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MAGNESIUM ALLOYS WITH HIGH MELTING POINT ADDITIONS

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FOREWORD

This report was prepared by Rensselaer Polytechnic Institute, Troy, New York, under USAF Contract No. AF 33(616)-2312. This contract was initiated under Project No. 7351, "Metallic Materials", Task No. 73514, "Improved Magnesium Alloys". It was administered under the direction of the Materials Laboratory, Directorate of Research, Wright Air Development Center, with Lt. R.D. Masteller acting as project engineer. The period of work covered by this report is 1 February 1954 to 31 January 1955.

Donation of 50 grams of swaged rhenium rod and 100 grams of potassium perrhenate by the Chase Copper and Brass Company, Waterbury 20, Connecticut, for use in this experimental work is gratefully acknowledged.

ABSTRACT

An exploratory investigation was made to determine the alloying characteristics and the influence on microstructures, mechanical properties and resistance to corrosion of small additions of titanium, hafnium, tantalum, nickel, cobalt, vanadium, boron, chromium, yttrium, rhenium, niobium, tungsten and molybdenum to magnesium and to selected magnesium-base alloys.

A potentially attractive method for the pronounced grain refinement of as-cast structure of magnesium-base alloys was found. Additions of small amounts of titanium dioxide and several forms of vanadium produced a moderate refinement in unalloyed magnesium. These additions were particularly effective when made to magnesium alloys with one or more soluble components. The mechanism of this action was believed to be extensive grain nucleation by stable, foreign nuclei in constitutionally supercooled liquid.

The solubility of titanium, hafnium, vanadium, boron, chromium, niobium, tungsten and molybdenum in magnesium was believed to be extremely limited. Additions of these elements to magnesium and to selected magnesium-base alloys did not influence significantly the mechanical properties or resistance to corrosion of hot rolled sheet. A consistent increase in tensile mechanical properties without loss in ductility in the as-extruded condition was associated with increased chromium additions to AZ31 composition reaching an optimum threshold at approximately 0.3 to 0.5% chromium, intended additions. The retention of rhenium and tantalum in magnesium and magnesium alloys was also believed to be of low magnitude and no improvement in mechanical properties or general resistance to corrosion was observed. Exceptionally high resistance to corrosion was exhibited by two alloys with additions of rhenium and two alloys with additions of tantalum to unalloyed magnesium in the form of hot rolled sheet. The result was considered significant but the specific cause for the benefit was not isolated.

Nickel and cobalt exhibited limited solid solubility in magnesium and magnesium alloys. Nickel additions produced a small improvement in room and elevated temperature mechanical properties of hot rolled sheet but lowered sharply the resistance to corrosion. Cobalt additions were less effective in improving mechanical properties and also lowered resistance to corrosion.

Microscopic examination indicated that the solid solubility of yttrium in magnesium was at least 0.5%. Yttrium additions to unalloyed magnesium produced an increase in tensile yield and ultimate strengths of 36 and 26%, respectively, in the form of hot rolled sheet at room temperature.

PUBLICATION REVIEW

This report has been reviewed and is approved.

FOR THE COMMANDER:

Richard R Kennedy

RICHARD R. KENNEDY
Chief, Metals Branch
Materials Laboratory
Directorate of Research

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INTRODUCTION

Statement of the Problem

The major purpose of this investigation was to determine the alloying characteristics, the influence on microstructure and the influence on mechanical properties of additions of titanium, hafnium, rhenium, yttrium and other high melting point elements to magnesium and to selected magnesium-base alloys. This study was an exploratory aspect of a more general problem, having as its ultimate goal the development of new, wrought magnesium-base alloys with improved mechanical and physical properties compared to those of present-day commercial alloys.

Scope of the Problem

Additions of titanium, hafnium, rhenium, yttrium, nickel, cobalt, tantalum, chromium, vanadium, columbium, boron, tungsten and molybdenum to magnesium and to selected magnesium alloys were evaluated. The scope of the evaluation of each addition element included studies to determine:

1. The results of previous work reported in the literature.
2. The most effective procedures for introducing the alloying addition and the relative retention of the addition.
3. The grain refining action of the alloying addition in primary structure and the retention of the effect in secondary structure.
4. The approximate extent of solid solubility of the alloying addition and the appearance and distribution of microconstituents.
5. The influence of the alloying addition on mechanical properties.
6. The influence of the alloying addition on the relative resistance to corrosion.

The general plan for study was similar for all alloying additions. Additions were made in one or more forms as metallic elements, salts of the elements and master alloys containing the desired addition element. As a general procedure, mechanical properties of 0.064 inch sheet in the hot rolled condition were determined at room temperature. Due to the limited experimental time available

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a determination of mechanical properties at the elevated temperatures 400 and 500°F was restricted to selected alloy compositions. A determination of as-cast mechanical properties at room temperature was limited to a portion of the experimental alloys prepared during the last half of the contract period.

Method for Presentation of Report

General experimental procedures for alloy preparation, mechanical testing, chemical analysis, microscopic examination and determination of relative resistance to corrosion are discussed in the following section. Specific deviations from these general experimental procedures, together with a review of literature and a presentation and discussion of results, are given in individual sections for each addition element.

EXPERIMENTAL PROCEDURE

Melting and Casting Alloys

Experimental alloy preparation followed general procedures recommended by The Dow Chemical Company, modified in details to permit introduction of high melting point and volatile components. The preparation of all alloys followed one or the other of two standardized procedures, designated according to the size of the melt. Melt Procedure I, used for a majority of the alloys prepared, produced 15 pound heats. Due to the expense of hafnium, yttrium, tantalum and rhenium, melt sizes were limited to approximately 200 grams and Melt Procedure II was developed and used for alloys with additions of these elements. Particular deviations from these two standardized procedures, when used, will be discussed in the individual sections of this report for the addition elements concerned.

The primary magnesium used in Melt Procedure I was Dow Pure grade notched ingot conforming to American Society for Testing Materials Specification B92-52 and guaranteed 99.8 percent magnesium. The primary magnesium used in Melt Procedure II was re-distilled magnesium in the form of condensed crystals. This material was purchased from The Dow Chemical Company and was certified to be at least 99.98 percent magnesium. The most significant impurities were 0.002 percent iron and 0.006 percent manganese. Manganese additions to experimental alloys prepared with Melt Procedure I were made with Dow "M" Alloy notched ingot conforming to American Society for Testing Materials Specification B93-51T. The "M" alloy ingot used had the following certified chemical analysis:

Manganese	1.61%
Copper	< 0.001%
Nickel	< 0.001%
Silicon	0.019%
Magnesium	balance

The identification of other alloying components and specifications of purity are given in the individual sections of this report for the addition elements concerned.

All alloys prepared according to Melt Procedure I were melted and alloyed in Amer-Mag(a) aluminized steel

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(a) Amer-Mag Crucibles, Type 2M51-026, 25 pound capacity, supplied by American Tank and Fabricating Company, 2284 Scranton Road, Cleveland 13, Ohio.

crucibles. Dow Pure and Dow M, if used, were melted down in a gas-fired crucible furnace under Dow 310 flux and the melt was refined, skimmed and dusted lightly with fresh flux. Temperature measurements were made with a chromel-alumel thermocouple in a steel immersion sheath and a Wheelco Indicating Pyrometer. Additions of alloying components were made in the temperature range 1400 - 1500°F, accompanied by thorough stirring with a steel tool designed to impart a gentle rolling motion to the melt. Alloying components in the forms of metal powder or dried granular salts were wrapped in paper and stirred into the melt. In alloys with intended zinc additions, these materials were wrapped in zinc foil. Larger solid addition forms were introduced in a special, perforated steel phosphorizing tool. Volatile additions of titanium tetrachloride were made by absorbing the liquid in barium chloride prior to the addition, and, as a second method, by introducing the titanium tetrachloride vapor directly into the melt. Melts were superheated 30 minutes at 1650-1700°F, cooled to 1350-1400°F, skimmed and poured into a cast iron mold, preheated to 300-400°F, under the protection of Dow 181 agent. The cast iron mold produced two ingot slabs for rolling, having the dimensions 5/8 inches thick, 3 inches wide and 8 inches long. Immediately prior to pouring, a representative sample of the melt was chill-cast into a ¼ inch diameter by 4 inch long pencil for spectrographic analysis. In addition, two tensile bars for the determination of as-cast mechanical properties were cast in a single, expendable, baked sand mold for a substantial number of the experimental alloys.

Melt Procedure II was developed to prepare heats of approximately 200 grams in size. Initial work with this procedure used Dixon(b) No. 1 clay-graphite crucibles. This practice was abandoned, however, when the results of an auxiliary investigation, described in Appendix I, associated the presence of an unidentified interdendritic network of microconstituents with the use of clay-graphite crucibles. The contamination was not encountered when using crucibles machined from Acheson(c) Grade C S graphite and these were adopted for standard procedure. Melt handling tools were graphite except for a skimming tool made from stainless steel sheet. Temperatures were determined by means of a chromel-alumel thermocouple in a graphite immersion sheath and a Brown Portable Potentiometer. Redistilled magnesium was melted down in a small electrical resistance furnace under Dow 220 flux, refined, skimmed and dusted lightly with fresh flux. Alloying additions were made at 1600-1700°F with techniques similar in principle to those described for Melt Procedure I except that a small

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(b) Supplied by F. B. Stevens Company, Detroit, Michigan

(c) Supplied by National Carbon Company, Niagara Falls, N.Y.

phosphorizing tool, machined from graphite, was substituted for the steel tool. Melts were superheated for 10 to 30 minutes at 1700°F, skimmed and poured at 1400-1500°F into a preheated cast iron mold. The mold utilized a big-end-up principle combined with a hot top to produce sound ingot slabs for rolling approximately 5/8 inches thick, 1½ inches wide and 4½ inches long. The entire melt was poured into this slab mold.

Initial plans for the experimental work of this program included the trial of a method to introduce high melting point elements as a liquid phase by arc melting above the surface of the magnesium melt and an examination of the possibility of preparing special master alloys similar in principle to the Dow K50. Although it was considered that both of these procedures had merit, neither was tried due to a lack of experimental time to devote to them.

Alloy Fabrication

Ingot slabs produced by Melt Procedure I for hot rolling were scalped along the sides and milled to ½ inch thickness prior to homogenization. Slabs were homogenized 1½ hours at 800°F and hot rolled at 800°F to 0.064 inch sheet on a two-high Oliver Mill with 3 inch diameter, 5 inch face rolls running at a speed of 16½ feet per minute. Roll temperature was maintained continuously at 400°F and ingots were reduced on a constant draft schedule between slab reheatings at 800°F for 20 minutes.

Ingot slabs produced by Melt Procedure II for hot rolling followed a similar schedule except that the initial breakdown passes were transverse to the long direction of the slab in order to obtain a slab 3 inches wide. Subsequent rolling to 0.064 inch sheet was carried out in the long direction of the slab.

Extrusion of experimental alloys was limited to a portion of the compositions in the magnesium-rhenium and magnesium-chromium systems. Alloys to be extruded were prepared according to Melt Procedure II, producing extrusion billets 3/4 inch diameter and 3 inches long. Billets were extruded in a laboratory extrusion container by the direct method, using a 100 ton capacity Watson-Stillman hydraulic press. Billets were extruded to 0.175 inch diameter rod, an extrusion ratio of 18, with a container temperature of 700°F and a speed of nominally 8 feet per minute after a four hour homogenization at 700°F in an auxiliary furnace.

Chemical Analyses

The chemical analyses of selected alloys with intended additions of titanium, rhenium, yttrium, nickel and cobalt were determined for selected alloys. Details of the procedures used are given in Appendix II.

Grain Size Measurements

As-cast grain size determinations were made for all experimental alloys prepared. Samples for this determination were removed from standardized locations in the ingots cast by both melt procedures. The determinations were made at 100X magnification by a comparative method, using a standard grain size rating chart supplied by The Dow Chemical Company. For sensibly equi-axed structures, grain size was expressed as an average grain diameter and for columnar structures the average length and width of the columnar grains was reported.

Mechanical Property Determination

Tensile yield and ultimate strengths, percentage elongation in two inches and compression yield strengths were determined at room temperature for 0.064 inch sheet in the as-hot rolled condition. The ultimate tensile strengths and percentages of elongation in two inches were determined for a limited number of selected compositions at 400°F and 500°F for the same condition of alloy preparation.

Room temperature mechanical properties were determined in a Southwork-Emery hydraulic testing machine using Templin Grips. Specimens for tensile properties were machined from blanks to a standard two inch gage length, 0.505 inches wide reduced section. Specimens for compression testing were 0.625 inches wide by 2.625 inches long. The rate of loading was approximately 1000 pounds per minute. Strain was followed with a Peters Extensometer or Compressometer and a Southwork-Emery Stress-Strain Recorder. Yield strengths were taken at 0.2 percent offset on the stress-strain curves.

Elevated temperature tensile properties were determined in the same tensile machine fitted with special pin grips for holding the specimen and an electrical resistance furnace with auxiliary apparatus to provide specimen temperature plus or minus 5°F of the nominal testing temperature control. Details of the specimen gripping arrangement and specimen dimensions are shown in Figure 1.

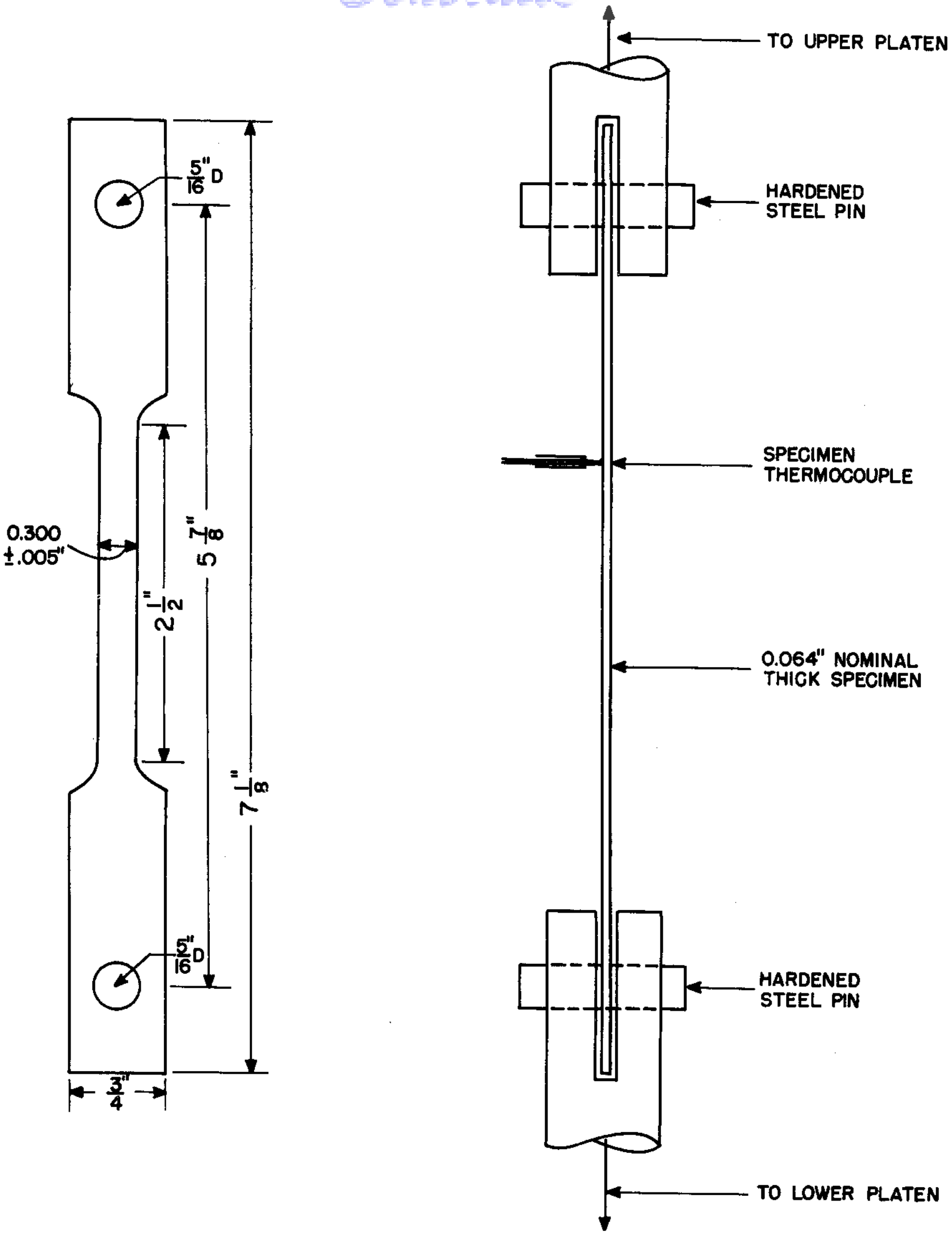

FIGURE 1 DRAWING TO SCALE

Specimen dimensions and arrangement for determination of tensile mechanical properties of 0.064 inch hot rolled sheet at elevated temperatures.

As-cast tensile mechanical properties were determined with a procedure similar to that used for the room temperature mechanical properties of hot rolled sheet except that strain to yield was followed manually by means of a Porter-Lipp strain gage clipped to the cast specimen.

Relative Resistance to Corrosion Determinations

Relative resistance to corrosion of selected alloys was determined by a 24 hour, static immersion in one normal sodium chloride solution, followed by visual examination and comparison. Specimens were one inch wide, three inches long, 0.064 inches thick sheet cut from as-hot rolled stock.

Prior to immersion, the specimens were cleaned first by dipping in 15 percent aqueous nitric acid and then by a five minute immersion in 15 percent aqueous chromic acid to remove stains left by the nitric acid dip. Following the chromic acid immersion the specimens were washed four times in boiling distilled water, dried in an air blast and immediately placed in the salt solution.

Test specimens were suspended in the salt solution and spaced ½ inches apart on a glass rod. The specimens were placed to avoid contact with a magnesium hydroxide precipitate which collected on the bottom of the vessel. In addition, the tops of the specimens were below an aerated layer at the surface of the solution formed by the evolution of hydrogen gas during the test.

The immersion test was made at room temperature in a 15 liter vessel allowing 300 milliliters of solution for each specimen. The approach to equilibrium was accelerated by adding 10 milliliters of 30 percent hydrogen peroxide solution to each liter of salt solution.

A strip of commercial AZ31 alloy sheet was immersed with each group of experimental specimens for a comparison standard. After removal from the test solution each specimen was washed in boiling water and dried in an air blast. One end of each specimen was cleaned in a 15 percent aqueous nitric acid solution to reveal the type and degree of attack.

A numerical rating system was used for evaluating the relative resistance to corrosion of each alloy compared to the commercial AZ31 standard specimens. This system was as follows:

Relative Resistance to Corrosion Number	Meaning
1	More resistant to corrosion than AZ31 alloy.
2	Resistance to corrosion comparable to AZ31 alloy.
3	Less resistant to corrosion than AZ31 alloy.
4	Considerably less resistant to corrosion than AZ31 alloy.
5	Specimen disintegrated and dropped to bottom of testing vessel.

A photograph of the comparison standards used in the evalution is shown in Figure 2

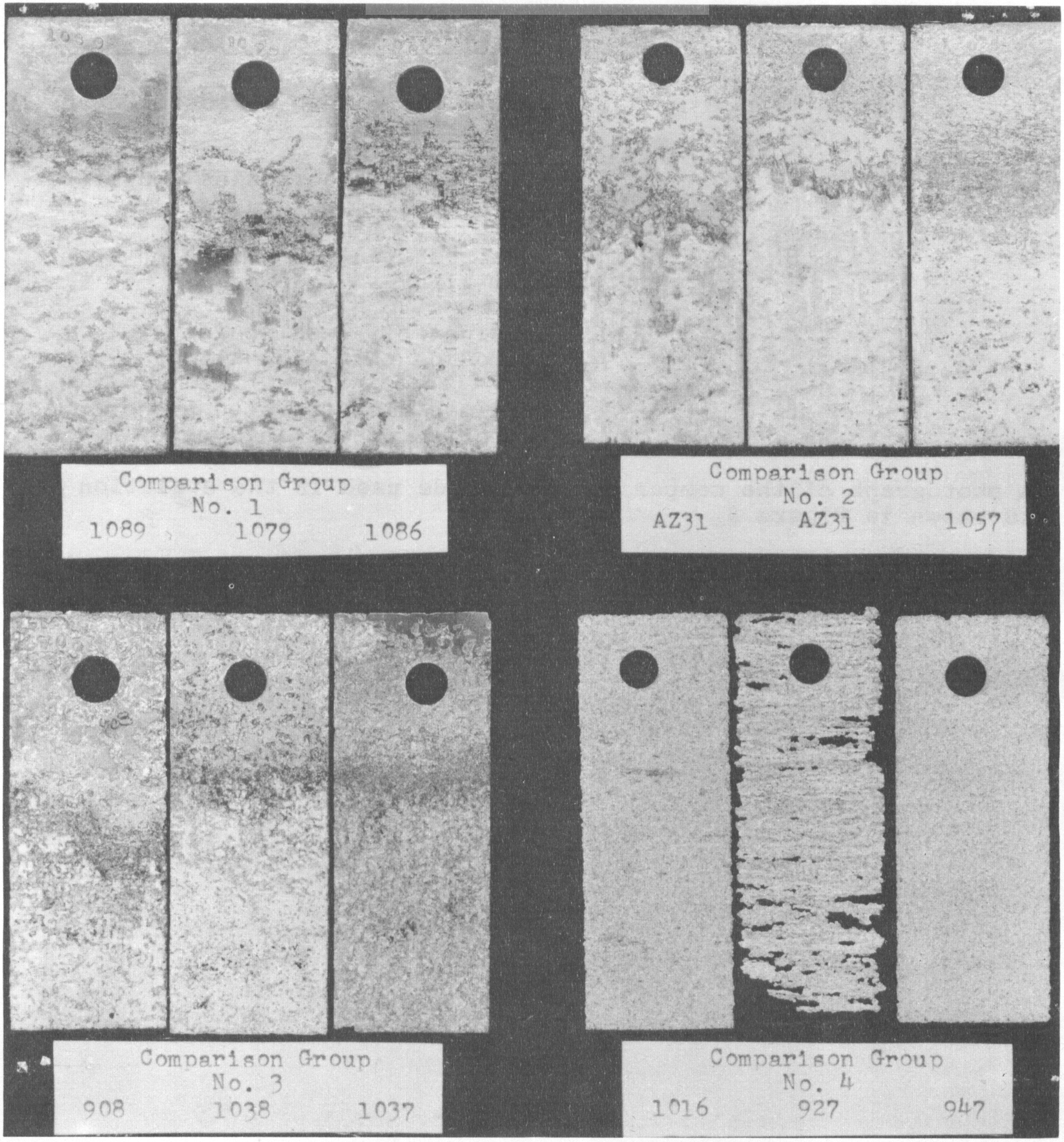

FIGURE 2

Comparison standards for visual evaluation of relative resistance to corrosion of experimental alloys.

MAGNESIUM - TITANIUM ALLOYS

Review of Literature

Although attempts have been made to introduce titanium into magnesium as early as 1938[1], and several patents[2,3] have been granted to protect the addition of titanium to certain magnesium alloys, only recently has any great interest been shown in titanium as an alloying addition to magnesium. The information available on the alloying behavior of titanium in magnesium was summarized by Carapella[4]. The solid solution of titanium in magnesium would be favored by the hexagonal close-packed structure of the low-temperature modification of titanium and the relative difference in atomic diameters of 9%. Due to an apparent alloying valence of zero in magnesium and its relative electronegativity, however, the solubility of titanium in magnesium would be expected to be restricted.

Kroll[5] reported on the feasibility of a number of alloying additions to magnesium and considered titanium an attractive possibility.

Aust and Pidgeon[6], in 1945, conducted an investigation to determine the solubility of titanium in magnesium. Additions of titanium as sheet, powder, and magnesium-base master alloy were tried, but none of the procedures produced alloys with more than trace amounts of titanium. Colorimetric analysis of the alloys produced showed a linear increase in the solubility of titanium with temperature in the range 650-850°C. The solubility of titanium in magnesium at its freezing point was reported as 0.0025%; 0.015% was given as the maximum solubility of titanium at 850°C.

Two recent investigations by Eisenreich[7,8] have dealt with the solubility of titanium in magnesium. The first investigation[7] considered the addition of titanium tetrachloride vapor to pure magnesium. The results indicated that the solubility of titanium in magnesium increased from about 0.003% at 655°C to 0.064% at 760°C. The presence of hydrogen was found to decrease the solubility of titanium; in several melts hydrogen was expelled by the addition of zirconium and the titanium solubility was increased to 0.115% at 800°C. Eisenreich drew the approximate equilibrium diagram and indicated a peritectic reaction at about 655°C. The second research[8] was devoted to the study of titanium additions to binary alloys of magnesium with silicon, manganese, and aluminum. Addition of titanium tetrachloride to these binary alloys was found to give only a trace of titanium in solution. It was reported that titanium additions did not decrease the as-cast grain size of these alloys and that significant grain coarsening was observed in the alloys magnesium + 1.4% silicon and magnesium + 0.6% zirconium when titanium tetrachloride was added. Eisenreich also reported that the solubility of aluminum, manganese, and silicon in magnesium was not affected by the addition of titanium.

Preparation of Experimental Alloys

A large portion of the magnesium-titanium alloys were prepared according to the standardized Melt Procedure I described in the Experimental Procedure section of this report. Deviations from this standard procedure are discussed below. Alloys were fabricated and mechanical properties were determined according to standard procedures described in the Experimental Procedure section.

Aluminum was added in the form of Alcoa commercial purity pig, specified to be greater than 99% aluminum. Zinc was added in the form of New Jersey Zinc Horsehead Special grade pig, specified to be greater than 99.99% zinc.

Titanium dioxide, titanium tetrachloride, and the absorbent barium chloride were added in the chemically pure form. Potassium fluotitanate was added as the technical purity salt. The titanium tetrafluoride and titanium tetrabromide used in this study were designated as purified.(a) The titanium sponge used was a fraction of Du Pont run A-2 and had a Brinell Hardness Number of 140. The manganese-titanium hardener used was specified to contain nominally 35% titanium, although an analysis was not available.

Zirconium was added as K30A (nominally 30% zirconium) supplied by Dow Chemical Company.

In general, when titanium compounds were added to the experimental alloys, the additions were made after the superheat at temperatures between 1600-1700°F, while the melts were cooling down to the pouring temperature. Alloying elements such as aluminum, zinc, zirconium, and the manganese-titanium hardener were added at 1500°F after meltdown and refining; when titanium sponge was added it was alloyed at 1700°F just after the melt was superheated.

Melts with the addition of titanium tetrachloride were prepared by measuring out the desired volume of liquid titanium tetrachloride and absorbing it in dried barium dichloride. About 40 grams of barium dichloride was used to absorb each millileter of titanium tetrachloride added.

(a) Supplied by A. D. Mackay, Inc., 198 Broadway, N.Y. 38, N.Y.

One melt, R-1425 (Dow Pure plus titanium), was made with the vapor-phase addition of titanium tetrachloride. The vapor was bubbled into the melt in the temperature range 1550-1500°F as the melt was cooling from the superheat. The vapor was produced in a small pressure vaporizer and was delivered to the melt at about 10 psi pressure and 290°F. Because of losses during heating up the vaporizer and alloying, the amount of titanium tetrachloride added could not be determined accurately (weighing before and after alloying was to be employed). Superheating was increased from the usual 15 minutes to 30 minutes for all alloys to which the manganese-titanium hardener was added; the standard superheat temperature was 1700°F for all types of alloys. In a few cases, alloys containing no aluminum were superheated only 10 minutes.

Chlorine fluxing was used with alloy R-1425 (Dow Pure plus titanium) to eliminate as much hydrogen as possible from the liquid melt; the melt was chlorine fluxed 7-8 minutes just prior to alloying the titanium tetrachloride vapor. The melt was fluxed at 1550°F, superheated 5 minutes at 1600°F, and allowed to air cool to 1550°F; when the melt had cooled to 1550°F the addition of vapor was started. After about 3-4 minutes of vapor introduction the temperature of the melt dropped to approximately 1500°F.

A summary of the alloys prepared and methods of preparation is given in Table I.

Exploratory Studies

At the outset of this investigation a small magnesium-titanium diffusion couple was prepared. The couple was composed of buttons ½ inch in diameter and ¼ inch long polished metallographically to a high luster on the mating surfaces. The polished surfaces were forced together and held securely during subsequent heat treatment by an axial force of clamping bolts. After sealing the clamp assembly into a Pyrex tube containing helium at a pressure of 400 millimeters of mercury, the couple was held for eleven days at 900°F. Metallographic examination of the couple sectioned to observe the interface indicated a distinct reaction on the titanium side. This condition appeared as a discrete line of microconstituents displaced a finite distance from the interface and a difference in contrast of the region between the interface and the microconstituents. No distinct evidence of diffusion was observed on the magnesium side. A tentative interpretation of these results was that the solid solubility of titanium in magnesium was extremely small. Additional work on this phase of the problem was abandoned because it was considered unlikely that its continuation would contribute significantly to the progress of the general investigation.

TABLE I

SUMMARY OF INTENDED COMPOSITIONS, AS-CAST GRAIN SIZE, AND LONGITUDINAL MECHANICAL PROPERTIES OF MAGNESIUM ALLOYS WITH ADDITIONS OF TITANIUM AS 0.064 INCH SHEET IN THE HOT-ROLLED CONDITION

Alloy Number	Intended Addition of Titanium				Average As-Cast Grain Diam., in.(c)	Longitudinal Mechanical Properties (d)		
						Kips/in^2		
	Base (a)	Method (b)	Form	Amount Wt. %		TYS	UTS	Elong. % 2 in.
R-1150	Mg	A	Master(e) Alloy	0.00015	0.004	(f)	(f)	(f)
R-1151	Mg	B	Ti Sponge Ti O_2	0.44 0.53	0.014	(f)	(f)	(f)
R-1152	Mg	B	Ti Sponge Ti O_2	0.9 1.1	0.015	(f)	(f)	(f)
R-1153	AZM331	B	Ti Sponge Ti O_2	0.065 0.079	0.001 to 0.002	(f)	(f)	(f)
R-1154	AZM331	B	Ti Sponge	1.4	0.005	(f)	(f)	(f)
R-1352	Mg	-	-	0.00	columnar 0.30" x 0.050"	17.6	26.6	6
R-1350	Mg	C	Ti O_2	0.13	0.070	14.2	22.3	8
R-1309	Mg	C	Ti O_2 -200 mesh	0.12	0.012	16.4	23.5	8
R-1413	Mg	C	Ti O_2 + 42 mesh	0.12	columnar 0.12" x 0.030"	16.0	27.0	6
R-1351	M1	-	-	0.00	0.12	21.2	26.8	9
R-1412	M1	C	Ti O_2	0.13	0.090	18.5	28.6	5
R-1308	Z3	-	-	0.00	0.008	34.7	37.5	6

TABLE I (Continued)

SUMMARY OF INTENDED COMPOSITIONS, AS-CAST GRAIN SIZE, AND LONGITUDINAL MECHANICAL PROPERTIES OF MAGNESIUM ALLOYS WITH ADDITIONS OF TITANIUM AS 0.064 INCH SHEET IN THE HOT-ROLLED CONDITION

	Intended Addition of Titanium					Longitudinal Mechanical Properties (d)		
						Kips/in^2		
Alloy Number	Base (a)	Method (b)	Form	Amount Wt. %	Average As-Cast Grain Diam., in. (c)	TYS	UTS	Elong. % 2 in.
R-1347	Z3	C	Ti O_2	0.13	0.002 to 0.003	30.2	37.6	8
R-1096	AZ31 0.2Mn	-	-	0.00	0.002 to 0.004	30.1	39.7	14.7
R-1055	AZ31 0.5Mn	-	-	0.00	0.003 to 0.010	35.4	41.8	10.5
R-1348	AZ31 0.2Mn	C	Ti O_2	0.13	0.001 to 0.004	28.8	42.0	6
R-1349	AZ33	C	Ti O_2	0.13	0.001 to 0.003	36.0	44.7	8
R-1189	AZM331	-	-	0.00	0.010	37.3	44.7	13.6
R-1188	AZM331	B	Ti Sponge Ti O_2	0.065 0.079	0.008 to 0.010	40.7	47.2	13.3
R-1175	Mg	-	-	0.00	0.015	17.4	25.8	5.0
R-1159	Mg	D	Ti Cl_4	0.03	0.012			
R-1160	Mg	D	Ti Cl_4	0.008	0.015	18.1	31.2	6.2
R-1161	Mg	D	Ti Cl_4	0.006	columnar 0.65" x 0.075"	16.8	30.2	7.0
R-1162	Mg	D	Ti Cl_4	0.012	columnar 0.75" x 0.065"	19.1	29.6	11.0
R-1163	Mg	D	Ti Cl_4	0.006	columnar 0.75" x 0.040"	17.7	30.9	10.0
R-1164	Mg	D	Ti Cl_4	0.003	0.012	18.7	32.2	9.0

TABLE I (Continued)

SUMMARY OF INTENDED COMPOSITIONS, AS-CAST GRAIN SIZE, AND LONGITUDINAL MECHANICAL PROPERTIES OF MAGNESIUM ALLOYS WITH ADDITIONS OF TITANIUM AS 0.064 INCH SHEET IN THE HOT-ROLLED CONDITION

Alloy Number	Intended Addition of Titanium				Average As-Cast Grain Diam., in. (c)	Longitudinal Mechanical Properties (d)		
	Base (a)	Method (b)	Form	Amount Wt. %		Kips/in² TYS	UTS	Elong. % 2 in.
R-1425	Mg	E	$TiCl_4$	-	columnar 0.40" x 0.060"	19.2	24.9	6
R-1182	Mg	F	$TiBr_4$	0.01	columnar 0.50" x 0.060"	17.3	25.0	4.2
R-1183	Mg	F	$TiBr_4$	0.04	columnar 0.40" x 0.060"	16.8	25.2	4.8
R-1241	Mg	G	TiF_4	0.085	columnar 0.60" x 0.065"	(g)	(g)	(g)
R-1247	Mg	G	TiF_4	0.045	-	(g)	(g)	(g)
R-1248	Mg	G	TiF_4	0.37	-	(g)	(g)	(g)
R-1249	Mg	H	K_2TiF_6	0.082	columnar 0.75" x 0.030"	17.1	25.7	5
R-1251	Mg	H	K_2TiF_6	0.14	columnar 0.75" x 0.065"	14.7	23.3	6
R-1253	Mg	J	Mn-Ti Hardener	2.6	columnar 0.55" x 0.060"	15.8	26.4	6
R-1254	Mg	J	Mn-Ti Hardener	1.0	0.090	15.2	21.8	8
R-1255	Mg	J	Mn-Ti Hardener	4.2	columnar 0.50" x 0.060"	17.3	25.4	5

TABLE I (Continued)

SUMMARY OF INTENDED COMPOSITIONS, AS-CAST GRAIN SIZE, AND LONGITUDINAL MECHANICAL PROPERTIES OF MAGNESIUM ALLOYS WITH ADDITIONS OF TITANIUM AS 0.064 INCH SHEET IN THE HOT-ROLLED CONDITION

Alloy Number	Intended Addition of Titanium Base (a)	Method (b)	Form	Amount Wt. %	Average As-Cast Grain Diam., in. (c)	Longitudinal Mechanical Properties (d) Kips/in^2 TYS	UTS	Elong. % 2 in.
R-1306	Z3	H	K_2TiF_6	0.21	0.005	22.4	34.2	20
R-1307	Z3	J	Mn-Ti	1.0	0.006	22.1	33.9	21
R-1257	KO	-	-	0.00	0.007	16.1	24.1	8
R-1258	KO	D	Ti Cl_4	0.026	columnar 0.70" x 0.060"	14.9	22.7	8
R-1294	KO	D	Ti Cl_4	0.052	0.060	13.7	24.2	7
R-1295	KO	D	Ti Cl_4	0.06	0.060	15.2	23.0	8
R-1296	KO	D	Ti Cl_4	0.04	0.090	17.4	25.4	8
R-1297	KO	H	K_2TiF_6	0.12	0.090	16.0	24.2	10
R-1303	ZK30	-	-	0.00	0.003	36.4	45.4	11
R-1304	ZK30	H	K_2TiF_6	0.21	0.006	25.5	36.7	16
R-1305	ZK30	H	K_2TiF_6	0.67	0.008	20.6	32.3	15

Notes

(a) The symbol "Mg" designates Dow Pure grade of magnesium.

(b) The procedures for the addition of titanium were:

A - Addition of an aluminum-magnesium titanium hardener (0.01% intended titanium).

Notes Continued

B - Dual addition of titanium dioxide and titanium sponge at 1700°F after the superheat.

C - Addition of titanium dioxide at 1700°F after the superheat.

D - Addition of titanium tetrachloride absorbed on barium dichloride at 1600°F after the superheat.

E - Addition of vapor-phase titanium tetrachloride in range of 1500-1500°F after superheating.

F - Addition of titanium tetrabromide at 1600°F after the superheat.

G - Addition of titanium tetrafluoride at 1600°F after the superheat.

H - Addition of potassium fluotitaniate at 1700°F after the superheat.

J - Addition of a manganese - 35% titanium hardener at 1500°F just after meltdown.

(c) The average as-cast grain size denotes a comparative determination from Dow Chemical Company standards; the grain size reported is the average diameter of the grains in the equiaxed zone unless otherwise noted. All grain size specimens were cut from the same relative position in the ingot structure.

(d) The values reported are an average of at least two tests.

(e) An experimentally prepared master alloy with an intended composition of 60% aluminum, 39% magnesium and 01% titanium.

(f) Small, exploratory heats of insufficient size for fabrication and testing.

(g) Not possible to hot roll because ingots contained extremely severe gas-type porosity.

As this study progressed a marked grain refinement in primary structure was observed in several alloys with addition of titanium to an AZM331 base. Alloy R-1153 (Dow M with additions of 0.14% titanium as titanium sponge and titanium dioxide) had a very fine grain structure. This discovery prompted casting of a duplicate (R-1188) and a control melt, identical except without the titanium addition (R-1189). Although both alloys displayed a relatively fine grain structure, more grain refinement was evident in the titanium-containing alloy. In addition, the mechanical properties of alloy R-1188 in the form of 0.064 inch hot-rolled sheet were significantly higher than those of alloy R-1189.

On the assumption that titanium dioxide was the cause of the pronounced grain refinement of primary structure in magnesium, an auxiliary investigation was made to explore more completely the behavior of this addition to magnesium and to magnesium alloys exhibiting a relatively small and a relatively large solidification interval. Small quantities (0.12 to 0.13%) of titanium dioxide were added to Dow Pure, and to the base compositions M1, Z3, AZ31, AZ33 and AZM331. The influence of the addition of titanium dioxide on primary microstructure in these cases is summarized in Figure 3. All sections shown were taken from the same relative location in the cast structure of the ingots.

Additions of titanium dioxide to Dow Pure produced a significant change in the microstructure, replacing a coarse, transcolumnar pattern with an equiaxed structure from the surface to center. There was a pronounced influence of the particle size of the titanium dioxide added, as indicated in the much finer and more uniform structure when the addition was a minus 200 mesh fraction (R-1309) than when added as a plus 42 mesh fraction (R-1413) or as a non-sized, as-received mixture of particles (R-1350).

The addition of titanium dioxide to Dow M suppressed the extent of the columnar structure but did not produce a marked refinement in grain size (R-1412 compared with R-1351). Additions to Z3, AZ31 and AZM331 base compositions resulted in an extremely fine, equiaxed grain structure throughout the cross-section (R-1347, R-1348 and R-1188 compared with R-1308, R-1055 and R-1189, respectively). The effectiveness of the titanium dioxide was reduced by the presence of manganese, as illustrated in the structure for R-1349 (AZ33 plus 0.13% titanium dioxide) compared with R-1188 (AZ33 plus saturation manganese plus 0.13% titanium dioxide).

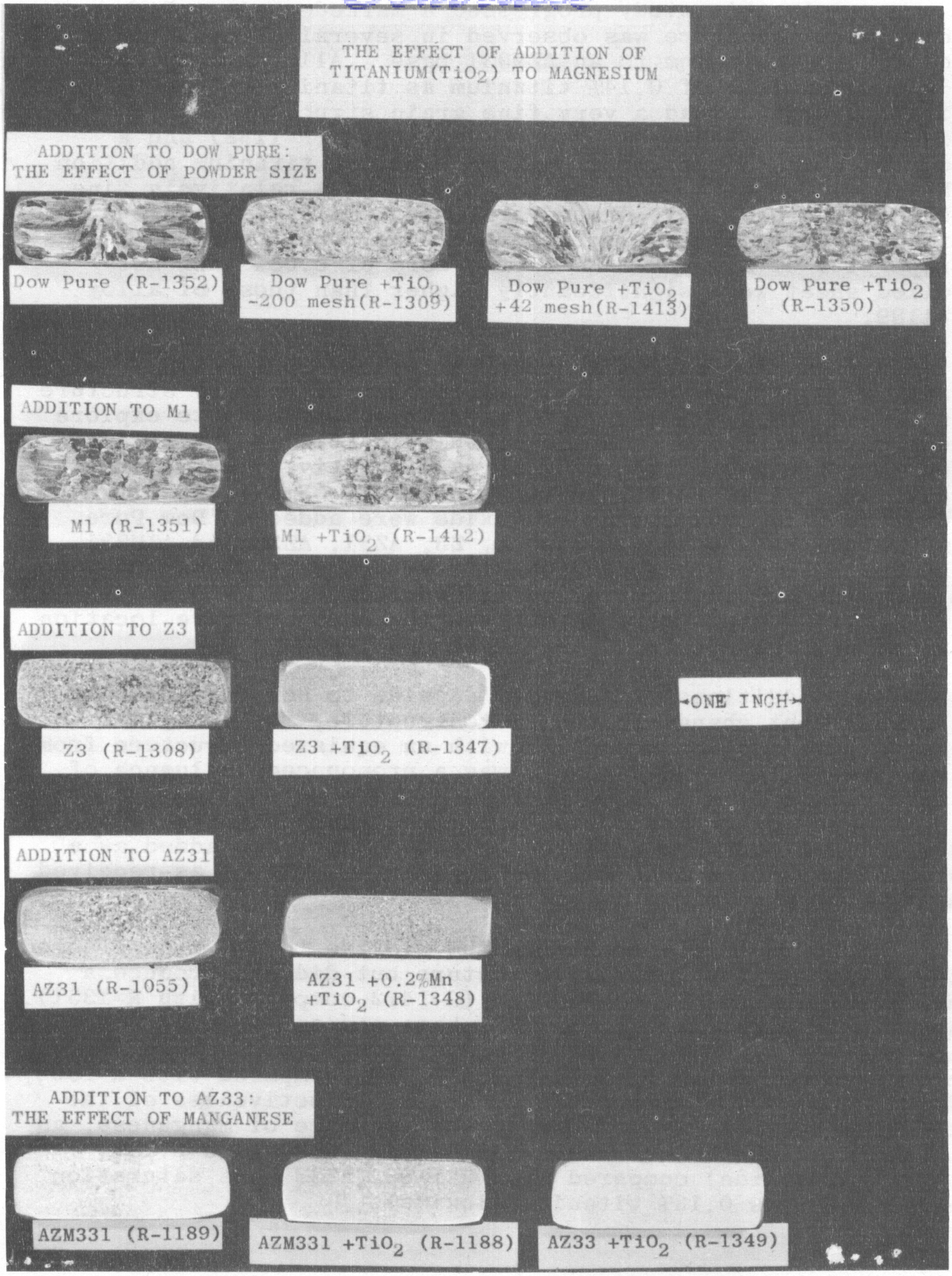

FIGURE 3

Magnification: 7/8X

Etch: Acetic
Picral

The influence of additions of titanium dioxide to magnesium and to magnesium alloys on as-cast macrostructure. Samples were prepared through number 3/0 emery paper and macroetched.

The calcium reduction of titanium tetrafluoride in the presence of zinc was suggested for evaluation. This proposal was studied for some time with the anticipation that zinc would dissolve the reduced titanium and provide a relatively low melting master alloy for later addition to magnesium. Using metallic zinc and calcium mixed with titanium tetrafluoride powder, no satisfactory master alloy was prepared. The reaction mixture was charged into a heavy steel bomb which was heated to 1900°F for as long as three hours. Small droplets, which behaved chemically like pure zinc, were found among the reaction products. A black pyrophoric powder, assumed to be a titanium compound, comprised a large volume of the reaction products. It was hoped that the zinc would melt and dissolve any of the titanium reduced by the calcium and the master alloy could be removed as chips. Because of the physical form of the zinc, from all the bomb reactions attempted, this idea was abandoned. A small piece of zinc was recovered from one of the bomb reactions, but it was not used to alloy titanium because it seemed to be unmelted reactant. A thin layer of zinc was left in the lowest part of the bomb from every run; the layer was too thin to be removed and used for alloying. This general idea was abandoned eventually as unworkable under the experimental conditions used.

Because of the slight solubility of titanium in aluminum, 0.19% titanium at the peritectic temperature 665°C, an attempt was made to prepare an aluminum-base master alloy containing titanium. An alloy with an intended composition of 60% aluminum, 39% magnesium, and 1.0% titanium was made by holding molten aluminum in contact with titanium sponge for several hours. After the sponge had dissolved, the proper amount of magnesium was added and the melt was cast immediately. The result was an extremely brittle master alloy. A portion of this master alloy was added to alloy R-1150 (magnesium plus aluminum - magnesium - titanium master alloy). Subsequent qualitative spectrographic analysis gave a positive indication of the presence of titanium in both the master alloy and alloy R-1150. This method of addition was not pursued, however, because observations indicated that it was no more effective in introducing titanium than other methods investigated.

Several of the alloys made when the program was initiated were analyzed for chemically dissolved titanium, deposited titanium, and total titanium by the colorimetric method suggested by Eisenreich[7]. Samples of the rolling slab riser were analyzed spectrophotometrically for the amount of total and dissolved titanium. The analysis technique required two samples for acid dissolution (only dissolved titanium is soluble in sulfuric acid while the total titanium may be determined by dissolution in nitric acid). Details of procedures used for qualitative spectrographic detection and for quantitative determination of titanium in magnesium are given in Appendix II. The amount of titanium present as a secondary phase, designated as deposited titanium, was expressed as the difference between the amount of titanium present and the amount of titanium in solid solution. Samples used for the analysis were too small to permit direct separation and weighing of the deposited titanium. The chemical analyses are given in Table II.

TABLE II

SPECTROPHOTOMETRIC ANALYSES FOR TITANIUM IN SELECTED MAGNESIUM-TITANIUM ALLOYS

Alloy	Intended Addition of Titanium Weight Percent	Chemical Analysis Soluble Ti	Chemical Analysis Total Ti	Deposited Ti (Difference)
R-1152	1.1	0.000	0.000	-
R-1153	0.14	0.000	0.000	-
R-1154	1.4	0.000	0.000	-
R-1159	0.03	0.002	0.004	0.002
R-1161	0.006	0.007	0.006	0.000
R-1162	0.012	0.012(a)	0.009(b)	-

(a) Average of two determinations
(b) Result of a single determination

Grain Refinement With Titanium Dioxide

Early in the program a study of the microstructure of alloy R-1152 (Dow Pure plus titanium addition as titanium sponge and titanium dioxide) was made. The microstructure showed a globular condition which was general throughout the structure. At high magnification each globular area was observed to contain a tiny, undissolved microconstituent; the microconstituents were believed to be associated with the titanium addition. The primary grain size was significantly smaller than other alloys with small additions of titanium to pure magnesium and it was believed that some grain refining in essentially pure metal can be traced to the addition of titanium dioxide.

Observations made during this study suggest that the mechanism of action of the titanium dioxide was that of a foreign nucleation material. The fact that the addition was more effective when made to magnesium alloys with one or more solute components exhibiting significant solid solubility than when made to unalloyed magnesium was believed to be strong evidence for the operation of constitutional supercooling during solidification. This condition could result from concentration gradients in the liquid and would be expected to increase significantly the nucleation tendencies of solid particles suspended in the liquid. Cibula[9] reported that grain refinement from additions of elements such as titanium, zirconium, columbium, boron, vanadium and others was much more pronounced when made to aluminum alloys exhibiting solid solutions than when made to unalloyed aluminum.

In the present investigation it was believed that the foreign nuclei were titanium dioxide and/or titanium monoxide produced by partial reduction with molten magnesium. A patent[10] granted to the Dominion Magnesium Company described the reduction of titanium dioxide to titanium monoxide by molten magnesium. It is believed possible that other compounds of titanium, including titanium carbide and titanium nitride, would be effective in this function although no attempt was made to study these materials.

Mechanical Properties

Longitudinal tensile mechanical properties were determined at room temperature with specimens of 0.064 inch sheet in the hot rolled condition, using procedures discussed in the Experimental Procedure section of this report. A summary of these properties is given in Table I.

Alloys R-1150 to R-1154 were made as exploratory melts of insufficient size for fabrication and testing. The addition of a 60% aluminum - 39% magnesium - 1.0% titanium master alloy to magnesium, R-1150, produced a relatively fine, equiaxed primary structure. The use of this form of addition was not pursued, however, because it was not considered as promising as the addition of titanium dioxide. Marked grain refinement of as-cast structure was associated with additions of titanium sponge and titanium dioxide. It was believed that titanium dioxide was the effective part of the addition and a more extensive study was made to determine the influence of this addition on mechanical properties.

The addition of titanium dioxide to magnesium and to base compositions M1, Z3 and AZ31 did not produce a significant change in the mechanical properties of 0.064 inch hot rolled sheet. The pronounced grain refinement of as-cast structures, illustrated in Figure 3, was accompanied by improved hot rolling characteristics compared with the same intended compositions without additions of titanium dioxide. Comparing alloys R-1188 and R-1189, the addition of titanium dioxide to AZM331 was associated with a distinct increase in tensile yield and ultimate strengths. As indicated in the mechanical properties of alloy R-1349 (AZ33 plus titanium dioxide), the presence of manganese was considered necessary for the improved mechanical strength and percentage elongation.

The microstructures of alloys R-1189 and R-1188 are compared in Figures 4 and 5. These structures appeared essentially the same although the grain size was noticeably more uniform and slightly finer in alloy R-1188. It was believed that this difference indicated that the initially finer as-cast structure of R-1188 provided a more uniform response to the conditions of fabrication of the sheet.

Additions of titanium tetrachloride to magnesium resulted in a coarse, columnar macrostructure in all cases studied. This observation was in agreement with evidence reported by Eisenreich[8]. Mechanical properties for alloys R-1159 to R-1164 indicated that additions of titanium tetrachloride absorbed in barium dichloride to magnesium produced a small improvement in tensile yield strength and a larger increase in tensile ultimate strength and percentage elongation,

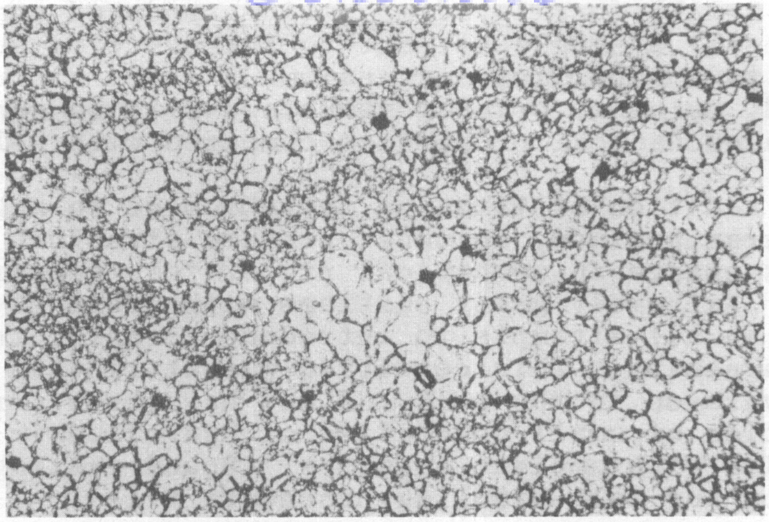

Figure 4

Specimen No: 2270 Magnification: 200X
Negative No: 700 Etch: Acetic Picral,
10 seconds

Longitudinal section of R-1189 (AZM331) sheet in the hot rolled condition. The average grain size ranged between approximately 0.0003 to 0.0004 inches and was less uniform in size than exhibited by R-1188, Figure 5. A uniform distribution of the manganese constituent in all parts of the structure was observed.

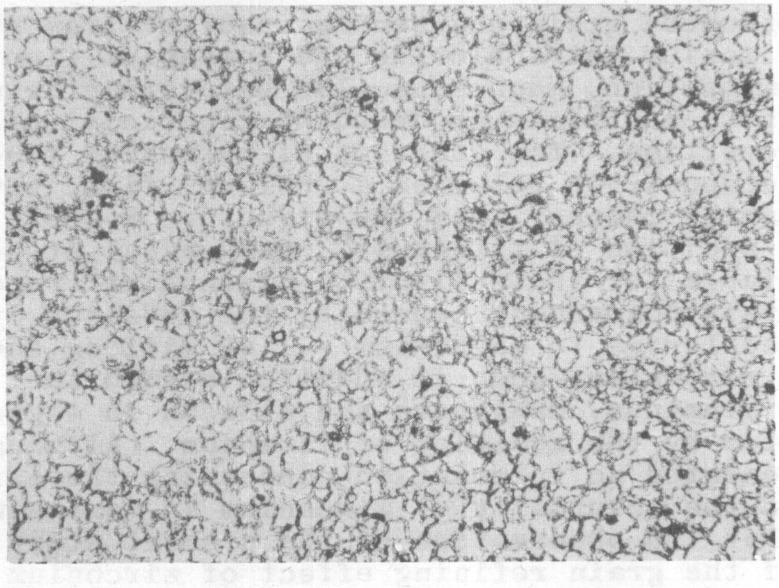

Figure 5

Specimen No: 2269 Magnification: 200X
Negative No. 699 Etch: Acetic Picral,
10 seconds

Longitudinal section of R-1188 (AZM331 plus 0.065% titanium sponge and 0.079% titanium dioxide) sheet in the hot rolled condition. The average grain size was 0.0003 that of R-1188, Figure 4, except for a more uniform grain size throughout the structure.

compared with R-1175 (unalloyed magnesium produced under the same conditions). A single attempt to introduce titanium tetrachloride as a vapor into magnesium, R-1425, produced a coarse grained, columnar primary structure with no sensible improvement in mechanical properties compared with R-1175.

The addition of titanium tetrabromide to magnesium produced a coarse grained, columnar primary structure and no significant change in mechanical properties, compared with alloy R-1175. Extremely gassy castings with gross cavities were obtained in all attempts to introduce titanium tetrafluoride in magnesium. This condition was attributed to the presence of hydrogen in the melt and may have been a result of the production of small quantities of hydrofluoric acid and its reaction with ambient moisture. Sound castings were not obtained by any melt handling procedure tried.

Additions of potassium fluotitanate and a manganese - 35% titanium hardener to magnesium produced coarse, as-cast macrostructures and no improvement in mechanical properties. The addition of both of these materials to base composition Z3, alloys R-1306 and R-1307, retained the uniform, equiaxed primary structure and produced a moderate, additional refinement compared with alloy R-1308 (a magnesium - 3% zinc alloy with no intended addition of titanium). Mechanical properties were not available to determine the influence of these additions.

Pronounced grain coarsening resulted from the addition of titanium tetrachloride and potassium fluotitanate to KO base composition, magnesium plus saturation level zirconium. These additions produced no beneficial effect on mechanical properties. The addition of potassium fluotitanate to ZK30 base composition retained a uniform, fine, equiaxed structure slightly coarser than the structure R-1303, (ZK30 alloy without addition of titanium). Mechanical properties were not available for these alloys. Eisenreich[8] reported significant grain coarsening caused by the addition of titanium tetrachloride to magnesium - 1.4% silicon and magnesium - 0.6% zirconium, and, in addition stated that the solubility of aluminum, manganese and silicon in magnesium was not affected by the addition of titanium. Although Eisenreich presented no information concerning the effect of titanium on the solubility of zirconium in magnesium, it is believed that the observation of the present study - an elimination of the grain refining effect of zirconium when added in combination with titanium tetrachloride - indicated a distinct decrease in the solubility of zirconium in magnesium in the presence of titanium.

Summary

The influence of additions of titanium on as-cast structure and on the mechanical properties of hot rolled magnesium alloy sheet was studied. Titanium was added to magnesium as titanium sponge, titanium dioxide, halides of titanium, potassium fluotitanate and as manganese - 35% titanium and 60% aluminum - 39% magnesium - 0.01% titanium hardeners. Some of these forms were added to magnesium alloy base compositions M1, Z3, AZ31, AZ33, AZM331 and KO.

The retention of titanium in magnesium was extremely small and no sensible improvement in mechanical properties was achieved. The most promising result of the study was the demonstration of an effective grain refinement of primary structure through the addition of titanium dioxide to magnesium and magnesium alloys. This effect was striking in unalloyed magnesium and there was a particle size dependence being more effective with finer particles of titanium dioxide. The action was moderate in M1 alloy but was pronounced in alloys exhibiting significant solid solution formation. Manganese reduced the effectiveness of the action. The general beneficial effect of the refinement was to improve hot working characteristics of the alloys. A significant improvement in tensile mechanical properties of AZM331 alloy was associated with the addition of titanium dioxide. The mechanism of operation of the effect was believed to be a foreign nuclei principle and it was considered likely that similar action would be obtained with other compounds of titanium or with other materials.

MAGNESIUM - HAFNIUM ALLOYS

Review of Literature

Carapella[4] reported that hafnium has a favorable size factor for alloying with magnesium, is hexagonal close packed in structure, and has an alloying valence of zero. These data indicate that hafnium could be expected to show some solid solubility in magnesium. Kroll[5] reported in 1945 that nothing was known about magnesium-hafnium alloys.

Preparation of Alloys

An experiment was performed to determine the effect of submerging hafnium metal in molten magnesium. A piece of high purity, hafnium crystal bar, obtained from the Atomic Energy Commission, weighing 68.0610 grams, was submerged in 908 grams of redistilled magnesium at 1600°F, and held for two hours. The melt was protected with Dow 310 flux. After the two hours at 1600°F, the hafnium was removed, cleaned in dilute acetic and then in dilute hydrochloric acid and weighed again. At this point the hafnium metal weighed 68.0142 grams, a loss in weight of 0.0468 grams or 0.069% of the total. The hafnium metal had essentially the same appearance after immersion as before. The 0.069% loss in weight was not considered significant. On the basis of these observations it was believed that the metallic hafnium did not alloy to any appreciable extent with the molten magnesium.

Fourteen 200 gram melts were made in the magnesium-hafnium alloy series following Melt Procedure II given in the Experimental Procedure Section of this report. The investigation was limited to hafnium additions to the base compositions magnesium, Z3 and ZK30 because it was believed that hafnium would not be compatible with other elements in magnesium. This belief was based on the fact that hafnium and zirconium have similar chemical behaviors and it is known that zirconium is incompatible in magnesium with all of the common alloying elements except zinc. The hafnium additions were made as metallic hafnium or as hafnium tetrachloride. These materials were obtained from the Atomic Energy Commission and were stated to be high purity, although chemical analyses were not supplied. The hafnium tetrachloride was dried in an oven at approximately 300°F for at least three hours prior to alloying. The additions of the hafnium tetrachloride and the hafnium sponge were made by wrapping them in paper, or, zinc sheet when zinc was to be an alloying element, and submerging the wrap beneath the melt surface. The zinc sheet used was 1/100 inch metal sheet of 99.99% purity(a). The

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(a) Obtained from the Fisher Scientific Company, Pittsburg, Pennsylvania.

zirconium additions were made in the form of Dow K30 master alloy containing nominally 30% zirconium. The melt was then stirred to provide the best possible conditions for solution of the hafnium in the magnesium.

It was believed that Melt Procedure II provided favorable conditions and the maximum possibility of obtaining a clean, flux-free solution of hafnium in magnesium. The melting and casting conditions for the magnesium-hafnium alloys are given in Table III. No difficulty was encountered in making these melts and all castings exhibited a satisfactory surface appearance.

As-Cast Grain Size

Metallographic specimens were taken from the bottom of each 200 gram casting in accordance with standardized procedures. Grain size determinations were made on the as-cast equiaxed structures and the results are reported in Table III. No particular trend was observed for the effect of hafnium on the as-cast grain size of magnesium base alloys, except when zinc was present in the alloy. Hafnium additions to a magnesium 3.0% zinc alloy reduced the as-cast grain size to the range obtained by the addition of saturation zirconium to the magnesium 3% zinc alloy. Hafnium had no effect on the as-cast grain size of a saturation zirconium 3.0% zinc-balance magnesium alloy.

Metallographic Observations

Microscopic examination of magnesium-hafnium alloys in the as-cast and hot rolled sheet conditions produced no distinct microstructural evidence of the presence of hafnium in the structure.

Mechanical Properties

The as-cast billets of the magnesium-hafnium alloy series were scalped and machined to 0.575 inch thickness. The billets were then homogenized, hot rolled to 0.064 inch sheet, longitudinal tensile blanks were sheared from the resulting sheet, flattened, machined to size, and tested following the procedure given in the Experimental Procedure section of this report. The mechanical properties are summarized in Table IV.

The data of Table IV indicate that hafnium had no beneficial affect on the room temperature mechanical properties of the magnesium base alloys used in this investigation.

TABLE III

MELTING AND CASTING CONDITIONS AND AS-CAST GRAIN SIZE FOR EXPERIMENTAL MAGNESIUM-HAFNIUM ALLOYS

Alloy Number	Intended Addition Weight Percent Hafnium	Intended Addition Weight Percent Other	Form of Hafnium Addition	Melt Procedure(a)	Average Grain Diameter, Inches
R-1311	-	-	-	A	0.023
R-1210	1.0	-	Metallic	B	0.007
R-1211	1.0	-	Tetra-chloride	B	0.040
R-1299	1.0	-	Metallic	B	0.013
R-1319	0.1	-	Metallic	A	0.040
R-1318	1.0	-	Metallic	A	0.015
R-1373	0.1	-	Tetra-chloride	A	0.015
R-1320	1.0	-	Tetra-chloride	A	0.030
R-1374	1.0	-	Tetra-chloride	A	0.020
R-1308	-	3.0Zn	-	C	0.025
R-1300	1.0	3.0Zn	Metallic	B	0.001
R-1392	0.1	3.0Zn	Metallic	A	0.003
R-1393	1.0	3.0Zn	Metallic	A	0.004
R-1341	-	0.7Zr 3.0Zn	-	A	0.003
R-1396	1.0	0.7Zr 3.0Zn	Metallic	A	0.003

(a) Melt procedures are given in the Experimental Procedure section of this report.
A means Melt Procedure II
B means Melt Procedure II using a Dixon No.4/0 clay graphite crucible
C means Melt Procedure I

The only effect observed was a lowering of the room temperature tensile yield and ultimate tensile strengths and an increase in ductility of the 0.7% zirconium 3.0% zinc-balance magnesium alloy with a 1.0% hafnium addition.

Resistance to Corrosion

Standard static resistance to corrosion tests were performed on the magnesium-hafnium alloy series. The results of this determination are given in Table V. Hafnium additions to magnesium and to the magnesium alloys studied did not alter the relative resistance to corrosion. An explanation for the consistently poor results for magnesium and magnesium-hafnium alloys was not obtained in an examination of the procedures used and the microstructures. Considering the possibility that a relatively high concentration of iron was present in these alloys, it was believed that the results indicated that either the retention of hafnium in the alloys was poor or that hafnium did not exhibit the beneficial capacity to remove iron from liquid solution possessed by zirconium.

Summary

Fourteen 200 grams melts were cast in the magnesium-hafnium alloy series. The hafnium was alloyed in the metallic or tetrachloride form. It was found that hafnium additions to a 3.0% zinc containing alloy reduced the as-cast grain size to the range obtained by the addition of saturation zirconium to the 3.0% zinc containing alloy. No observable evidence of hafnium was found in the microstructures of the as-cast or as-hot rolled alloys. The data collected showed no beneficial effect of hafnium on the magnesium base alloys investigated with respect to mechanical properties or resistance to corrosion.

TABLE IV

ROOM TEMPERATURE MECHANICAL PROPERTIES OF 0.064 INCH MAGNESIUM-HAFNIUM ALLOY SHEET IN THE HOT-ROLLED CONDITION

Alloy Number	Intended Addition Weight Percent		Longitudinal Tensile Properties(a)		
			Kips per sq.in.		Elongation
	Hafnium	Other	TYS	UTS	% in 2 in.
Pure Mg(b)	-	-	14.0	27.0	16.0
Pure Mg(c)	-	-	27.0	37.0	9.0
R-1311	-	-	11.4	21.3	7.0
R-1299(d)	1.0 sponge	-	11.1	21.2	7.0
R-1319	0.1 sponge	-	9.6	21.4	6.8
R-1318	1.0 sponge	-	10.4	22.0	6.2
R-1373	0.1 $HfCl_4$	-	9.7(e)	21.2(e)	4.5(e)
R-1320	1.0 $HfCl_4$	-	10.3	22.0	6.0
R-1374	1.0 $HfCl_4$	-	10.3(e)	21.5(e)	5.5(e)
R-1308(f)	-	3.0Zn	29.4	36.5	17.0
R-1300(d)	1.0 sponge	3.0Zn	28.3(e)	36.2(e)	14.5(e)
R-1392	0.1 sponge	3.0Zn	29.2	37.7	11.8
R-1393	1.0 sponge	3.0Zn	30.0(e)	37.6	15.3
R-1341	-	0.7Zr 3.0Zn	38.5	46.7	8.3
R-1396	1.0 sponge	0.7Zr 3.0Zn	33.6	41.7	14.8

(a) Properties reported are an average of three specimens for each alloy unless otherwise noted.

(b) Properties taken from "Metals Handbook", 1948, p.1014, Annealed condition.

(c) Properties taken from "Metals Handbook", 1948, p.1014, Hard rolled condition.

(d) Alloy melted in clay-graphite crucible giving possible contamination. (See Appendix I)

(e) Properties reported are an average of two specimens.

(f) Alloy melted in AMER-MAG crucible.

TABLE V

RELATIVE RESISTANCE TO CORROSION OF 0.064 INCH HOT-ROLLED MAGNESIUM-HAFNIUM ALLOY SHEET COMPARED TO COMMERCIAL FS1-0 ALLOY SHEET

Alloy Number	Intended Addition Weight Percent		Relative Resistance to Corrosion (a)
	Hafnium	Other	
R-1311	-	-	5
R-1299(b)	1.0 Metallic	-	5
R-1319	0.1 Metallic	-	5
R-1318	1.0 Metallic	-	5
R-1373	0.1 Tetrachloride	-	5
R-1320	1.0 Tetrachloride	-	5
R-1374	1.0 Tetrachloride	-	5
R-1308(c)	-	3.0Zn	4
R-1300(b)	1.0 Metallic	3.0Zn	3
R-1392	0.1 Metallic	3.0Zn	3
R-1393	1.0 Metallic	3.0Zn	3
R-1341	-	0.7Zr 3.0Zn	3
R-1396	1.0 Metallic	0.7Zr 3.0Zn	3

(a) The relative resistance to corrosion was determined according to the procedure and rating scheme described in the Experimental Procedure section of this report.

(b) Alloy melted in clay-graphite crucible giving possible contamination (see Appendix I).

(c) Alloy melted in AMER-MAG crucible.

MAGNESIUM - TANTALUM ALLOYS

Review of Literature

Carapella[4] reported that tantalum has a favorable size factor for alloying with magnesium, is body-centered cubic in structure, and has an alloying valence of zero. From these data it was expected that tantalum would show little, if any, solid solubility in magnesium. Kroll[5] stated in 1945 that nothing was known about magnesium-tantalum alloys.

Preparation of Alloys

An experiment was carried out to determine the effect of submerging tantalum wire in molten magnesium. A coil of 0.015 inch diameter tantalum wire, weighing 0.8904 gms., was submerged in 207.5 gms. of redistilled magnesium held at 1600°F. The melt was protected with Dow 310 flux. The coil of tantalum wire was removed after two hours at 1600°F, cleaned in dilute acetic acid and then in concentrated hydrochloric acid, and weighed again. The tantalum coil then weighed 0.8700 gms., a loss in weight of 0.0204 gms. or 2.28% of the total. This weight loss was considered significant. The tantalum wire showed a discoloration, and metallographic examination of a cross-section of the wire exhibited what was believed to be evidence of some attack by the magnesium on the tantalum. On the basis of these observations it was believed that the metallic tantalum was wet by the molten magnesium and showed a tendency to alloy with it.

Sixteen 200 gm. melts were made in the magnesium-tantalum alloy series following Melt Procedure II, discussed in the Experimental Procedure section of this report. Tantalum was added to magnesium and to base compositions Z3, ZM30, ZM31 and ZK30 in the form of metallic powder, tantalum pentachloride, and tantalum potassium fluoride. The tantalum powder used in this investigation was guaranteed 99.9% pure and minus 325 mesh(a). The tantalum chloride was designated anhydrous and purified(a). The tantalum potassium fluoride was C.P. grade(b). The conditions of melting and casting used are listed in Table VI.

(a) Obtained from A. D. Mackay, Inc., 198 Broadway, New York 38, New York

(b) Obtained from Fisher Scientific Co., Pittsburg, Pennsylvania

TABLE VI

MELTING AND CASTING CONDITIONS AND AS-CAST GRAIN SIZE FOR EXPERIMENTAL MAGNESIUM-TANTALUM ALLOYS

Alloy Number	Intended Addition Weight Percent		Tantalum Added As	Melt Procedure(a)	Average Grain Diameter Inches
	Tantalum	Other			
R-1311	-	-	-	A	0.023
R-1289	0.1	-	Powder	B	0.007
R-1322	0.1	-	Powder	A	0.025
R-1290	1.0	-	Powder	B	0.020
R-1333	1.0	-	Powder	A	0.017
R-1291	0.1	-	TaK_2F_7	B	0.023
R-1337	0.1	-	TaK_2F_7	A	0.017
R-1293	1.0	-	TaK_2F_7	B	0.023
R-1334	1.0	-	TaK_2F_7	A	0.017
R-1346	0.1	-	$TaCl_5$	A	0.030
R-1342	1.0	-	$TaCl_5$	A	0.035
R-1308	-	3.0Zn	-	C	0.025
R-1336	0.1	3.0Zn	Powder	A	0.002
R-1335	1.0	3.0Zn	Powder	A	0.002
R-1344	-	3.0Zn 0.5Mn	-	A	0.004
R-1339	1.0	3.0Zn 0.5Mn	Powder	A	0.003
R-1259	-	3.0Zn 1.2Mn	-	C	0.007
R-1343	1.0	3.0Zn 1.2Mn	Powder	A	0.006
R-1341	-	3.0Zn 0.7Zr	-	A	0.003
R-1345	1.0	3.0Zn 0.7Zr	Powder	A	0.002

(a) Melt procedures are given in the Experimental Procedure section of this report.

A means Melt Procedure II

B means Melt Procedure II except that the alloy was melted in a Dixon 4/0 clay-graphite crucible

C means Melt Procedure I

The addition of tantalum as a tantalum potassium fluoride caused excessive melt activity even after the compound had been dried at 300°F at least one month. This activity was believed to have resulted from a violent reduction of the tantalum potassium fluoride by the magnesium and not by any entrapped moisture on the compound or the melt handling tools.

As-Cast Grain Size

The results of as-cast grain size determinations on the equiaxed structures of the magnesium-tantalum system alloys are given in Table VI. Metallographic specimens were taken from the bottom of each casting in accordance with standarized procedures. These measurements indicated that tantalum powder additions to magnesium base alloys had a grain refining tendency, especially in the presence of zinc. This observation was noted on each base composition to which tantalum was added. The relatively small average grain size of alloy R-1289 (0.1% tantalum powder-balance magnesium) was attributed to melt contamination derived from a new clay-graphite crucible used for the melt (see Appendix I). The additions of tantalum to redistilled magnesium as $TaCl_5$ exhibited a tendency to enlarge the average grain size of the alloys.

Metallographic Observations

Metallographic observations showed no distinct evidence of the presence of tantalum in the as-cast or as-hot rolled condition.

Mechanical Properties

The as-cast billets of the magnesium-tantalum alloy series were scalped and machined to 0.575 inch thickness. The billets were then homogenized and hot rolled to 0.064 inch sheet following the standardized procedures given in the Experimental Procedure section of this report. Longitudinal tensile blanks were sheared from the hot rolled sheet, flattened, machined into test specimens, and tested following standardized procedures. Mechanical properties of magnesium-tantalum alloys are given in Table VII. The results indicated that tantalum additions had no significant effect on the mechanical properties of magnesium and the magnesium base alloys used in this investigation.

TABLE VII

ROOM TEMPERATURE MECHANICAL PROPERTIES OF 0.064 INCH MAGNESIUM - TANTALUM ALLOY SHEET IN THE HOT-ROLLED CONDITION

Alloy Number	Intended Addition Weight Percent		Longitudinal Tensile Properties(a) Kips per sq.in.		
	Tantalum	Other	TYS	UTS	Elongation % in 2 in.
Pure Mg(b)	-	-	14.0	27.0	16.0
Pure Mg(c)	-	-	27.0	37.0	9.0
R-1311	-	-	11.4	21.3	7.0
R-1289(d)	0.1 powder	-	10.6	21.1	5.8
R-1322	0.1 powder	-	10.1	21.5	6.8
R-1290(d)	1.0 powder	-	11.6	21.5	5.5
R-1333	1.0 powder	-	9.9	21.3	6.8
R-1291(d)	0.1 TaK_2F_7	-	9.8	20.5	6.5
R-1337	0.1 TaK_2F_7	-	12.6	22.7	3.0
R-1293(d)	1.0 TaK_2F_7	-	9.9	21.1	7.2
R-1334	1.0 TaK_2F_7	-	9.2	21.7	5.0(e)
R-1346	0.1 $TaCl_5$	-	12.4(e)	22.8(e)	4.2(e)
R-1342	1.0 $TaCl_5$	-	10.9	22.0	4.3
R-1308(f)	-	3.0Zn	29.4	36.5	17.0
R-1336	0.1 powder	3.0Zn	24.4	34.8	17.9
R-1335	1.0 powder	3.0Zn	24.4	35.4	16.8
R-1344	-	0.5Mn 3.0Zn	26.5	37.6	9.8
R-1339	1.0 powder	0.5Mn 3.0Zn	26.5	37.9	9.2
R-1259(f)	-	1.2Mn 3.0Zn	33.3	41.5	9.0
R-1343	1.0 powder	1.2Mn 3.0Zn	31.5(e)	41.7(e)	8.5(e)
R-1341	-	0.7Zr 3.0Zn	38.5	46.7	8.3
R-1345	1.0 powder	0.7Zr 3.0Zn	38.5(e)	46.8	10.0

(a) Properties reported are an average of three specimens for each alloy unless otherwise noted.

(b) Properties taken from "Metals Handbook",1948,p.1014. Annealed condition.

(c) Properties taken from "Metals Handbook",1948,p.1014. Hard rolled condition.

(d) Alloy melted in clay-graphite crucible giving possible contamination (see Appendix I).

(e) Properties reported are an average of two specimens.

(f) Alloy melted in AMER-MAG crucible.

Resistance to Corrosion

Specimens from the magnesium-tantalum alloy series were subjected to the standard static resistance to corrosion test. The details of this test are given in the Experimental Procedure section of this report. The results of the determination for the magnesium-tantalum alloy series are given in Table VIII. No specific trend for the effect of tantalum on the magnesium base alloys was noted.

It was observed, however, that alloys R-1290 (1.0 tantalum intended-balance magnesium), R-1291 (0.1 tantalum intended-balance magnesium), and R-1337 (0.1 tantalum intended-balance magnesium) possessed exceptionally good relative resistance to corrosion. A comparison of these three alloys with a commercial FS1-0 sheet specimen used as a control specimen during the test is shown in Figure 6. In Figure 6, the surface markings on alloy R-1337 were stains resulting from a nitric acid cleaning solution after the test was completed and were not formed during the test. The possibility that melt contamination from a clay-graphite crucible (see Appendix I) was responsible for the attractive result for alloy R-1291 was considered unlikely since alloy R-1337 was an intended duplicate except for melting in a graphite crucible. A review of all details of alloy preparation and handling produced no explanation for the cause of high relative resistance to corrosion. The result was believed to be significant.

Summary

Sixteen 200 gm. melts were cast in the magnesium-tantalum alloy series. The tantalum additions were in the form of metallic powder, tantalum chloride, or tantalum potassium fluoride. No observable evidence of tantalum was found in the microstructures of the as-cast or as-hot rolled alloys. It was observed that tantalum additions in the form of a metallic powder reduced the as-cast grain size of the magnesium base alloys, especially those containing a zinc addition. The data showed no beneficial effect of tantalum on the as-hot rolled mechanical properties of the magnesium base alloys used in this investigation. Certain tantalum containing alloys exhibited exceptionally good corrosion resistance compared with commercial FS1-0 alloy. This result was considered significant but no experimental explanation for its occurrence was observed.

TABLE VIII

RELATIVE RESISTANCE TO CORROSION OF 0.064 INCH HOT-ROLLED MAGNESIUM-TANTALUM ALLOY SHEET COMPARED TO COMMERCIAL FS1-0 ALLOY SHEET

Alloy Number	Intended Addition Weight Percent Tantalum	Intended Addition Weight Percent Other	Relative Resistance to Corrosion (a)
R-1311	-	-	5
R-1289(b)	0.1 powder	-	5
R-1322	0.1 powder	-	5
R-1290(b)	1.0 powder	-	1
R-1333	1.0 powder	-	5
R-1291(b)	0.1 TaK_2F_7	-	1
R-1337	0.1 TaK_2F_7	-	1
R-1293(b)	1.0 TaK_2F_7	-	4
R-1334	1.0 TaK_2F_7	-	5
R-1346	0.1 $TaCl_5$	-	5
R-1342	1.0 $TaCl_5$	-	4
R-1308(c)	-	3.0Zn	4
R-1336	0.1 powder	3.0Zn	3
R-1335	1.0 powder	3.0Zn	3
R-1344	-	0.5Mn 3.0Zn	4
R-1339	1.0 powder	0.5Mn 3.0Zn	4
R-1259(c)	-	1.2Mn 3.0Zn	4
R-1343	1.0 powder	1.2Mn 3.0Zn	4

TABLE VIII (Continued)

RELATIVE RESISTANCE TO CORROSION OF 0.064 INCH HOT-ROLLED MAGNESIUM-TANTALUM ALLOY SHEET COMPARED TO COMMERCIAL FS1-O ALLOY SHEET

Alloy Number	Intended Addition Weight Percent		Relative Resistance to Corrosion (a)
	Tantalum	Other	
R-1341	-	0.7Zr 3.0Zn	3
R-1345	1.0 powder	0.7Zr 3.0Zn	4

(a) The relative resistance to corrosion was determined according to the procedure and rating scheme given in the Experimental Procedure section of this report.

(b) Alloy melted in clay-graphite crucible giving possible contamination (see Appendix I).

(c) Alloy melted in AMER-MAG steel crucible.

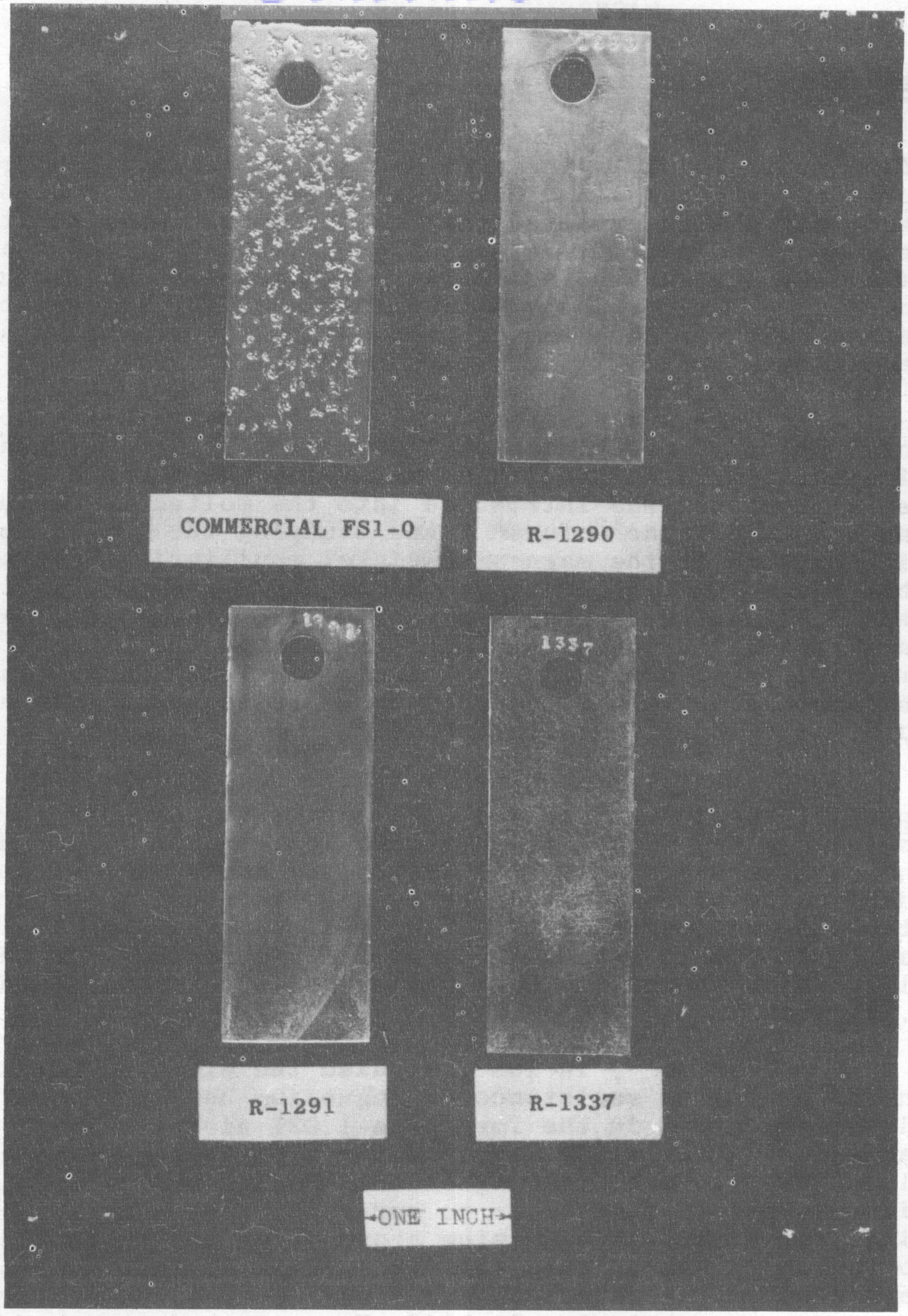

FIGURE 6
Photograph showing the improved relative resistance to corrosion of alloys R-1290 (magnesium - 1.0 tantalum, intended), R-1291 (magnesium - 0.1 tantalum, intended), and R-1337 (magnesium - 0.1 tantalum, intended) compared to commercial FS1-0 alloy sheet.

MAGNESIUM - NICKEL ALLOYS

Review of Literature

Carapella[4] reported that nickel has an unfavorable size factor for alloying with magnesium, is face centered cubic in structure, and has an alloying valence of zero. From these data it is expected that nickel should show limited, if any, solid solubility in magnesium. Alico[11] stated that there is a tendency for the solubility of a metal in magnesium to increase with increasing temperature when the size factor is unfavorable for room temperature solubility of the metal in magnesium.

Gann and Winston[12], in 1927, investigated the possibility of alloying nickel to magnesium. No evidence of nickel solid solubility in magnesium was found when the metallic nickel was introduced into the molten magnesium. Haughton and Payne[13] found, when studying the magnesium rich portion of the magnesium nickel equilibrium diagram, that the solubility of nickel in liquid magnesium was less than 0.10 percent. They stated that the amount of nickel in solution depends on the temperature and the time at temperature, the dissolved nickel increasing with increasing temperature or time at temperature. These authors found a eutectic at 23.5% nickel and 946°F.

McDonald[14] stated, in 1940, that nickel is a "possibly desirable" addition to magnesium. In his work, McDonald added nickel to magnesium in metallic form. Grube and coworkers[15] stated that increasing amounts of nickel added to CM-62 composition increased the tensile properties at 600°F but decreased the creep resistance of CM-62 alloy. Later, in 1951, Grube and coworkers[16] found that the CM alloy which showed the best resistance to creep contained 0.25% nickel.

Davies[17], in 1948, studied the effect of nickel on the corrosion resistance of magnesium base alloys. The nickel was added in the form of a 1.02% nickel-balance magnesium master alloy. The master alloy was made by alloying nickel shot to sublimed magnesium. Davies emphasized that with respect to resistance to corrosion, there is a tolerance limit for nickel in magnesium above which the resistance to corrosion is poor. This tolerance limit is reported to depend on the manganese in solution, decreasing with decreasing manganese content. In 1942, Hanawalt and coworkers[18] studied the effect of nickel on the corrosion resistance of magnesium and its alloys. They added nickel to magnesium in the form of a master alloy. The results showed that nickel has a deleterious effect on the corrosion resistance of

MAGNESIUM - NICKEL ALLOYS

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Preparation of Alloys

Four preliminary 50 gm. melts were cast to determine the effect of nickel on the microstructure of magnesium alloys and to see what complications and difficulties, if any, would be encountered in preparing the alloys. The melts were made in Dixon Number 1 clay graphite crucibles(a) using Dow 310 flux for protection. The nickel was added to molten Dow pure magnesium at 1500°F as a fine metallic powder, wrapped in paper, submerged beneath the melt surface and stirred with a graphite rod. The powder was specified to be at least 98% nickel and had a particle size of approximately 6 microns(b). The melts were superheated 5 minutes at 1700°F, cooled to 1400°F and poured into a graphite mold held at 400°F. The graphite mold had a cylindrical cavity, 1 inch in diameter. Intended nickel additions of 0, 0.10, 1.00 and 10.00% were cast in this manner.

No experimental difficulty was encountered in this procedure but metallographic observations indicated that the nickel recovery was low. Metallographic specimens were taken from the centers of the castings and examination showed what was believed to be an insoluble eutectic structure along grain boundaries and throughout the matrix. Observations of this structure at 1500X indicated clearly that this constituent contained at least two phases believed to be a magnesium rich solid solution containing a slight amount of nickel and the intermediate phase Mg_2Ni. From these investigations it was concluded that the addition of a nickel powder modified the microstructure of a magnesium base alloy and that a procedure for the melting and casting of magnesium-nickel alloys could be established without experiencing great difficulties.

Twenty magnesium base-nickel containing alloys were made following Melt Procedure I outlined in the Experimental Procedure section of this report. Nickel was added to molten magnesium and magnesium base alloys in the form of a metallic powder, a magnesium -70% nickel master alloy or as an anhydrous nickelous chloride. The nickel addition was wrapped in either paper or zinc foil, depending on whether zinc was an intended addition, submerged beneath the melt surface, and stirred for approximately 1 minute.

(a) Supplied by F. B. Stevens, Incorporated, Detroit, Michigan.
(b) Supplied by A. D. Mackay Incorporated, 198 Broadway, New York 38, New York.

Nickel additions were made to magnesium base alloys containing varying amounts of zinc, manganese, and zirconium.

The nickel powder used in these studies was the same as that used in the preliminary investigations of the magnesium-nickel alloy series. The master alloy was designated 70% nickel-balance magnesium. The nickelous chloride was analyzed 99.9% purity with rare earths and alkali metals being the major impurities(a). No difficulty was encountered in adding the nickel to the molten magnesium. The melting and casting conditions for the magnesium-nickel alloy series are given in Table IX.

Chemical Analysis

Selected magnesium-nickel alloys were analyzed for nickel concentration to determine the best method of alloying nickel to magnesium. The specimens analyzed were sections from the risers of the rolling slab castings, adjacent to the billet that was used for rolling. The method of analysis is given in Appendix II. The results of the analyses are given in Table IX.

These results indicate that the best method of addition of nickel to magnesium, with regard to recovery, was as a fine metallic powder. This result was based on a comparison of the values for an intended addition of 1.0% nickel. The incongruous analyses for the lower intended nickel concentration ranges may have been the result of nickel segregation in the sample or due to pick-up of nickel remaining in the crucible from a previous melt.

As-Cast Grain Size

As-cast grain size determinations were made on the equiaxed structures of the magnesium-nickel alloy series. The grain size determinations were made on metallographic specimens taken from the center of the riser on the rolling slab casting adjacent to the rolling slab. The results of these determinations are given in Table IX. These results indicate that nickel imparts small to moderate grain refinement of primary structure in magnesium and magnesium base alloys. Raising the alloying temperature from 1500°F to 1700°F or increasing the superheating time from 15 to 30 minutes had a tendency to increase the grain size of magnesium

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(a) Supplied by J. T. Baker Chemical Company, Phillipsburg, New Jersey.

TABLE IX

MELTING AND CASTING CONDITIONS AND AS-CAST GRAIN SIZE FOR EXPERIMENTAL MAGNESIUM-NICKEL ALLOYS

Alloy Number	Intended Addition Weight Percent		Nickel Analysis Weight Percent(a)	Nickel Added As	Average Grain Diameter Inches
	Nickel	Other			
R-1166	-	-	None	-	0.020 - 0.040
R-1167	0.01	-	None	powder	0.023 - 0.027
R-1168	0.10	-	0.13	powder	0.023 - 0.027
R-1169	1.0	-	0.96	powder	0.013
R-1314(b)	1.0	-	-	powder	0.040
R-1315(c)	1.0	-	-	powder	0.020
R-1316(d)	1.0	-	-	powder	0.040
R-1238(e)	2.2	-	-	powder	0.027
R-1239(c)	2.2	-	-	powder	0.017
R-1170	0.01	-	0.02	70Ni-30Mg hardener	0.030
R-1171	0.10	-	0.10	70Ni-30Mg hardener	0.027
R-1172	1.0	-	0.47	70Ni-30Mg hardener	0.023 - 0.027
R-1173	0.14	-	0.10	$NiCl_2$	0.033 - 0.050
R-1174	1.0	-	0.66	$NiCl_2$	0.023
R-1384	-	0.5Mn 3.0Zn	-	-	0.005
R-1380	1.0	0.5Mn 3.0Zn	-	powder	0.006
R-1259	-	1.2Mn 3.0Zn	-	-	0.007
R-1378	0.1	1.2Mn 3.0Zn	-	powder	0.009
R-1379	1.0	1.2Mn 3.0Zn	-	powder	0.007
R-1385	-	0.7Zr	-	-	0.050
R-1381	0.1	0.7Zr	-	powder	0.005 - 0.035
R-1382	1.0	0.7Zr	-	powder	0.010
R-1341(f)	-	0.7Zr 3.0Zn	-	-	0.003
R-1383	1.0	0.7Zr 3.0Zn	-	powder	0.005

(a) Nickel analysis determined by the procedure given in Appendix II.

(b) Melt Procedure I used except that the nickel powder was added at 1700°F instead of 1500°F.

(c) Melt Procedure I used except that superheating was done at 1850°F instead of 1700°F.

(d) Melt Procedure I used except that the nickel powder was added at 1700°F instead of 1500°F and the superheating was extended from 15 to 30 minutes.

(e) Melt Procedure I used except that the superheating time was extended from fifteen to thirty minutes.

(f) Melt made using Melt Procedure II outlined in the Experimental Proecdure section of this report.

base alloys containing 1.0% intended nickel concentration. The grain size of the alloys where the nickel addition was in powder form appeared to be smaller than that produced by equivalent intended nickel concentrations of magnesium-nickel hardener or the anhydrous nickelous chloride. This may have been due, however, to the fact that it was believed that the powder form of nickel addition resulted in the highest percentage of nickel recovery. Comparing the values for R-1185 and R-1382, the intended addition of 1.0% nickel reduced the as-cast grain size of the magnesium - 0.7% intended zirconium alloy by a factor of five. It was believed, however, that this result should be regarded as tentative since the zirconium concentration in the two alloys was not determined.

Metallographic Observations

As-cast metallographic specimens of the magnesium-nickel alloy series showed an interdendritic network of eutectic structure which increased in extent with increased nickel additions. Figure 7 shows the as-cast microstructure of alloy R-1239 (magnesium - 2.2% nickel intended). The eutectic is seen in the interstices of magnesium-nickel solid solution dendrites. Resolution of the phases present in the eutectic is illustrated in Figure 8. The influence of hot rolling is shown in Figure 9 for the same alloy illustrated in Figure 7, R-1239. The thermal treatment apparently resulted in some agglomeration of the intermediate phase in the eutectic. Mechanical working displaced the network into longitudinal stringers with distinct evidence of the beginning of a breakdown in continuity. Figure 10 illustrates the appearance of the as-cast microstructure of alloy R-1382 (magnesium - 0.7% zirconium - 1.0% nickel intended). The magnesium-nickel eutectic is shown dispersed throughout the interstices of solid solution dendrites. The zirconium had no apparent effect on the microstructure of the magnesium-nickel alloy.

The microstructure of alloy R-1383 (magnesium - 0.7% zirconium - 3.0% zinc - 1.0% nickel intended), Figures 11 and 12, illustrated a more continuous network that was believed to be made up of both zinc-rich and nickel-rich phases. The existence of a multiphase network is clearly illustrated.

Room Temperature Mechanical Properties

Three magnesium-nickel binary alloys were cast directly into tensile bars in a baked sand mold and were

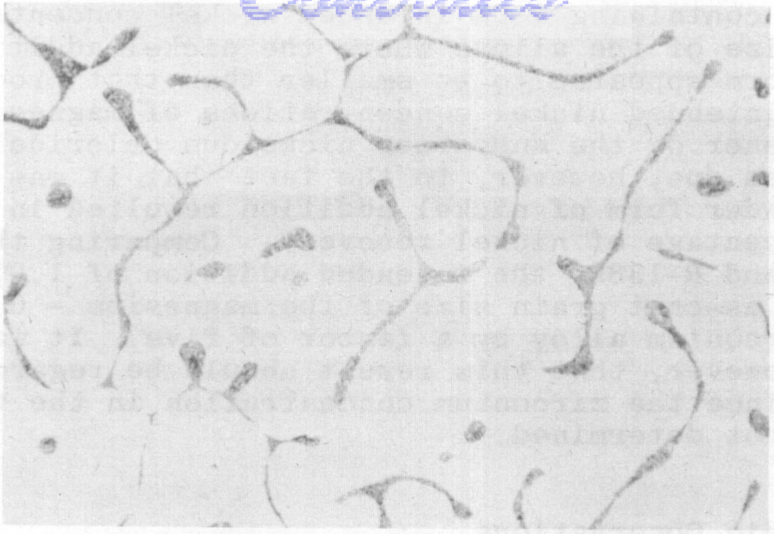

Figure 7

Negative No: 645 Magnification: 500X
Specimen No: 2377 Etch: As-polished

As-cast microstructure of alloy R-1239 (magnesium-2.2% nickel, intended) revealing a relatively large amount of eutectic structure in the interstices of magnesium-nickel solid solution dendrites.

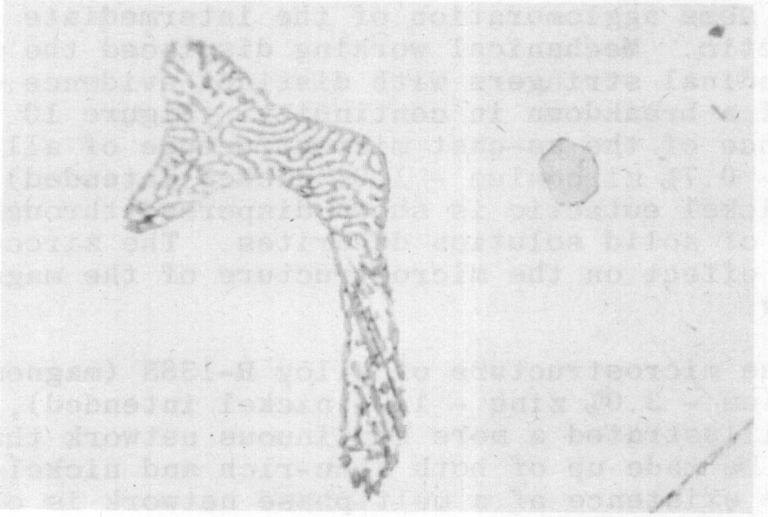

Figure 8

Negative No: 611 Magnification: 200X
Specimen No: 2282 Etch: As-polished

As-cast microstructure of alloy R-1169 (magnesium-1.0% nickel, intended) showing the phases present in the eutectic. These are believed to be a magnesium-nickel solid solution and Mg_2Ni.

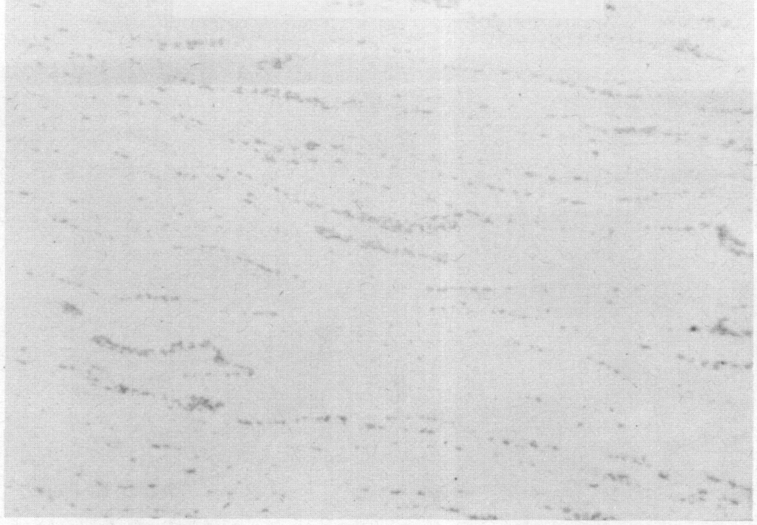

Figure 9

Negative No: 643 Magnification: 500X
Specimen No: 2519 Etch: As-polished

Longitudinal section of alloy R-1239 (magnesium - 2.2% nickel, intended) in the hot rolled condition. Stringers of the eutectic network are shown aligned in the direction of working and there appeared to be a tendency toward agglomeration of the intermediate phase and the beginning of a breakdown in the continuity of the network.

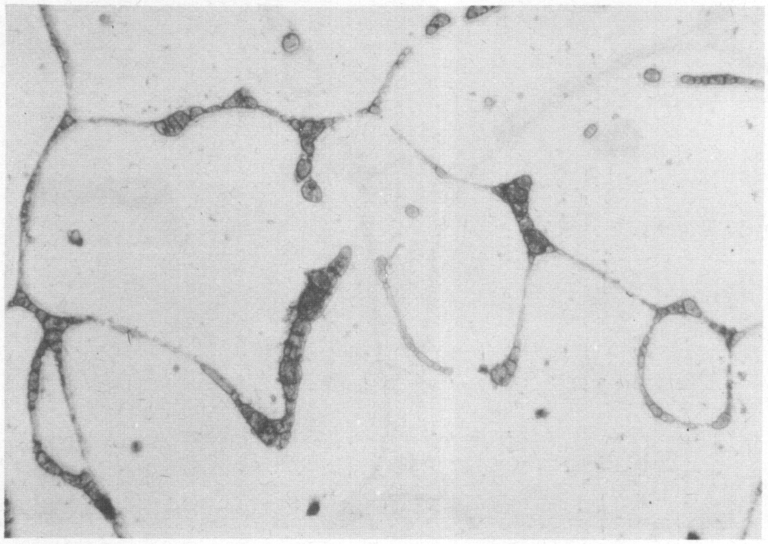

Figure 10

Negative No: 686 Magnification: 500X
Specimen No: 2622 Etch: 10 sec. glycol

As-cast microstructure of alloy R-1382 (magnesium - 1.0% nickel - 0.7% zirconium, intended) showing magnesium - nickel eutectic dispersed throughout the interstities of solid solution dendrites. The zirconium had no apparent effect on the microstructure of the magnesium-nickel alloy.

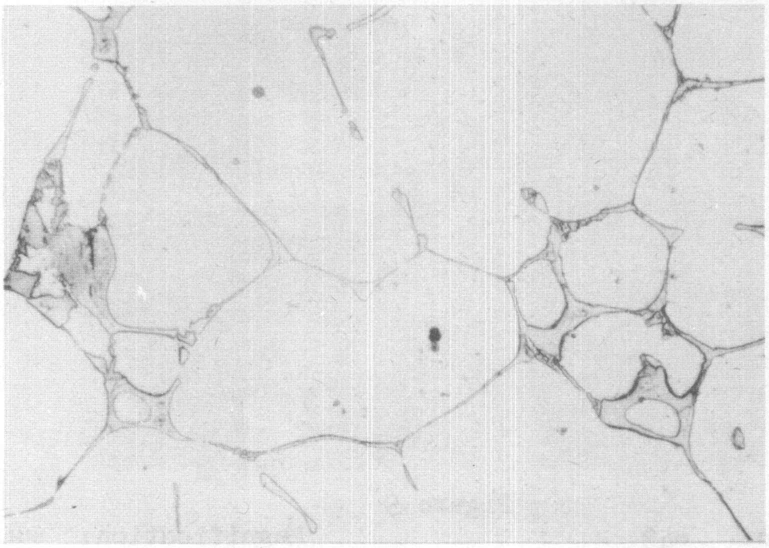

Figure 11

Negative No: 689 | Magnification: 500X
Specimen No. 2623 | Etch: 10 sec. glycol

As-cast microstructure of alloy R-1383 (magnesium - 0.7% zirconium - 3.0% zinc - 1.0% nickel, intended) showing an interdendritic network believed to be made up of both zinc rich and nickel rich phases.

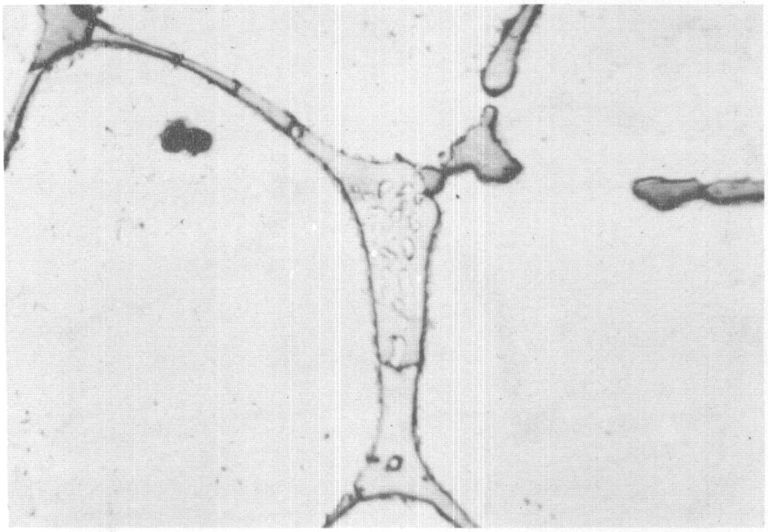

Figure 12

Negative No: 692 | Magnification: 2000X
Specimen No: 2623 | Etch: 10 sec. glycol

As-cast microstructure of same alloy and condition as Figure 11. The increased magnification and resolution illustrates the presence of a multiphase network.

tested following the procedures outlined in the Experimental Procedure section of this report. The results of these tests are reported in Table X.

TABLE X

MECHANICAL PROPERTIES OF BINARY MAGNESIUM-NICKEL AS-CAST TEST BARS

Alloy Number	Intended Nickel Addition wt.%	Mechanical Properties(a) Kips per sq.in. TYS	UTS	Elongation % in 2 in.
Mg (b)	-	3.0	12.0	6.0
R-1352	-	3.05	13.8	6.5
R-1314(c)	1.0 powder	2.24	17.1	8.7
R-1315(d)	1.0 powder	2.69	20.2	11.3
R-1316(e)	1.0 powder	2.73	20.2	8.7

(a) Properties reported are the average of two specimens for each alloy.

(b) Properties taken from "Metals Handbook" 1948, p.1014.

(c) Melt alloyed at 1700°F instead of 1500°F.

(d) Alloy superheated at 1850°F instead of 1700°F.

(e) Melt alloyed at 1700°F instead of 1500°F and superheating time extended from 15 to 30 minutes.

The data in Table X indicate that the intended addition of 1.0% nickel to magnesium improved the ultimate tensile strength and percentage elongation but lowered tensile yield strength compared to the properties reported for unalloyed magnesium. Mechanical properties for the experimental unalloyed magnesium agreed well with the handbook values for sand-cast magnesium. Due to limited experimental time a determination of the influence of nickel on the as-cast mechanical properties of magnesium alloys was not attempted.

The magnesium-nickel base alloys were hot rolled to 0.064 inch sheet and longitudinal mechanical properties were determined in the hot rolled condition following standard procedures described in the Experimental Procedure section of this report. A summary of the mechanical properties at room temperature is given in Table XI.

The addition of 2.2% nickel to magnesium, R-1238 and R-1239, increased the strength properties and the percentage elongation compared with commercial purity magnesium receiving the same mechanical and thermal treatment, R-1166. Compared with alloy R-1245 (magnesium - 1.2 manganese, intended), the nickel additions produced a similar strength increase and a greater increase in ductility than the manganese addition over the values of these properties for unalloyed magnesium, R-1166. The mechanical properties of the magnesium-nickel alloys R-1238 and R-1239 were comparable to values reported by McDonald[14].

Alloy R-1378 (magnesium - 1.2% manganese, 3.0% zinc, 0.1% nickel, intended) exhibited attractive strength properties in the hot rolled condition. It was noted that the nickel addition in alloy R-1381 (magnesium - 0.7% zirconium - 0.1% nickel intended) was associated with increased strength properties for the magnesium-zirconium base alloy. In both cases, however, no further increase in properties was observed with an increased nickel addition. It was believed that in the presence of certain alloying elements, the beneficial effect of adding nickel reached a maximum at some value below the 0.1% intended composition. It seems probable that this maximum value is near the maximum solid solubility of nickel in magnesium.

Elevated Temperature Mechanical Properties

The mechanical properties of selected magnesium-nickel base alloys at 400 and 500°F were determined following the method of tensile testing described in the Experimental Procedure section of this report. The results of these tests are given in Table XII. Specimen temperatures listed in Table XII were measured and followed throughout the testing cycle with a chromel alumel thermocouple touching the specimen.

The results in Table XII indicate that nickel raises the longitudinal mechanical properties of commercial purity magnesium, although the effect levels off at increasing nickel contents and in some instances even shows a tendency to decrease. The intended addition of 1.0% nickel to magnesium-manganese-zinc alloys raised considerably the longitudinal ultimate tensile strength at 400°F but the effect

TABLE XI

LONGITUDINAL ROOM TEMPERATURE MECHANICAL PROPERTIES OF 0.064 INCH MAGNESIUM-NICKEL ALLOY SHEET IN THE HOT-ROLLED CONDITION

Alloy Number	Intended Addition Weight Percent		Longitudinal Mechanical Properties(a) Kips per sq. in.			Elongation
	Nickel	Other	CYS	TYS	UTS	% in 2 in.
Pure Mg(b)	-	-	-	14.0	27.0	16.0
Pure Mg(c)	-	-	-	27.0	37.0	9.0
R-1166	-	-	9.3	18.0	25.3	7.5
R-1167	0.01 powder	-	9.1	16.3	24.2	5.0
R-1168	0.1 powder	-	9.9	16.8	24.4	10.0(d)
R-1169	1.0 powder	-	12.1	18.4	26.1	10.5(d)
R-1314	1.0 powder	-	10.6	19.2	26.9	6.5
R-1315	1.0 powder	-	10.4	19.3	26.9	5.5
R-1316	1.0 powder	-	10.2	20.1	27.1	5.3
R-1238	2.2 powder	-	13.0	19.6	29.2	9.2
R-1239	2.2 powder	-	14.1	20.1	29.1	9.0(d)
R-1170	0.01 hardener	-	9.4	17.1	24.2	10.0(d)
R-1171	0.1 hardener	-	10.4	16.5	24.3	11.5
R-1172	1.0 hardener	-	10.9	16.4	23.9	10.8
R-1173	0.14 $NiCl_2$	-	11.1	15.2	23.5	9.5
R-1174	1.0 $NiCl_2$	-	11.7(d)	17.7	23.8	10.0
R-1384	-	0.5Mn 3.0Zn	24.0	34.0	42.0	5.3
R-1380	1.0 powder	0.5Mn 3.0Zn	21.4(e)	30.9	37.8	2.7
R-1245	-	1.2Mn	13.2	20.1	28.5	5.5
R-1259	-	1.2Mn 3.0Zn	22.2	33.3	41.5	9.0
R-1378	0.1 powder	1.2Mn 3.0Zn	25.8	34.8	43.1	4.3
R-1379	1.0 powder	1.2Mn 3.0Zn	25.5	33.3	39.8	1.5
R-1385	-	0.7Zr	10.1	16.8	25.5	5.5
R-1381	0.1 powder	0.7Zr	11.4(d)	21.0	28.9	6.0(d)
R-1382	1.0 powder	0.7Zr	12.2	19.1	28.7	10.3
R-1341(f)	-	0.7Zr 3.0Zn	-	38.5	46.7	8.3
R-1383	1.0 powder	0.7Zr 3.0Zn	21.4(d)	29.3	36.8	5.3

(a) Notes are found on next page.

Notes Continued

(a) Properties reported are an average of three specimens for each alloy unless otherwise noted.

(b) Properties taken from "Metals Handbook" 1948, p.1014, annealed condition.

(c) Properties taken from "Metals Handbook" 1948, p.1014, hard rolled condition.

(d) Properties reported are an average of two specimens for each alloy.

(e) Properties reported are for one specimen for each alloy.

(f) Alloy melted following Melt Procedure II given in the Experimental Procedure section of this report.

TABLE XII

LONGITUDINAL ELEVATED TEMPERATURE MECHANICAL PROPERTIES OF 0.064 INCH MAGNESIUM-NICKEL ALLOY SHEET IN THE HOT-ROLLED CONDITION

	Intended Composition Weight Percent		Specimen Temperature	Longitudinal Mechanical Properties (a)	
Alloy Number	Nickel	Other	± 5°F	Kips per sq.in. UTS	Elongation % in 2 in.
FS1-0	-	3.0Al 1.0Zn 0.2Mn	400	20.0	18.0
			500	18.0	46.0(b)
FS1-H24	-	3.0Al 1.0Zn 0.2Mn	400	21.4	14.0
			500	17.3	43.5
R-1166	-	-	405	15.2	20.0
			498	11.5	28.0
R-1168	0.10 powder	-	400	19.1	12.0
			500	14.9	27.5
R-1169	1.0 powder	-	400	14.4(b)	21.0
			502	15.6	32.5
R-1238	2.2 powder	-	400	18.2	21.0
			502	14.9	42.5
R-1384	-	0.5Mn 3.0Zn	400	23.7	20.0
			498	18.7	21.0
R-1380	1.0 powder	0.5Mn 3.0Zn	400	25.0	21.0
			500	15.8	34.5
R-1259	-	1.2Mn 3.0Zn	400	23.2	21.0
			502	19.3	22.5
R-1379	1.0 powder	1.2Mn 3.0Zn	400	29.1	22.0
			502	20.4	22.5
R-1385	-	0.7Zr	402	15.9	13.0
			500	13.6	17.0

TABLE XII (Continued)

LONGITUDINAL ELEVATED TEMPERATURE MECHANICAL PROPERTIES OF 0.064 INCH MAGNESIUM-NICKEL ALLOY SHEET IN THE HOT-ROLLED CONDITION

Alloy Number	Intended Composition Weight Percent		Specimen Temperature ± 5°F	Longitudinal Mechanical Properties (a)	
	Nickel	Other		Kips per sq.in. UTS	Elongation % in 2 in.
R-1382	1.0 powder	0.7Zr	400	18.5	19.5
			502	15.4	28.0
R-1341(c)	-	0.7Zr 3.0Zn	398	25.8	22.5
			502	24.4	41.5
R-1383	1.0 powder	0.7Zr 3.0Zn	400	19.4	21.0
			502	15.2	15.5

(a) Properties reported are for one specimen for each alloy.

(b) Results are in doubt due to testing irregularities.

(c) Alloy melted using Melt Procedure II.

was nullified when the temperature was raised to 500°F, as observed in alloys R-1384, R-1380, R-1259, and R-1379. It was observed that an intended addition of 1.0% nickel raised the elevated temperature properties of the magnesium - 0.7% zirconium intended alloy (R-1385 and R-1382), but reduced significantly the elevated temperature properties of the magnesium - 0.7% zirconium - 3.0% zinc, intended alloy (R-1341 and R-1383).

Resistance to Corrosion

Standard static resistance to corrosion tests were performed on the magnesium base nickel alloys following the method given in the Experimental Procedure section of this report. The results of these tests are summarized in Table XIII.

Summary

Twenty alloys were prepared by adding nickel to magnesium and to selected magnesium alloys with manganese, zinc and zirconium additions. The addition of nickel as a six micron powder resulted in the greatest recovery of this element in comparison with other methods of addition. Nickel additions produced a small or moderate refinement of primary grain structure. Microstructural evidence of nickel was the presence of a eutectic in the interstices of primary dendrites. Zirconium produced no recognized structural effect on this condition but the combined addition of zinc and zirconium with nickel produced a relatively massive multiphase interdendritic network.

Mechanical properties of hot rolled sheet at room temperature indicated that an intended addition of 2.2% nickel increased the tensile properties a small amount and the compressive yield strength and percentage elongation a significant amount compared with unalloyed magnesium receiving the same mechanical and thermal treatments. This change was slightly greater than obtained with a magnesium - 1.2% manganese binary alloy. An addition of 0.1% nickel to magnesium base alloys with manganese, zinc and zirconium produced moderate strength and percentage elongation increases; a nickel addition of 1% to these same alloys produced no additional increase in mechanical properties, indicating a threshold of effectiveness near 0.1% nickel.

The tensile mechanical properties of hot rolled sheet at 400°F were improved by additions of nickel to magnesium and to magnesium alloys containing manganese and zinc and zirconium but decreased these properties for alloys containing zinc and zirconium. These beneficial effects were not realized at the testing temperature of 500°F.

The relative resistance to corrosion was sharply decreased by nickel additions to experimental alloys, a result with ample agreement in the literature.

TABLE XIII

RELATIVE RESISTANCE TO CORROSION OF 0.064 INCH HOT-ROLLED MAGNESIUM-NICKEL ALLOY SHEET COMPARED TO COMMERCIAL FS1-0 ALLOY SHEET

Alloy Number	Intended Addition Weight Percent		Nickel Analysis Weight Percent	Relative Resistance to Corrosion (a)
	Nickel	Other		
R-1166	-	-	None	2
R-1167	0.01 powder	-	None	3
R-1168	0.1 powder	-	0.13	5
R-1169	1.0 powder	-	0.96	5
R-1314	1.0 powder	-	-	5
R-1315	1.0 powder	-	-	5
R-1316	1.0 powder	-	-	5
R-1238	2.2 powder	-	-	5
R-1239	2.2 powder	-	-	5
R-1170	0.01 hardener	-	0.02	4
R-1171	0.10 hardener	-	0.10	5
R-1172	1.0 hardener	-	0.47	5
R-1173	0.14 $NiCl_2$	-	0.10	5
R-1174	1.0 $NiCl_2$	-	0.66	5
R-1384	-	0.5Mn 3.0Zn	-	3
R-1380	1.0 powder	0.5Mn 3.0Zn	-	5
R-1259	-	1.2Mn 3.0Zn	-	4
R-1378	0.1 powder	1.2Mn 3.0Zn	-	3
R-1379	1.0 powder	1.2Mn 3.0Zn	-	5
R-1385	-	0.7Zr	-	1
R-1381	0.1 powder	0.7Zr	-	5
R-1382	1.0 powder	0.7Zr	-	5
R-1341(b)	-	0.7Zr 3.0Zn	-	3
R-1383	1.0 powder	0.7Zr 3.0Zn	-	5

(a) Relative resistance to corrosion symbols explained in the Experimental Procedure section of this report.

(b) Alloy melted following Melt Procedure II.

MAGNESIUM - COBALT ALLOYS

Review of Literature

Carapella[4] reported that cobalt has an unfavorable size factor for alloying with magnesium, is hexagonal close-packed in structure, and has an alloying valence of zero. From these data it was expected that cobalt would show limited, if any, solid solubility in magnesium. Alico[11] stated that there is a tendency for the solubility of a metal in magnesium to increase with increasing temperature if the size factor is unfavorable for room temperature solubility of the metal in magnesium.

Wetherill[19], in 1935, published results of investigations on a series of magnesium-cobalt alloys. These alloys had a maximum cobalt analysis of 4.79 weight percent. Wetherill stated that a "probable eutectic" was indicated at 1175°F and approximately 5.0% cobalt. The amount of cobalt in the final alloy was dependent on the temperature reached during melting and the time at this temperature, increasing as these factors increased. Metallic cobalt was added to molten magnesium in these investigations under a chloride-flouride flux covering.

Shul'gin[20], in 1940, studied magnesium-cobalt alloys melted in air and in a vacuum. The resulting alloys were tested at room and elevated temperatures in the as-cast, as-forged and heat treated conditions. Cobalt additions to 0.62% were studied and it was found that the additions had little effect on the mechanical properties. Metallographic examination showed no free cobalt in any alloy in any condition.

Grube and coworkers[15], in 1946, stated that cobalt improved the room temperature tensile properties, while increasing the grain size of magnesium base alloys. An alloy of 1.5% cobalt, 10.0% cerium, 2.0% manganese, balance magnesium, produced good tensile properties at room temperature and at 600°F.

Beck[21] states that cobalt is insoluble in magnesium and has a negligible effect on the hardness and strength of magnesium. Beck also states that cobalt increases the risk of corrosion and should not be used in magnesium alloys.

Preparation of Alloys

Fifteen large melts were made in the magnesium-cobalt alloy series, following Melt Proedure I outlined in the Experimental Procedure section of this report. The cobalt additions were made in the form of a metallic powder or an anhydrous cobaltous chloride. The cobalt metal powder was nickel free, cobalt metal, C.P. grade(a). The cobaltous chloride used was certified 99.9% purity with the major impurity being nickel. The alloying additions were submerged beneath the melt surface wrapped in either paper or zinc foil, depending on whether zinc was an intended alloying element or not. The addition was stirred into the melt for approximately one minute. No trouble was encountered in making these alloys. The cobalt additions were made to base alloys containing varying amounts of magnesium, zinc, zirconium, and manganese. These data are assembled in Table XIV. The zirconium was added as Dow K30 master alloy, containing nominally 30% zirconium.

Chemical Analysis

Chemical analyses were performed on selected magnesium-cobalt alloys to determine the best method for alloying cobalt to magnesium. The analyses were performed on sections of the slab casting risers, adjacent to the rolling billet. The method of analysis is given in Appendix II. The results of the analysis are listed in Table XIV. The results in Table XIV indicated that the best method of addition of cobalt to magnesium, with regard to the percent recovery, was as a fine metallic powder. This conclusion was based on a comparison of the percent recovery of alloys R-1186 and R-1191 where the higher cobalt intended concentrations would tend to minimize any error occurring from cobalt pick up from the previous melts.

As-Cast Grain Size

The results of as-cast grain size determinations on the equiaxed structures of the magnesium-cobalt alloy series are given in Table XIV. The grain size determinations were made on metallographic specimens taken in accordance with the standardized procedures from the center of the riser of the rolling slab mold, adjacent to the slab. No definite trend was observed for the effect of cobalt on the grain size of magnesium base alloys. It was noted, however, that the as-cast grain size of the magnesium - 0.7%

(a) Obtained from the Fisher Scientific Company

TABLE XIV

MELTING AND CASTING CONDITIONS AND AS-CAST GRAIN SIZE FOR EXPERIMENTAL MAGNESIUM-COBALT ALLOYS

Alloy Number	Intended Addition Weight Percent		Cobalt Analysis Weight Percent(a)	Cobalt Added As	Average Grain Diameter Inches
	Cobalt	Other			
R-1184	-	-	None	-	0.027
R-1185	0.1	-	0.022	powder	0.023-0.040
R-1186	1.0	-	0.39	powder	0.040
R-1190	0.04	-	0.012	$CoCl_2$	0.040
R-1191	0.86	-	0.13	$CoCl_2$	0.027
R-1317	0.1	-	-	$CoCl_2$	0.045
R-1384	-	0.5Mn 3.0Zn	-	-	0.005
R-1367	1.0	0.5Mn 3.0Zn	-	powder	0.005
R-1259	-	1.2Mn 3.0Zn	-	-	0.007
R-1365	0.1	1.2Mn 3.0Zn	-	powder	0.009
R-1366	1.0	1.2Mn 3.0Zn	-	powder	0.007
R-1385	-	0.7Zr	-	-	0.050
R-1375	0.1	0.7Zr	-	powder	0.045
R-1376	1.0	0.7Zr	-	powder	0.025
R-1341(b)	-	0.7Zr 3.0Zn	-	-	0.003
R-1377	1.0	0.7Zr 3.0Zn	-	powder	0.008

(a) Cobalt analysis determined by the procedure given in Appendix II.

(b) Melt made using Melt Procedure II.

intended zirconium base alloys decreased with increasing cobalt content. The opposite effect was observed with the addition of 3.0% zinc to the base alloy.

Metallographic Observations

As-cast metallographic specimens of the cobalt containing magnesium base alloys showed that the cobalt was distributed throughout the castings as an intergranular and to a lesser extent an interdendritic constituent assumed to be cobalt-rich. Figure 13 shows the as-cast microstructure of alloy R-1186 (magnesium - 0.39% cobalt analysis). The cobalt-constituent was observed at the grain boundaries and to some extent along an interdendritic network. Figure 14 shows this cobalt constituent at a magnification of 2000X. The cobalt-rich particles were resolved and clearly seen. Figure 15 illustrates the effect of hot rolling on the microstructure of the alloy shown in Figures 13 and 14. The cobalt constituent was strung out in the direction of rolling.

The as-cast microstructure of alloy R-1367 (magnesium - 0.5% manganese, 3.0% zinc, and 1.0% cobalt intended) is shown in Figure 16. The zinc addition did not produce a recognized influence on the distribution of the cobalt constituent. The usual coring around the zinc containing phase in a magnesium alloy was noted in this specimen but is not clearly defined in Figure 16.

Wetherill[19] reported a microstructure of magnesium-cobalt alloys similar to the magnesium-copper eutectic. This is essentially the same microstructure as shown in Figures 13 and 14 of this report. It is therefore believed that the cobalt in the as-cast magnesium base alloys used in this investigation was distributed along grain boundaries and to some extent interdendritically in the form of a eutectic.

Mechanical Properties at Room Temperature

As-cast mechanical properties were determined for several magnesium base cobalt alloys. Two tensile bars for each melt were cast in a baked sand mold and were tested following procedures outlined in the Experimental Procedure section of this report. The results of these tests are given in Table XV.

The results in Table XV indicate that the addition of 1.0% cobalt as a powder to magnesium increased the as-cast tensile properties moderately. It was observed that the addition of 1.0% cobalt powder to a magnesium- 1.2%

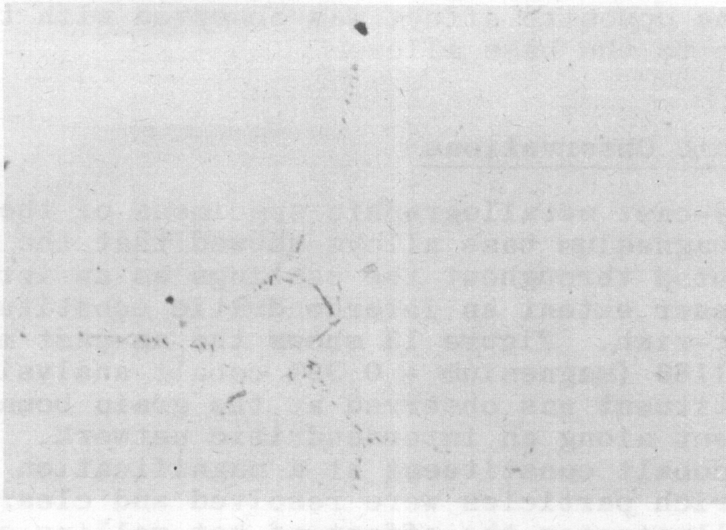

Figure 13

Negative No: 657 Magnification: 500X
Specimen No: 2357 Etch: As-polished

As-cast microstructure of alloy R-1186 (magnesium - 0.39% cobalt analyzed) showing the cobalt constituent distributed primarily along grain boundaries.

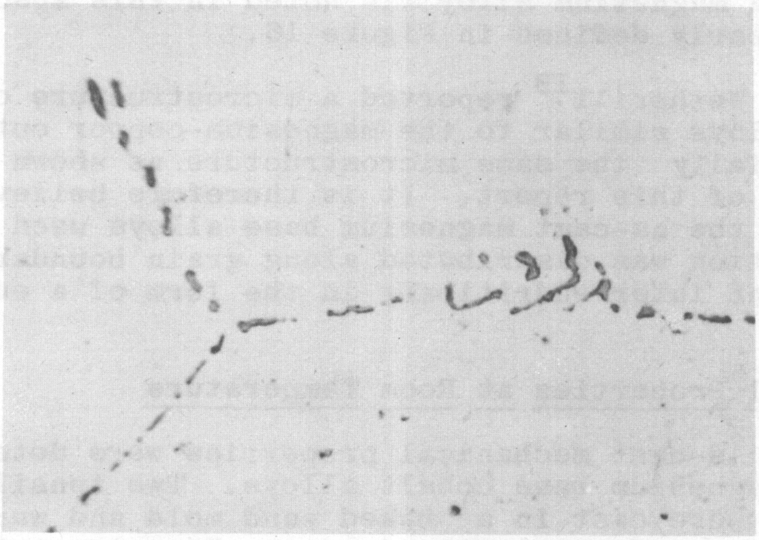

Figure 14

Negative No: 614 Magnification: 2000X
Specimen No: 2357 Etch: As-polished

As-cast microstructure of alloy R-1186 (magnesium - 0.39% cobalt analyzed) is shown with the cobalt constituent clearly resolved.

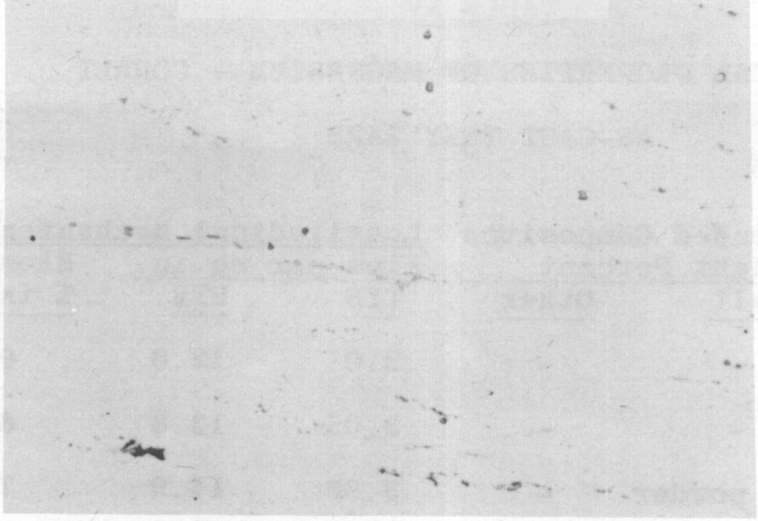

Figure 15

Negative No: 644	Magnification: 500X
Specimen No: 2508	Etch: As-polished

Longitudinal section of as-hot rolled microstructure of alloy R-1186 (magnesium - 0.39% cobalt analyzed) revealing the creak down of the as-cast cobalt phase distribution into stringers which are aligned with the rolling direction.

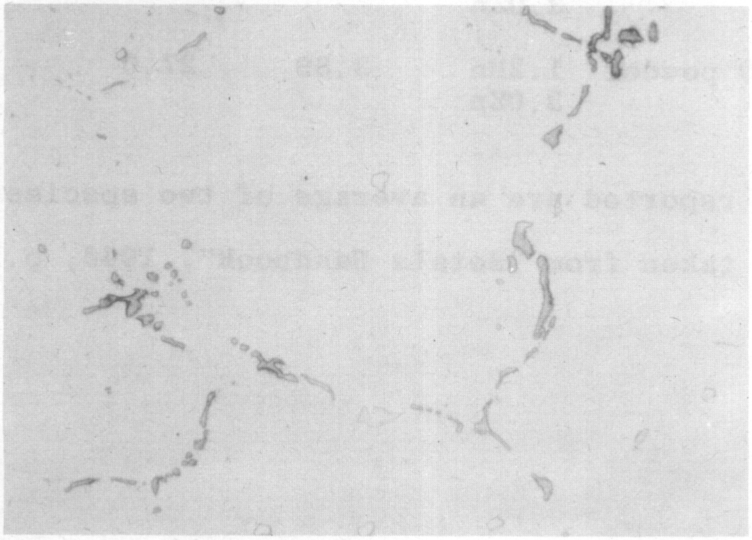

Figure 16

Negative No: 688	Magnification: 500X
Specimen No: 2611	Etch: 10 sec. glycol

As-cast microstructure of alloy R-1367 (magnesium - 0.5% manganese - 3.0% zinc - 1.0% cobalt intended) showing the white zinc and the dark cobalt containing phases.

TABLE XV

MECHANICAL PROPERTIES OF MAGNESIUM - COBALT

AS-CAST TEST BARS

	Intended Composition Weight Percent		Longitudinal Mechanical Properties(a)		
			Kips per sq.in.		Elongation
Alloy Number	Cobalt	Other	TYS	UTS	% in 2 in.
Pure Mg(b)	-	-	3.0	12.0	6.0
R-1352	-	-	3.05	13.8	6.5
R-1186	1.0 powder	-	3.96	14.9	7.5
R-1190	0.04 $CoCl_2$	-	3.47	12.4	4.0
R-1191	0.86 $CoCl_2$	-	2.65	10.9	6.7
R-1317	0.1 $CoCl_2$	-	1.48	13.9	7.5
R-1259	-	1.2Mn 3.0Zn	4.52	23.8	6.7
R-1365	0.1 powder	1.2Mn 3.0Zn	3.77	23.3	7.5
R-1366	1.0 powder	1.2Mn 3.0Zn	3.89	27.0	12.2

(a) Properties reported are an average of two specimens.

(b) Properties taken from "Metals Handbook", 1948, p.1014.

manganese - 3.0% zinc alloy increased the ultimate tensile strength and percentage elongation but decreased the tensile yield strength.

The magnesium-cobalt alloys were hot rolled to 0.064 inch sheet and longitudinal mechanical properties were determined in the hot rolled condition following standard procedures described in the Experimental Procedure section of this report. A summary of the mechanical properties at room temperature is given in Table XVI. The results in Table XVI indicate that cobalt showed no consistent beneficial effect on the room temperature mechanical properties of the magnesium base alloys used in this investigation. An elevation of the strength properties for the alloy containing 1.2% manganese and 3.0% zinc was noted with the cobalt addition. The strength elevation was not increased with increasing cobalt content but the effect was consistent over all cobalt contents. A check on the as-cast grain sizes of these alloys showed that the increased strength properties were not associated with a significant trend in the as-cast grain sizes.

The addition of cobalt to a magnesium base alloy containing 0.7% zirconium and 3.0% zinc, lowered significantly the tensile yield and ultimate tensile strengths of the alloy. The as-cast grain size of the alloy was increased from 0.003 inches to 0.008 inches with the addition of 1.0% cobalt. The decrease in the strength properties of the alloy may have been related to increased as-cast grain size with the addition of 1.0% cobalt.

Mechanical Properties at Elevated Temperatures

Mechanical properties at elevated temperatures were determined for selected magnesium - cobalt alloys following procedures outlined in the Experimental Procedure section of this report. The results of these tests are given in Table XVII. No significant improvement in mechanical properties was observed for cobalt additions to the alloys studied except for the magnesium - 0.7 zirconium alloy.

Resistance to Corrosion

Standard static resistance to corrosion tests were performed on the magnesium cobalt alloys. The details of this test are given in the Experimental Procedure section of this report. The results for the magnesium cobalt alloys are reported in Table XVIII. The results of Table XVIII show that cobalt generally decreased the resistance to cor-

TABLE XVI

ROOM TEMPERATURE MECHANICAL PROPERTIES OF 0.064 INCH MAGNESIUM - COBALT ALLOY SHEET IN THE HOT-ROLLED CONDITION

Alloy Number	Intended Addition Weight Percent		Longitudinal Mechanical Properties(a)			
			Kips per sq. in.			Elongation % in 2 in.
	Cobalt	Other	CYS	TYS	UTS	
Pure Mg(b)	-	-	-	14.0	27.0	16.0
Pure Mg(c)	-	-	-	27.0	37.0	9.0
R-1184	-	-	9.6	15.6	23.9	7.8
R-1185	0.1 powder	-	9.9	16.2	23.2	8.2
R-1186	1.0 powder	-	11.0	17.1	23.7	11.2
R-1190	0.04 $CoCl_2$	-	9.5	15.5(e)	22.9	8.7
R-1191	0.86 $CoCl_2$	-	11.0	17.0	24.0	11.5
R-1317	0.1 $CoCl_2$	-	8.4	17.7	25.9	5.2
R-1384	-	0.5Mn 3.0Zn	24.0	34.0	42.0	5.3
R-1367	1.0 powder	0.5Mn 3.0Zn	22.1	32.8	40.0	4.5
R-1259	-	1.2Mn 3.0Zn	22.2	33.3	41.5	9.0
R-1365	0.1 powder	1.2Mn 3.0Zn	25.6	35.5	43.5	5.7
R-1366	1.0 powder	1.2Mn 3.0Zn	24.9	35.3	42.8	6.8
R-1385	-	0.7Zr	10.1	16.8	25.5	5.5
R-1375	0.1 powder	0.7Zr	13.0	16.3	25.6	5.8
R-1376	1.0 powder	0.7Zr	11.3	17.7	26.7	10.0
R-1341(d)	-	0.7Zr 3.0Zn	-	38.5	46.7	8.3
R-1377	1.0 powder	0.7Zr 3.0Zn	20.6	31.7	39.1	7.8

(a) Notes are found on following page.

TABLE XVI (Continued)

ROOM TEMPERATURE MECHANICAL PROPERTIES OF 0.064 INCH MAGNESIUM - COBALT ALLOY SHEET IN THE HOT-ROLLED CONDITION

(a) Properties reported are an average of three specimens for each alloy unless otherwise noted.

(b) Properties taken from "Metals Handbook", 1948, p.1014, annealed condition.

(c) Properties taken from "Metals Handbook", 1948, p.1014, hard rolled condition.

(d) Alloy melted in graphite crucible following Melt Procedure II.

(e) Properties reported are an average of two specimens.

TABLE XVII

LONGITUDINAL ELEVATED TEMPERATURE MECHANICAL PROPERTIES OF 0.064 INCH MAGNESIUM-COBALT ALLOY SHEET IN THE HOT-ROLLED CONDITION

Alloy Number	Intended Addition Weight Percent		Specimen Temperature ± 5°F	Longitudinal Mechanical Properties (a)	
	Cobalt	Other		Kips per sq.in. UTS	Elongation % in 2 in.
FS1-0	-	-	400	20.0	18.0
			500	18.0	46.0 (b)
FS1-H24	-	-	400	21.4	14.0
			500	17.3	43.5
R-1166	-	-	405	15.2	20.0
			498	11.5	28.0
R-1185	0.1 powder	-	402	15.9	13.0
			502	12.6	16.5
R-1186	1.0 powder	-	398	15.3	12.5
			500	13.2	22.0
R-1384	-	0.5Mn 3.0Zn	400	23.7	20.0
			498	18.7	21.0
R-1367	1.0 powder	0.5Mn 3.0Zn	400	22.9	21
			502	15.0	[illegible].5
R-1259	-	1.2Mn 3.0Zn	400	23.2	21.0
			502	19.3	22.5
R-1366	1.0 powder	1.2Mn 3.0Zn	400	22.4	21.0
			498	20.7	25.0
R-1385	-	0.7Zr	402	15.9	13.0
			500	13.6	17.0
R-1376	1.0 powder	0.7Zr	398	20.7	12.5
			500	14.4	26.0
R-1341(c)	-	0.7Zr 3.0Zn	398	25.8	22.5
			502	24.4	41.5

TABLE XVII (Continued)

LONGITUDINAL ELEVATED TEMPERATURE MECHANICAL PROPERTIES OF 0.064 INCH MAGNESIUM-COBALT ALLOY SHEET IN THE HOT-ROLLED CONDITION

Alloy Number	Intended Addition Weight Percent Cobalt	 Other	Specimen Temperature ± 5 °F	Longitudinal Mechanical Properties (a) Kips per sq.in. UTS	 Elongation % in 2 in.
R-1377	1.0 powder	0.7Zr 3.0Zn	398	26.7	26.5
			502	18.7	25.0

(a) Properties reported are the result of one specimen for each alloy.

(b) Result in doubt due to testing irregularities.

(c) Alloy melted following Melt Procedure II.

TABLE XVIII

RELATIVE RESISTANCE TO CORROSION OF 0.064 INCH HOT-ROLLED MAGNESIUM - COBALT ALLOY SHEET COMPARED TO COMMERCIAL FS1-0 ALLOY SHEET

Alloy Number	Intended Addition Weight Percent Cobalt	Intended Addition Weight Percent Other	Cobalt Analysis Weight Percent	Relative Resistance to Corrosion(a)
R-1184	-	-	None	3
R-1185	0.1 powder	-	0.022	5
R-1186	1.0 powder	-	0.39	5
R-1190	0.04 $CoCl_2$	-	0.012	4
R-1191	0.86 $CoCl_2$	-	0.13	5
R-1317	0.1 $CoCl_2$	-	-	5
R-1384	-	0.5Mn 3.0Zn	-	3
R-1367	1.0 powder	0.5Mn 3.0Zn	-	4
R-1259	-	1.2Mn 3.0Zn	-	4
R-1365	0.1 powder	1.2Mn 3.0Zn	-	4
R-1366	1.0 powder	1.2Mn 3.0Zn	-	4
R-1385	-	0.7Zr	-	1
R-1375	0.1 powder	0.7Zr	-	4
R-1376	1.0 powder	0.7Zr	-	5
R-1341(b)	-	0.7Zr 3.0Zn	-	3
R-1377	1.0 powder	0.7Zr 3.0Zn	-	3

(a) The relative resistance to corrosion was determined according to the scheme outlined in the Experimental Procedure section of this report.

(b) Alloy melted in graphite crucible following Melt Procedure II.

rosion of the magnesium base alloys used in this investigation. In no instance did cobalt improve the corrosion resistance of a magnesium base alloy although in some instances the presence of 3.0% zinc did serve to reduce considerably the deleterious effect of the cobalt.

Summary

Fifteen large melts were made in the magnesium-cobalt alloy series. Cobalt additions in the form of a metallic powder resulted in the best percentage recovery. No definite trend was noted for the effect of cobalt on the as-cast grain size of magnesium base alloys. Metallographic observations indicated that the cobalt was dispersed throughout the castings as a cobalt rich interdendritic and intergranular constituent.

Cobalt increased the as-cast tensile strength of magnesium base alloys but had slight effect on the tensile yield strength. Cobalt showed no consistent beneficial effect on the as-hot rolled mechanical properties of magnesium base alloys. No beneficial effect of cobalt was observed on the elevated temperature properties of magnesium base alloys. It was noted, however, that cobalt increased the tensile strength of a magnesium-0.7% zirconium alloy at 400°F.

Cobalt was found to decrease the corrosion resistance of magnesium base alloys.

MAGNESIUM - VANADIUM ALLOYS

Review of Literature

Vanadium is a Group V transition metal with an alloying valence of zero, a body centered cubic crystal structure and a density of 6.0. Its melting point is 3150°F, ± 90°F[24]; which is higher than that of any of the common alloying elements in magnesium.

Vanadium has an unfavorable atomic size factor for appreciable solubility in magnesium according to Carapella[4]. The Dow Chemical Company[25] has reported that vanadium alloys with magnesium only to a few hundredths percent at the most. They added vanadium to magnesium in amounts up to one percent. No data could be found in the literature on the effects of vanadium on the mechanical properties or resistance to corrosion of magnesium.

Preparation of Experimental Alloys

Eight experimental alloys were cast containing additions of vanadium. All were prepared essentially according to the standardized Melt Procedure I described in the Experimental Procedure section of this report. Minor deviations from this procedure are described below. Alloys were fabricated into 0.064 inch sheet and tested for mechanical properties and resistance to corrosion according to the standard procedures described in the Experimental Procedure section.

Aluminum additions were in the form of Alcoa commercial purity pig specified to be greater than 99% aluminum. Zinc was added as New Jersey Zinc Horsehead Special grade pig specified to be greater than 99.99% zinc.

Vanadium was added in three different forms: vanadium metal powder, aluminum-vanadium master alloy and divanadyl tetrachloride. The recovery of vanadium was not investigated by spectrographic or chemical means and no conclusions as to the relative effectiveness of the different forms of additions were justified from the limited metallographic evidence of vanadium. The vanadium metal powder(a) was 20 mesh size and specified to be 99.5% pure. The aluminum-vanadium master alloy(b) was eight mesh size and had the following specified analysis:

(a) Supplied by A. D. Mackay, Inc., 198 Broadway, New York 38, New York.

(b) Supplied by Electro Metallurgical Company, Niagara Falls, New York.

Vanadium	80 - 85%
Aluminum	12 - 16%
Silicon	1% (approximately)
Iron	1% (approximately)
Oxygen	0.25% (approximately)

The divanadyl tetrachloride[a] was specified to be chemically pure.

Divanadyl tetrachloride and aluminum-vanadium master alloy additions were wrapped in paper and stirred into the melt. All alloy additions were added at 1450°F prior to superheating. The melts were then stirred for approximately two minutes, skimmed, refluxed and finally superheated 10 minutes at 1650°F. The only exception to this schedule was alloy R-1165 (Dow Pure -0.30% Vanadium) which was alloyed at 1600°F and superheated 15 minutes at 1700°F.

Chlorine gas fluxing, where carried out, was started immediately after the melt temperature reached 1450°F and continued for five minutes with the furnace turned off. It was found that the melt cooled to approximately 1400°F during chlorination. After this treatment the melt was again brought up to 1450°F and the alloy additions were added. The chlorination apparatus and procedure are described in detail in the Magnesium-Chromium Alloys section of this report.

A summary of the alloys prepared and their melting and casting conditions and as-cast grain size is given in Table XIX.

Metallographic Observations

Examination of the as-cast microstructure of magnesium-vanadium binary and magnesium-vanadium-aluminum ternary alloys revealed what appeared at low magnification to be many small, round pits scattered across the specimen surface. This condition was evident on both as-polished and etched surfaces and could not be eliminated by etching and repolishing with extreme care to avoid pitting attack. The number of pits observed in the microstructure increased with increasing intended vanadium content and they were therefore believed to be

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(a) Supplied by A. D. Mackay, Inc., 198 Broadway, New York 38, New York.

TABLE XIX

MELTING AND CASTING CONDITIONS AND AS-CAST GRAIN SIZE FOR EXPERIMENTAL MAGNESIUM-VANADIUM ALLOYS

Alloy Number	Intended Additions Weight Percent V	Intended Additions Weight Percent Other	Melt Procedure(a)	Vanadium Added As	Average Grain Diameter, Inches
R-1352	-	-	B	-	Large, Columnar
R-1165	0.30	-	A	$(VO)_2Cl_4$	0.060(b)
R-1410	0.50	-	A	$(VO)_2Cl_4$	0.075
R-1411	0.50	-	A	Powder	0.050(b)
R-1423	0.50	0.09Al	A	Master Alloy	0.040(b)
R-1424	1.00	0.17Al	A	Master Alloy	0.060(b)
R-1364	-	3.00Al 1.00Zn 0.50Mn	B	-	0.011
R-1429	0.30	3.00Al 1.00Zn 0.30Mn	B	Master Alloy	0.005
R-1427	0.50	3.00Al 1.00Zn 0.30Mn	B	Master Alloy	0.006
R-1428	1.00	3.00Al 1.00Zn 0.30Mn	B	Master Alloy	0.004

(a) Melt Procedures are given in the Experimental Procedure section of this report.
A means Melt Procedure I.
B means Melt Procedure I with five minutes of chlorination at 1450°F prior to alloying.

(b) Grain size determined on equiaxed grains in center of casting cross section. Grains at edges of casting were predominantly large and columnar.

associated with the vanadium in the alloys. The appearance of this condition is shown in Figure 17 which is a photomicrograph of the as-cast structure of alloy R-1165 (Magnesium -0.30% Vanadium, intended).

Investigation of this condition at high magnification showed that each of the pits was centered about a tiny particle and that the circular area around the particle was broad and usually darker than the particle itself as well as the surrounding matrix. In many cases this dark area consisted of concentric light and dark rings. The outer edge in all cases was a nearly perfect circle. The depth of pitting was not over about 0.002 millimeters and most of the cross-section of the pit except for a thin ring adjacent to the central particle could be brought into clear focus with the surrounding surface area at magnifications as high as 800X. The appearance of several of the pits is shown at this magnification in Figure 18.

Two different mechanisms were considered as possibly being the cause of this condition. The first was that tiny particles of vanadium or a foreign constituent related to the vanadium addition were nucleated and precipitated during freezing. According to this mechanism of formation the dark annular rings surrounding the particles were not a true structural condition but an artifact caused by electrochemical or mechanical attack of the surrounding matrix specimen preparation. The second mechanism considered was that vanadium formed a peritectic with magnesium and that the small particles were the peritectic constituent and the annular rings were evidence of peritectic walling.

Lack of experimental time precluded further investigation of this condition and no additional data fostering either mechanism was obtained. It was noted, however, that the fact that the condition showed up in the as-polished as well as the etched condition was contrary to the peritectic reaction mechanism because peritectic walling would normally be revealed only by etching. On the other hand, the perfectly round shape of the dark annular rings and the fact that the depth differential over their broad surface was fairly constant and of small magnitude was considered equally contrary to a mechanism involving pit formation by mechanical erosion or electrochemical attack. The foreign particle precipitation mechanism was, therefore, also considered inadequate to completely explain the observed condition.

Microscopic examination of AZ31 base alloys to which vanadium had been added did not reveal any of the small pits. Figure 19 is a photomicrograph of alloy

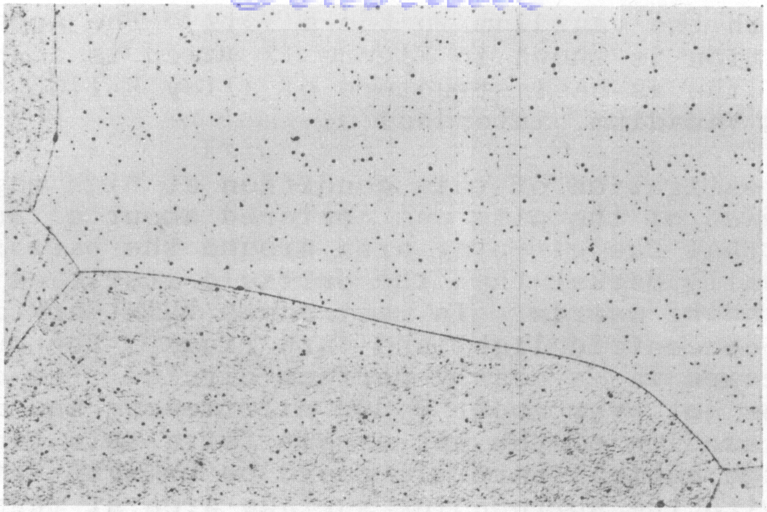

Figure 17

Negative No:	695	Filter:	Wratten	Magnification:	100X
Specimen No:	2722		58B	Etch:	15 sec. in acetic glycol

As-cast microstructure of alloy R-1165 (magnesium - 0.30% vanadium, intended) showing typical appearance of small pits found in alloys containing vanadium.

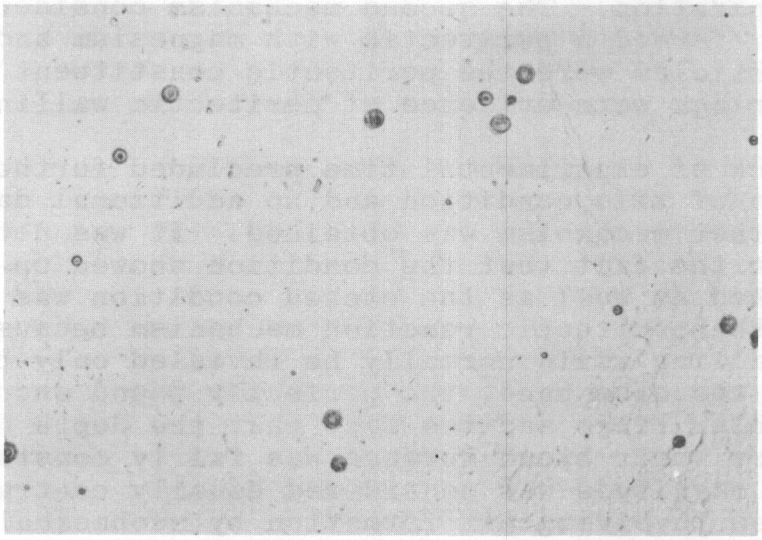

Figure 18

Negative No:	696	Filter:	Wratten	Magnification:	800X
Specimen No:	2722		47	Etch:	15 sec. in acetic glycol

As-cast microstructure of alloy R-1165 showing the same condition as in Figure 17 but at a higher magnification to illustrate the presence of a tiny microconstituent in the center of each depression and the broad, shallow appearance of the annular rings.

R-1428 (AZ31 - 0.3% Manganese - 1.0% Vanadium) in the as-cast condition. Either the vanadium constituent was soluble in this case or it formed an intermetallic compound with manganese or zinc and settled out of the melt. Examination of as-hot rolled microstructure was carried out on representative alloys. Of significance was the fact that the small, shallow pits observed in the as-cast microstructures of alloys of magnesium-vanadium and magnesium-aluminum-vanadium were not evident after hot rolling. The appearance of the as-hot rolled microstructure of alloy R-1423 (Magnesium - 0.50% Vanadium - 0.09% Aluminum, intended) is shown in Figure 20. The extremely fine grain size of this alloy considering the small aluminum content was thought to be due primarily to the vanadium addition.

Grain Refining Effect of Vanadium Additions

Microscopic examination of cross-sections cut from the rolling ingot risers showed that vanadium imparted significant grain refinement in all of the alloys to which it was added. This effect is shown in Figure 21 which is a photograph of microetched cross-sections of all of the vanadium bearing alloys cast during the project.

Alloy R-1352 was a casting of Dow Pure magnesium with no alloy additions and it exhibited a very coarse columnar grain configuration completely into the center of the casting. Addition of 0.3% vanadium in the form of divanadyl tetrachloride, alloy R-1165, confined the columnar structure to the edges of the casting and produced a central portion of large but decidedly equiaxed grains. Increasing the vanadium content to 0.5% added as divanadyl tetrachloride, alloy R-1410, further reduced the extent of the columnar structure. Addition of 0.5% vanadium metal powder, alloy R-1411, suppressed the extent of the columnar structure an amount equivalent to that caused by a 0.3% addition of divanadyl tetrachloride.

A vanadium addition in the form of aluminum - 85% vanadium master alloy, produced a very large degree of both suppression of the columnar range and grain size reduction on alloy R-1428 (Magnesium - 0.5% Vanadium - 0.09% Aluminum). However, effects were less pronounced when the vanadium content was increased to 1.0% and the aluminum to 0.17% as in alloy R-1424.

Addition of the aluminum - 85% vanadium master alloy reduced the grain size of already equiaxed AZ31 alloy. This effect is shown for AZ31 base alloys R-1429, R-1427 and R-1428 which had intended vanadium additions of 0.3%, 0.5%

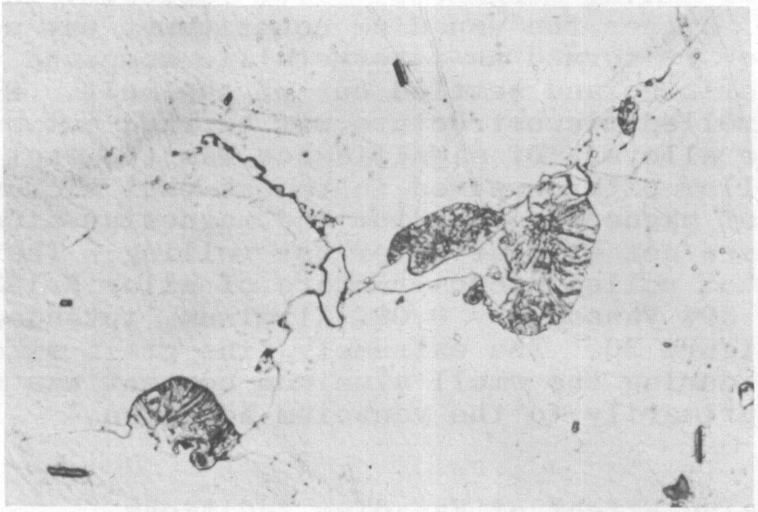

Figure 19

Negative No: 701 Filter: Wratten Magnification: 800X
Specimen No: 2724 47 Etch: 18 sec. in acetic glycol

As-cast microstructure of alloy R-1428 (AZ31 - 0.30% manganese - 1.0% vanadium, intended). The microstituents present are cream colored $Mg_{17}Al_{12}$, slate grey manganese and the magnesium - $Mg_{17}Al_{12}$ eutectic.

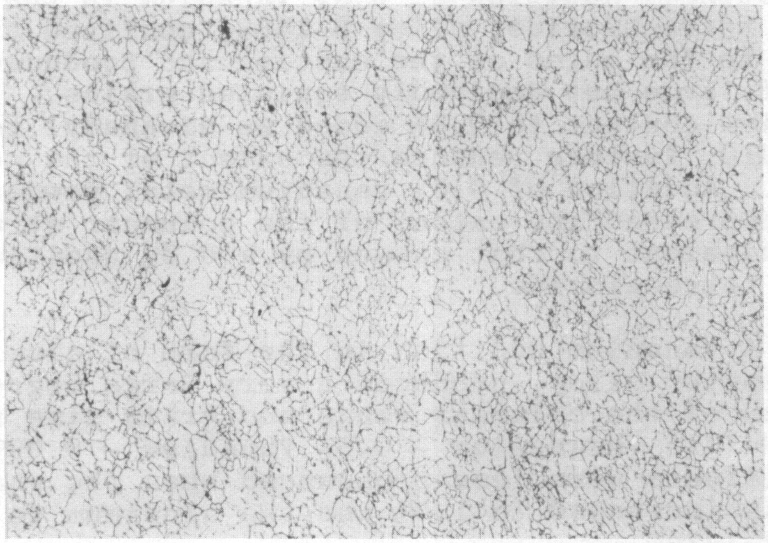

Figure 20

Negative No: 693 Filter: Wratten Magnification: 100X
Specimen No: 2721 58B Etch: 15 sec. in acetic glycol

As-hot rolled microstructure of alloy R-1423 (magnesium - 0.50% vanadium - 0.09% aluminum, intended). The average grain diameter is about 0.0007 inches.

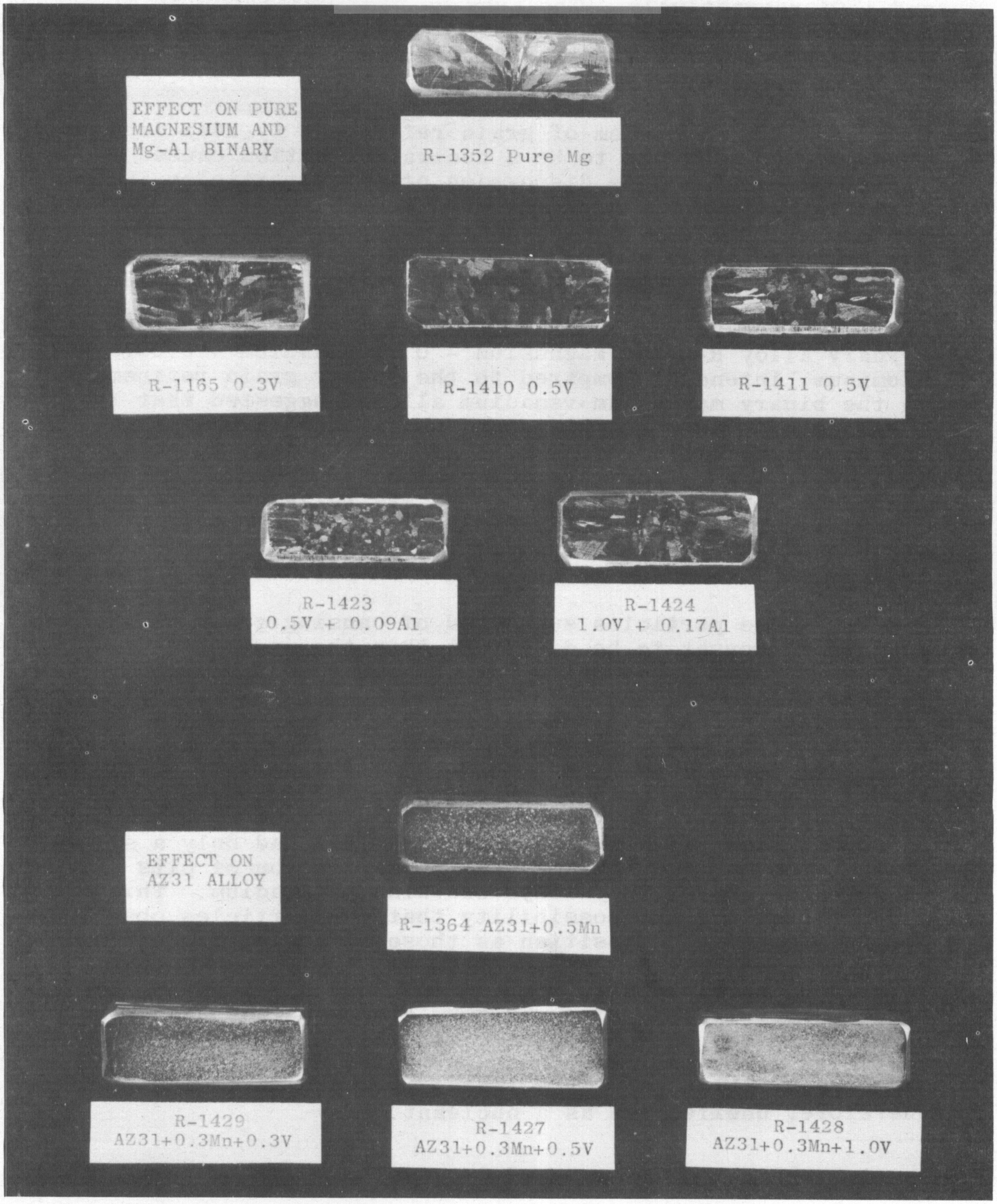

Figure 21 - Photograph of macroetched cross sections cut from the rolling ingot risers of vanadium bearing alloys.

Vanadium was added to alloys R-1165 and R-1410 in the form of divanadyl tetrachloride, to alloy R-1411 in the form of 20 mesh powder, and to all other alloys shown, in the form of aluminum - 85% vanadium master alloy.

and 1.0% respectively. The average grain diameter of alloy R-1364 was 0.011 inches, whereas, the average grain diameter of alloys R-1429, R-1427 and R-1428 was 0.005, 0.006 and 0.004 inches, respectively.

The mechanism of grain refinement by additions of vanadium was believed to be a nucleation action caused by the presence of a fine dispersion of solid particles in the melt just before freezing. In the Magnesium-Titanium Alloys section of this report a like mechanism was postulated for the grain refining action of additions of titanium dioxide to magnesium and magnesium alloys.

The very marked grain refinement shown in the ternary alloy R-1423 (Magnesium - 0.5% Vanadium - 0.09% Aluminum, intended) compared to the lesser grain refinement in the binary magnesium-vanadium alloys suggested that the presence of a more soluble component in the base alloy increased the grain refining effect of the less soluble addition. This effect was noted also for the additions of titanium dioxide and in both cases was believed to be evidence of constitutional supercooling during melt solidification. The presence of a similar effect was noted by Cibula[9] for additions of vanadium to aluminum rich solid solutions.

The particles suspected of causing grain refinement were thought to be different than the particles associated with the shallow pitting discussed previously in this section of the report. This conclusion was based on the lack of correlation between the observed grain refinement and the observed number of shallow, round surface pits for alloys R-1423 and R-1424 (Magnesium - 1.0% Vanadium - 0.17% Aluminum, intended). Alloy R-1423 had a large degree of grain refinement and only a moderate amount of the shallow pits, whereas, alloy R-1424 had only a slight grain refinement but the largest concentration of pits observed in any of the alloys containing vanadium. This did not preclude the possibility that the particles observed were of the same composition as those effecting nucleation and grain refinement. It was thought very possible that an optimum particle size might exist for a maximum nucleating effect and that this size was submicroscopic and hence not observed in the microstructure. If this were true the observed particles might well have been particles of the nucleating constituent which were much larger than the optimum size and, therefore, uneffective as a nucleant.

Mechanical Properties

Longitudinal tension and compression blanks were sheared from 0.064 inch sheet hot rolled according to the schedule described in the Experimental Procedure section of this report. These blanks were flattened and specimens were machined from them and tested following standardized procedures. The mechanical properties of magnesium-vanadium, magnesium-vanadium-aluminum and AZ31 vanadium alloys are shown in Table XX. The results indicated that vanadium had no significant effect on the mechanical properties of magnesium and the magnesium base alloys in this investigation.

Resistance to Corrosion

Specimens for the magnesium-vanadium alloy series were subjected to the standard static resistance to corrosion test described in the Experimental Procedure section of this report. The results of this test are summarized in Table XXI. Vanadium did not significantly affect the relative resistance to magnesium-aluminum and AZ31 base alloy compositions studied.

Summary

Eight 15 pound melts were cast in the magnesium-vanadium series. Vanadium additions were in the form of metallic powder, divanadyl tetrachloride and a master alloy containing 85% vanadium, balance aluminum. The comparative merits of these methods of adding vanadium were not determined with the limited data obtained. Microstructural evidence of vanadium in the form of small particles surrounded by relatively broad annular rings which appeared to be shallow pits was observed in the magnesium vanadium binary and magnesium-vanadium-aluminum ternary alloys but not in the AZ31 base compositions. It was observed that vanadium additions reduced the as-cast grain size and lessened the extent of columnar structures in the castings. No significant effects on either the mechanical properties or relative resistance to corrosion were caused by vanadium additions.

TABLE XX

ROOM TEMPERATURE MECHANICAL PROPERTIES OF 0.064 INCH MAGNESIUM-VANADIUM ALLOY SHEET IN THE HOT-ROLLED CONDITION

Alloy Number	Intended Addition Weight Percent		Longitudinal Mechanical Properties (a)			
	Vanadium	Other	Kips per sq. in. CYS	TYS	UTS	Elongation % in 2 in.
Pure Mg(b)	-	-	-	14.0	27.0	16.0
Pure Mg(c)	-	-	-	27.0	37.0	9.0
R-1352(d)	-	-	10.2	17.7	26.6	6.0
R-1165	0.30 $(VO)_2Cl_4$	-	-	19.4	31.6	5.0
R-1410	0.50 $(VO)_2Cl_4$	-	11.6	18.5	27.5	3.8
R-1411	0.50 powder	-	10.2	17.5	27.6	4.8
R-1423	0.50 Master Alloy	0.09Al	12.6	17.8	27.0	3.8
R-1424	1.00 Master Alloy	0.17Al	12.7	18.3	26.7	4.3
AZ31(b)	-	3.0Al 1.0Zn 0.3Mn	16.0	22.0	37.0	21.0
AZ31(c)	-	3.0Al 1.0Zn 0.3Mn	29.0	33.0	42.0	11.0
R-1364(d)	-	3.0Al 1.0Zn 0.5Mn	21.0	34.2	43.6	12.3
R-1429(d)	0.30 Master Alloy	3.0Al 1.0Zn 0.3Mn	18.8	32.7	40.2	9.0
R-1427(d)	0.50 Master Alloy	3.0Al 1.0Zn 0.3Mn	18.9	33.3	40.9	11.0
R-1428(d)	1.00 Master Alloy	3.0Al 1.0Zn 0.3Mn	18.3	30.1	40.1	11.3

(a) Notes are found on next page.

Notes Continued

(a) Properties reported are an average of two specimens unless otherwise stated.

(b) Properties in annealed condition. Data obtained from Metals Handbook, ASM, 1948 edition, pp.1014-1021.

(c) Properties in hard rolled condition. Data obtained from Metals Handbook, ASM, 1948 edition, pp.1014-1021.

(d) Melt was chlorinated for five minutes at 1450°F prior to alloying.

TABLE XXI

RELATIVE RESISTANCE TO CORROSION OF 0.064 INCH HOT-ROLLED MAGNESIUM-VANADIUM ALLOY SHEET COMPARED TO COMMERCIAL FS1-0 ALLOY SHEET

Alloy Number	Intended Addition Weight Percent: Vanadium	Intended Addition Weight Percent: Other	Relative Resistance to Corrosion (a)
R-1352(b)	-	-	1
R-1165	0.30 $(VO)_2Cl_4$	-	2
R-1410	0.50 $(VO)_2Cl_4$	-	2
R-1411	0.50 powder	-	2
R-1423	0.50 Master Alloy	0.09Al	2
R-1424	1.00 Master Alloy	0.17Al	2
R-1364(b)	-	3.00Al 1.00Zn 0.50Mn	4
R-1429(b)	0.30 Master Alloy	3.00Al 1.00Zn 0.30Mn	3
R-1427(b)	0.50 Master Alloy	3.00Al 1.00Zn 0.30Mn	3
R-1428(b)	1.00 Master Alloy	3.00Al 1.00Zn 0.30Mn	3

(a) The relative resistance to corrosion was determined according to the procedure and rating scheme described in the Experimental Procedure section of this report.

(b) Melt was chlorinated for five minutes at 1450°F prior to alloying.

MAGNESIUM - BORON ALLOYS

Review of Literature

Boron is classed as a metalloid element and is in Group III of the Periodic Table. Its physical properties are relatively unknown due to the difficulty of obtaining high purity samples until comparatively recently. According to data edited by Hampel[26] its density is about 2.30, its crystal structure has been reported as either tetragonal or orthorhombic and its melting point has been reported by one investigator to be about 4352°F and by another to be between 3632°F and 3767°F. Boron would be expected to be insoluble in magnesium due to an atomic size difference of 38% reported by Carapella[4].

The Dow Chemical Company[27] reported an investigation on the addition of boron to magnesium. The recovery was very low, less than one part per million being found in the alloy after an addition of 1.68 percent. It was reported that this low recovery was somewhat improved when the addition was made by bubbling boron trichloride through the melt.

Preparation of Alloys

Three experimental 15 pound melts were made with intended additions of boron. All were prepared according to the standardized Melt Procedure I described in the Experimental Procedure section of this report. All of the additions were in the form of powder or fine granules and were added wrapped in paper to prevent their floating on the melt surface during alloying.

Boron additions were made using calcium boride(a) and boron nitride(b) powders and granular manganese boride(c). The calcium boride and boron nitride powders were, respectively, 100 and 200 mesh. Both were specified to be purified and the boron nitride was stated to be 90% boron. The manganese boride was roughly 40 mesh but included large quantities of fines. No specifications as to its purity were available.

Addition of calcium boride produced large quantities of a light residue which floated to the melt surface and seemed to supplement the Dow 310 flux as a protective covering. Very little oxidation was noted during superheating of this melt. This condition was thought to be due to calcium rather than to the boron in the addtion.

(a) Supplied by the Fisher Scientific Company, New York 14, New York

(b) Supplied by A. D. Mackay, Inc., 198 Broadway, New York 38, New York

(c) Supplier unknown.

Heavy residues were noted in the crucible bottom after alloying manganese boride but this was believed due to the large quantity of manganese and not to any effect of the boron.

The melting and casting conditions and as-cast grain size of experimental magnesium boron alloys are summarized in Table XXII.

The ingots were scalped,homogenized,and rolled to 0.064 inch sheet and the sheet was tested for mechanical properties according to the standardized procedures described in the Experimental Procedure section of this report.

TABLE XXII

MELTING AND CASTING CONDITIONS AND AS-CAST GRAIN SIZE OF EXPERIMENTAL MAGNESIUM-BORON ALLOYS

Alloy Number	Intended Addition Weight Percent Boron	Other	Form of Boron Addition	Melt Procedure(a)	Average Grain Diameter, Inches
R-1416	0.5	-	BN	I	very coarse, columnar
R-1415	1.0	5.1Mn	MnB	I	0.100
R-1414	3.0	1.7Ca	CaB_6	I	very coarse, columnar

(a) Melt procedures are described in detail in the Experimental Procedure section of this report.

As-Cast Grain Size

The as-cast grain size was determined according to standard procedures described in the Experimental Procedure section of this report. Boron nitride and calcium boride additions, alloys R-1416 (Magnesium - 0.5% Boron) and R-1414 (Magnesium - 3.0% Boron - 1.7% Calcium), respectively, did not affect the grain size. The primary macrostructure in both of these cases was transcolumnar similar to the structure observed in alloy R-1352 (Pure Magnesium).

Addition of manganese boride, alloy R-1415 (Magnesium - 1.0% Boron - 5.1% Manganese) eliminated the columnar structure but did not materially reduce the grain size. This effect was believed to be due either to the manganese or to impurities in the manganese boride addition rather than to boron in the alloy.

Metallographic Observations

Examination of the as-cast microstructures of all experimental magnesium-boron alloys did not reveal distinct evidence of the presence of boron. Of significance was the absence of the manganese constituent and the presence of an extensive interdendritic network in alloy R-1415 (Magnesium - 1.0% Boron - 5.1% Manganese). The absence of the manganese constituent indicated that manganese boride was not dissociated during alloying and that it was probably the main constituent in the heavy residue which settled to the crucible bottom after alloying. The interdendritic network was very similar in appearance to the contamination condition, described in Appendix I, which was found in alloys prepared in clay-graphite crucibles according to experimental Melt Procedure II. Alloy R-1415, however, was prepared in an AMER-MAG aluminized steel crucible according to Melt Procedure I, suggesting that the interdendritic network was due to contamination by impurities in the manganese boride addition.

Mechanical Properties

The mechanical properties of experimental magnesium - boron additions are reported in Table XXIII. No significant effects due to boron on the mechanical properties were evident from these data.

Resistance to Corrosion

The relative resistance to corrosion of experimental magnesium-boron alloys was determined according to standardized procedures described in the Experimental Procedure section of this report. The results of the determination are given in Table XXIV.

No significant trend for the effect of boron on the relative resistance to corrosion of magnesium was noted. The very low relative resistance to corrosion of alloy R-1415 was attributed to the previously described interdendritic network caused by impurities.

TABLE XXIII

ROOM TEMPERATURE MECHANICAL PROPERTIES OF 0.064 INCH MAGNESIUM-BORON ALLOY SHEET IN THE HOT-ROLLED CONDITION

Alloy Number	Intended Addition Weight Percent		Longitudinal Tensile Properties(a) Kips per sq. in.			Elongation
	Boron	Other	CYS	TYS	UTS	% in 2 in.
Pure Mg(b)	-	-	-	14.0	27.0	16.0
Pure Mg(c)	-	-	-	27.0	37.0	9.0
R-1352	-	-	10.2	17.7	26.6	6.0
R-1416	0.5 (BN)	-	10.2	18.9	28.5	4.8
R-1415	1.0 (MnB)	5.1Mn	11.4	17.8	27.5	3.8
R-1414	3.0 (CaB_6)	1.7Ca	10.7	18.1	27.3	4.3

(a) Properties reported are an average of two specimens unless otherwise stated.

(b) Annealed condition properties from ASM "Metals Handbook", 1948, p.1014.

(c) Hard rolled condition properties from ASM "Metals Handbook", 1948, p.1014.

TABLE XXIV

RELATIVE RESISTANCE TO CORROSION OF 0.064 INCH HOT-ROLLED MAGNESIUM-BORON ALLOY SHEET COMPARED TO COMMERCIAL FS1-0 ALLOY SHEET

Alloy Number	Intended Addition Weight Percent Boron	Intended Addition Weight Percent Other	Relative Resistance to Corrosion (a)
R-1352(b)	-	--	1
R-1416	0.5 (BN)	--	2
R-1415	1.0 (MnB)	5.1Mn	5
R-1414	3.0 (CaB)	1.7Ca	2

(a) The relative resistance to corrosion was determined according to the standard procedure and rating scheme described in the Experimental Procedure section of this report.

(b) Melt was chlorinated for five minutes at 1450°F prior to alloying.

Summary

Three 15 pound melts were cast in the magnesium-boron series. The boron additions were in the form of calcium boride, manganese boride and boron nitride. No observable evidence of boron was found in the microstructures of the as-cast alloys. No significant effects due to the boron addition were evident in the mechanical properties or relative resistance to corrosion of the alloys of this series.

MAGNESIUM - CHROMIUM ALLOYS

Review of Literature

Chromium is a transition element of Group VI with a normally body centered cubic lattice, a density of 7.19 and a melting point of 3430 ± 20°F[24]. It has an alloying valence of zero and an atomic size differing from that of magnesium by 15% according to Carapella[4]. This borderline atomic size factor coupled with high electronegativity compared to magnesium would be expected to produce low solubility in magnesium and highly stable intermetallic compounds.

Recent work at Rensselaer Polytechnic Institute[28] has indicated that chromium additions to AZ31 base alloys produced a small but significant increase in the mechanical properties of rolled sheet. The introduction of chromium was accomplished by stirring electrolytic chromium powder or aluminum-chromium hardeners into the melt at 1600°F followed by superheating at 1700°-1800°F. Compositions were prepared with intended chromium additions up to 1.00 weight percent but the maximum chromium recovery was found to be only 0.021 weight percent. Optimum mechanical properties were found for the chromium bearing, AZ31 base alloys which contained 0.50% manganese and therefore the manganese content was believed critically related to the ability of the chromium to impart increased strength.

Johnson[29] and Anderson and Johnson[30] reported significant improvements in mechanical properties compared to commercial values for alloys containing small additions of combinations of chromium, antimony, strontium and barium to AZ63 and AZ31 base compositions in cast and wrought form, respectively. They report qualitative data which indicated that chromium was recovered in the alloys to which it was added. Chromium was stated to be an important addition, although it was indicated that the maximum improvement in mechanical properties was associated with double combinations of the four addition elements investigated.

Beck[31] and Sauerwald[32] reported that chromium cannot be alloyed with magnesium or magnesium-aluminum alloys. Grube and coworkers[33,16] added single additions of chromium to a limited number of magnesium melts and found no improvements in mechanical properties.

Morioka[34] reported that chromium could be added to magnesium-base alloys containing aluminum, zinc and manganese by introducing lumps of chromium trichloride into the melt at about 1600°F. This method of introduction produced measurable chromium recoveries of from 0.001 to 0.061 weight percent. He reported that the resulting alloys had increased resistance to corrosion. Beck[31], however, reported that small amounts of chromium present as traces of a second phase reduced the resistance to corrosion.

Veazey[35] and Hanawalt and McDonald[36] have patented magnesium alloys with chromium additions. Veazey added from 0.01 to 0.10 percent chromium to magnesium in the form of anhydrous chromic chloride, chromium sesquioxide and metallic chromium and claimed recoveries as high as 0.08 percent. His alloys were made using a high density flux which settled to the bottom preventing formation of a flux coating over the alloy addition and, thereby, increasing the surface of the alloy exposed to molten magnesium.

Preparation and Evaluation of Magnesium-Chromium Hardeners

Initial experimental work consisted of an attempt to make a magnesium-chromium hardener having a large amount of mechanically entrapped metallic chromium similar to the zirconium in Dow K50 magnesium-zirconium hardener. It was thought that such a hardener, if it could be made, would be a more suitable method for the introduction of chromium into magnesium than methods previously attempted. Four alloys were cast in attempts to make such a hardener.

The hardeners were made by stirring repeatedly small additions of electrolytic chromium powder or anhydrous chromium trichloride into molten, high purity magnesium, anticipating that the magnesium eventually would become saturated with mechanically entrapped particles of massive chromium. The electrolytic chromium powder(a) had a particle size range minus 100-plus 170 mesh and had the following specified impurities expressed in weight percent:

Carbon	0.02	Copper	$<$0.01
Iron	0.02	Lead	0.001
Oxygen	0.62	Sulphur	0.038
Nickel	0.011		

The anhydrous chromium trichloride(b) was 8 to 12 mesh particle size and was a purified grade.

(a) Supplied by the Electro Metallurgical Corporation, Niagara Falls, New York.

(b) Supplied by the Fisher Scientific Company, New York 14, New York.

All of the hardeners were prepared as 100 gram melts in Dixon No. 4/0 clay-graphite crucibles using Dow 220 flux for protection. A vertical tube electric resistance furnace was used for melting and the castings were poured in a 3/4 inch diameter, cylindrical, preheated, graphite mold. Additions of chromium powder were wrapped in paper, submerged beneath the melt surface and stirred with a graphite rod. In all cases the total chromium addition was divided into several portions each of which was added and stirred into the melt separately. The chromium trichloride addition was wrapped in aluminum foil, submerged under the melt surface and stirred with a steel phosphorizing tool rather than a graphite rod. No superheating was done so as to prevent serious oxidation during the prolonged stirring. All hardeners were poured at 1400°F.

The melting and casting conditions and as-cast grain size of these hardeners are listed in Table XXV.

TABLE XXV

MELTING AND CASTING CONDITIONS AND AS-CAST GRAIN SIZE FOR MAGNESIUM-CHROMIUM HARDENERS

Hardener Alloy Number	Base Alloy	Intended Addition Wt. % Cr	Form of Addition	Alloying Temp., °F	Average Grain Diameter, Inches
R-1222	Pure Mg	50	Powder	1450	0.050 x 0.100
R-1223(a)	Pure Mg	50	Powder	1500	---
R-1224	Pure Mg	50	Powder	1500	large, columnar
R-1225	AZ31	16	$CrCl_3$	1450	0.010

(a) Casting was scrapped due to excessive oxide and flux inclusions.

Metallographic examination showed that the electrolytic powder additions produced columnar grains with an average width of 0.050 inches and length of 0.10 to 0.30 inches. This large grain size coupled with the lack of evidence of a deep purple microconstituent in the matrix, characteristic of previously observed alloys with analyzed chromium contents, was believed to indicate that the attempt to make hardeners with electrolytic chromium powder was unsuccessful.

Examination of the microstructure of hardener alloy R-1225 (AZ31 - 0.30% Manganese - 16% Chromium, intended) revealed that a large addition of chromium in the form of anhydrous chromium trichloride introduced an unidentified purple microconstituent into the alloy. The fine particle size of this constituent made positive recognition uncertain but the constituent appeared similar to the purple constituent observed previously in alloys with additions of chromium. When etched in acetic glycol, however, it lost its characteristic dull purple color and appeared brownish-gray. The particles were quite large and in most cases segregated together in large clusters. No evidence of alloying with magnesium was noticed at the interface between the particles and the surrounding matrix. The as-polished and etched appearances of this condition are shown in Figures 22 and 23, respectively.

The possibility that the unidentified constituent was the manganese constituent was examined carefully. The manganese constituent was observed in alloy R-1225 and it did not appear the same as the unidentified constituent under various conditions of specimen surface treatment. In particular, the unidentified constituent clustered in groups of fine particles, usually in close proximity to a clear phase believed to be $Mg_{17}Al_{12}$, as illustrated in Figure 23. This was not a characteristic behavior of the manganese constituent in AZ31 composition.

A large amount of non-metallic inclusions were observed in the microstructure of alloy R-1225. This condition was attributed to the prolonged stirring and melt disturbance caused by repeated additions of small portions of the total intended chromium addition.

Further study of the hardeners was not pursued in order to devote more experimental effort to the other aspects of the investigation of chromium additions to magnesium.

Preparation of Experimental Alloys for Extrusion and Rolling

Extrusion billets 3/4 inches in diameter and three inches long were prepared for the magnesium-chromium and AZ31-chromium alloy systems using anhydrous chromium trichloride for introducing chromium. The melt procedure used was essentially Melt Procedure II described in the Experimental Procedure section of this report.

Ten alloys were prepared as 100 gram melts in Dixon Number 4/0 clay-graphite crucibles. They were melted in a vertical tube electric resistance furnace using Dow 220 flux for protection and poured into a cylindrical graphite mold. Redistilled, high purity magnesium was used for the magnesium-chromium alloys and Dow Pure notched ingot for the AZ31 chromium alloys. Alcoa aluminum pig, specified 99.8%, New Jersey Horse-

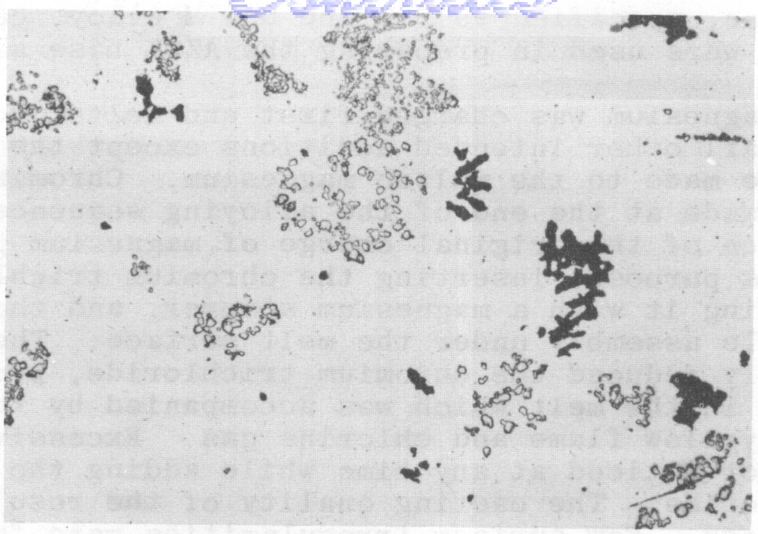

Figure 22

Negative No: 703 Magnification: 100X
Specimen No: M-2391 Etch: As-polished

Microstructure of hardener alloy R-1225 (AZ31 - 0.30% manganese - 16% chromium, intended) showing the segregated purple constituent believed to be related to the chromium addition. The dark areas are evidence of flux and oxide inclusions. Chromium was added as anhydrous chromium trichloride.

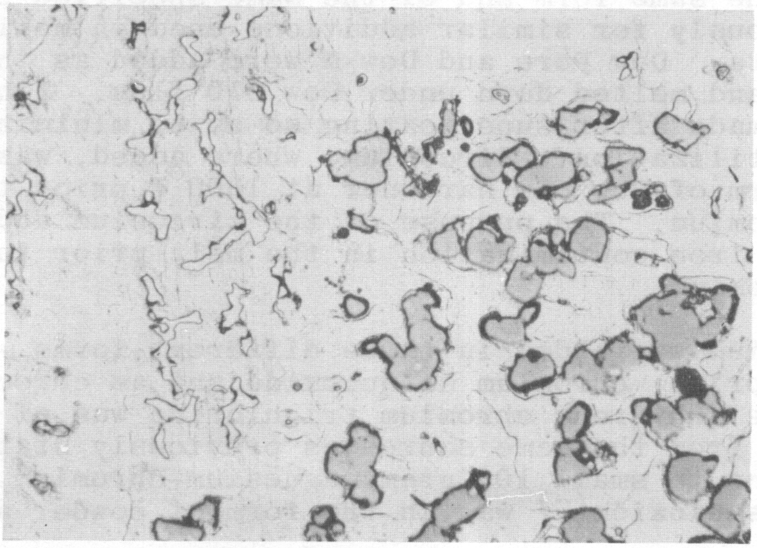

Figure 23

Negative No: 705 Magnification: 500X
Specimen No: M-2391 Etch: 12 seconds in acetic glycol

Same condition as in Figure 22 but at a higher magnification and etched to reveal the segregation of cream colored $Mg_{17}Al_{12}$ intermetallic constituent.

head special zinc, specified 99.99% and Dow M alloy, certified 1.61% manganese were used in preparing the AZ31 base alloys.

The magnesium was charged first and melted down. Following this all other intended additions except the chromium trichloride were made to the molten magnesium. Chromium trichloride additions were made at the end of the alloying sequence by drilling a hole in a piece of the original charge of magnesium previously reserved for this purpose, inserting the chromium trichloride into the hole, plugging it with a magnesium stopper, and then submerging the whole assembly under the melt surface. The molten magnesium readily reduced the chromium trichloride, producing a mild reaction in the melt which was accompanied by the evolution of a yellow flame and chlorine gas. Excessive melt oxidation was not noticed at any time while adding the anhydrous chromium trichloride. The casting quality of the resulting alloys was generally good. Few surface irregularities were found on the castings.

Fifteen experimental alloys for rolling to 0.064 inch sheet were cast. All ingots for rolling with the exception of R-1426 were prepared as 15 pound melts in Amer-Mag aluminized steel crucibles according to Melt Procedure I described in the Experimental Procedure section of this report. Alloy R-1426 was prepared as a 200 gram melt in an Acheson graphite crucible according to Melt Procedure II.

Aluminum, zinc and manganese additions to 15 pound melts were in the same form and of the same specified purity as stated previously for similar additions used in making extrusion billets. Dow Pure and Dow M were added as the initial charge and melted down under Dow 310 flux. Zinc additions were made after superheating so as to minimize loss of zinc by volatilization. Zirconium, where added, was introduced in the form of Dow K50 hardener at 1600°F prior to the addition of chromium. The purpose of the zirconium additions was to minimize iron contamination in the melt prior to the addition of chromium.

Chromium was added in three different forms - anhydrous chromium trichloride, chromium sesquioxide and as chromic flouride trihydrate. The anhydrous chromium trichloride was of the same purity and from the same source as previously stated for similar additions to small 100 gram magnesium-chromium melts. The chromium sesquioxide(c) was in the form of powder and had the

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(c) Supplied by the Fisher Scientific Company, New York 14, New York.

following certified analysis:

Ammonia(NH_3)	0.05%
Sulphate(SO_4)	0.1%
Chloride(Cl)	0.003%
Iron(Fe)	0.03%
Substances not precipitated by NH_4OH	0.5%

Chromic fluoride trihydrate, $CrF_3 \cdot 3H_2O$, was prepared just before use from purified chromic fluoride enneahydrate, $CaF_3 \cdot 9H_2O$(d), by heating 25 hours in a drying oven at 250°F. According to Mellor[37] the enneahydrate loses three moles of water at 221°F forming the hexahydrate and the hexahydrate loses three more moles of water, becoming the trihydrate, after about eight hours at 140°-160°F. Formation of the anhydrous fluoride could have been accomplished, according to Mellor, by heating the trihydrate in a stream of hydrogen flouride at 1200°F. This was not done because the added experimental effort was not justified in light of the questionable benefit of addition of large amounts of chromium fluoride to magnesium. The trihydrate was considered suitable from a safety standpoint for small additions.

All chromium additions were made just prior to superheating after first alloying all other additions except zinc which was added after superheating. Anhydrous chromium chloride and chromium sesquioxide additions were made at 1600°F. The chromium fluoride trihydrate was added at 1450°F to minimize reaction during evolution of the water of hydration. All chromium additions were wrapped in paper and stirred into the melt with an iron ladle. After alloying the chromium, each melt was stirred for approximately three minutes with an iron rod.

The rare earth addition to alloy R-1397 (Magnesium - 3.0% Zinc - 0.5% Zirconium - 2.0% Rare Earth - 0.2% Chromium, intended) was made at 1450°F prior to adding chromium, in the form of standard grade rare earth chloride(e) wrapped in paper. A large amount of pink colored, metallic residue containing much entrained oxide and flux was recovered from the crucible bottom after pouring this melt. It was associated mainly with the rare earth addition because it could be felt on the bottom of the crucible immediately following the addition of rare earth chloride.

(d) Supplied by the Fisher Scientific Company, New York 14, New York.

(e) Supplied by the Metallo-Chemical Corporation, 117 Liberty Street, New York, New York. An analysis of this product was not supplied but was stated to be a mixture of rare earth chlorides.

TABLE XXVI

MELTING AND CASTING CONDITIONS AND AS-CAST GRAIN SIZE FOR EXPERIMENTAL MAGNESIUM-BASE ALLOYS WITH CHROMIUM ADDITIONS INTRODUCED AS ANHYDROUS CHROMIUM TRICHLORIDE

Alloy Number	Intended Addition Weight Percent Chromium		Melt Procedure (a)	Superheat Conditions Temp. °F		Average Grain Diameter, Inches
	Chromium	Other		Temp. °F	Time Min.	
R-1194	-	-	A	1450	6.5hrs.	large, columnar
R-1226	-	-	A	1400	30	0.030
R-1352	-	-	B	1640	15	large, columnar
R-1227	0.05	-	A	1500	20	large, columnar
R-1228	0.10	-	A	1500	20	0.040 x 0.070
R-1353	0.10	-	B	1750	15	large, columnar
R-1229	0.30	-	A	1500	20	0.035(b)
R-1230	0.50	-	A	1500	20	0.050
R-1354	0.50	-	B	1740	15	0.065
R-1231	1.00	-	A	1500	20	0.040(b)
R-1355	1.00	-	B	1775	15	large, columnar
R-1356	0.10	0.20Zr	B	1740	15	large, columnar
R-1358	0.10	0.50Zr	B	1850	15	0.050 x 0.080
R-1357	0.50	0.20Zr	B	1740	15	large, columnar
R-1359	0.50	0.05Zr	B	1740	15	0.040(b)
R-1360	0.10	1.00Zn 0.20Zr	B	1740	15	0.045
R-1361	0.10	3.00Zn 0.60Zr	B	1740	15	0.004
R-1397	0.20	3.00Zn 0.50Zr 2.00R.E.	B	1650	10	0.005
R-1398	0.20	2.00Zn 0.70Zr 3.00Th	B	1650	10	0.004
R-1426	-	3.00Al 1.00Zn 0.30Mn	C	1500	21hrs.	0.011

TABLE XXVI (Continued)

MELTING AND CASTING CONDITIONS AND AS-CAST GRAIN SIZE FOR EXPERIMENTAL MAGNESIUM-BASE ALLOYS WITH CHROMIUM ADDITIONS INTRODUCED AS ANHYDROUS CHROMIUM TRICHLORIDE

Alloy Number	Intended Addition Weight Percent		Melt Procedure (a)	Superheat Conditions		Average Grain Diameter, Inches
	Chromium	Other		Temp. °F	Time Min.	
R-1364	-	3.00Al 1.00Zn 0.50Mn	B	1740	15	0.011
R-1232	0.05	3.00Al 1.00Zn 0.30Mn	A	1500	20	0.035
R-1233	0.10	3.00Al 1.00Zn 0.30Mn	A	1500	20	0.020
R-1362	0.10	3.00Al 1.00Zn 0.50Mn	B	1740	15	0.003
R-1234	0.30	3.00Al 1.00Zn 0.30Mn	A	1500	2hrs.	0.025
R-1235	0.50	3.00Al 1.00Zn 0.30Mn	A	1500	2hrs.	0.020
R-1363	0.50	3.00Al 1.00Zn 0.50Mn	B	1620	5	0.060
R-1236	1.00	3.00Al 1.00Zn 0.50Mn	A	1500	2hrs.	0.050 x 0.075

(a) Melt procedures are given in the Experimental Procedure section of this report.

A means Melt Procedure II using a Dixon Number 4/0 clay-graphite crucible, 100 gram melt size, and a three inch long, 3/4 inch diameter cylindrical graphite ingot mold.

B means Melt Procedure I with chlorination for five minutes at 1450°F prior to alloying.

C means Melt Procedure II.

(b) Grain size determined on equiaxed grains at center of casting cross section. Grains at edge of casting were predomenantly large and columnar.

TABLE XXVII

MELTING AND CASTING CONDITIONS AND AS-CAST GRAIN SIZE FOR EXPERIMENTAL MAGNESIUM BASE ALLOYS WITH CHROMIUM ADDITIONS INTRODUCED AS CHROMIUM SESQUIOXIDE AND CHROMIUM FLUORIDE

Alloy Number	Intended Addition Weight Percent Chromium	Other	Form of Addition	Melt Procedure(a)	Average Grain Diameter, Inches
R-1421	0.05	-	$Cr F_3 \cdot 3H_2O$	I	0.050 x 0.075
R-1422	0.10	-	$Cr F_3 \cdot 3H_2O$	I	large, columnar
R-1417	0.10	-	Cr_2O_3	I	large, columnar
R-1418	0.50	-	Cr_2O_3	I	large, columnar
R-1419	1.00	-	Cr_2O_3	I	large, columnar
R-1420	0.50	3.00Al 1.00Zn 0.50Mn	Cr_2O_3	I	0.010

(a) Melt procedures are given in the Experimental Procedure section of this report.

The thorium addition to alloy R-1398 (Magnesium - 2.0% Zinc - 0.7% Zirconium - 3.0% Thorium - 0.2% Chromium, intended) was made at 1450°F, prior to alloying chromium, in the form of magnesium - 30% thorium hardener (f) ingot.

Chlorine gas fluxing, where carried out, was done for the purpose of removing hydrogen from the melt. The removal of hydrogen was considered beneficial both in reducing pinhole porosity in the castings and in possibly increasing the recovery of alloy additions. The assembly for melt chlorination was similar to the portable chlorination apparatus described in a Dow Chemical Company Bulletin[38]. A neoprene hose led from the chlorine tank to one end of a steel pipe into the other end of which was cemented a graphite tube. After first obtaining a steady flow of chlorine the graphite tube was immersed in the melt and rotated slowly around the inside of the crucible. Graphite was used for introducing the chlorine gas rather than iron because of its greater resistance to the corrosive action of hot chlorine and molten magnesium and to minimize the pick-up of iron by the melt.

A summary of the melting and casting conditions and as-cast grain size of all alloys prepared is given in Tables XXVI and XXVII. Table XXVI includes all alloys having chromium added in the form of anhydrous chromium trichloride and Table XXVII includes the alloys having chromium added in the form of chromium sesquioxide and chromic fluoride trihydrate.

Effect of Chromium on As-Cast Grain Size

Macroscopic examination of cross sections from as-cast ingot risers indicated that in some cases chromium additions had a marked grain refining effect. Comparison of alloys R-1227, 1228, 1229, 1230 and 1231 which were magnesium base alloys with respective additions of 0.05, 0.10, 0.30, 0.50 and 1.00 percent chromium, showed that increasing the amount of chromium added as anhydrous chromium trichloride produced significant reductions in both the extent of columnar structure and the grain size of the 100 gram extrusion billets.

This effect, however, was not present in the similarly prepared alloy series R-1232, 1233, 1234, 1235 and 1236 which were AZ31 base alloys with respective chromium additions of 0.05, 0.10, 0.30, 0.50 and 1.00 percent in the form of anhydrous chromium trichloride. No marked trends were noted in this series but it was thought significant that none of the alloys except R-1362

(f) Supplied by the Dow Chemical Company, Midland, Michigan.

had as fine a grain size as alloys R-1426 and R-1364 AZ31 alloys without intended additions of chromium.

In both the pure magnesium base and AZ31 series of chromium bearing alloys it was noted that grain refinement and reduction of the extent of the columnar area was much less for an intended addition of 1.0 percent chromium than for an intended addition of 0.5 or 0.3 percent chromium. This suggested an optimum intended chromium addition for maximum grain refinement of from 0.3 to 0.5 percent.

No significant effects upon the as-cast grain size were noted for chromium sesquioxide and chromic fluoride trihydrate additions to magnesium. Single additions or combinations of zinc, zirconium, thorium or rare earths in combination with chromium added as anhydrous chromium trichloride, likewise, produced no significant effects on the as-cast grain size that were attributed to the chromium addition.

As a general observation, the addition of chromium to magnesium and to magnesium-base alloys was ineffective as a means to produced refinement of primary grain structure. This agreed in effect with results reported by Cibula[9] that chromium additions to aluminum were less effective in primary structure grain refinement than addition of other elements such as titanium, vanadium and zirconium.

Metallographic Observations

Examination of the as-cast and wrought microstructures of all experimental magnesium-chromium alloys did not reveal distinct evidence of the presence of a deep-purple microconstituent, with the exception of the special hardener alloy R-1225 discussed above. Several microstructural conditions observed in AZ31 base compositions with additions of chromium prepared as small melts were not detected in comparable alloys prepared as 15 pound melts. These effects, therefore, were considered to be associated with the method of preparing the alloy and not to a characteristic influence of the chromium.

As-extruded microstructures of the alloys with additions of chromium were fine grained. The structure of alloy R-1235 (AZ31 - 0.3% Manganese - 0.5% Chromium, intended), illustrated in Figure 24, exhibited a general distribution of extremely fine equiaxed grains mingled with a longitudinal pattern of slightly coarser grain structure. The as-extruded microstructure of hardener alloy R-1225 (AZ31 - 0.3% Manganese - 16% Chromium, intended) developed a coarser grain structure than R-1235, and, in addition, exhibited longitudinal stringers of undissolved microconstituents. A typical example of this structure is shown in Figure 25. The microstructural conditions in these two alloys may have resulted from chromium additions.

The microstructures of hot rolled sheet were not influenced by additions of chromium to magnesium or to magnesium base alloys.

Metallographic Evaluation of Magnesium-Chromium Crucible Residues

Investigations of the microstructure of chromium bearing alloys cast during the present research and also during past work at Rensselaer[28] indicate that chromium was not retained in the melts to an appreciable degree in either soluble or massive form when added in amounts of one percent or less. Stirring in very large quantities of chromium in attempts to make magnesium-chromium hardener alloys likewise did not produce significant microstructural evidence of retained chromium except in the one case of previously described hardener alloy R-1225 (AZ31 - 0.3% Manganese - 16% Chromium, intended). In nearly all cases where attempts were made to add chromium, however, extensive residues remained in the bottom of the crucible after pouring. Furthermore, it was generally observed that the quantity of residue present was roughly proportional to the amount of the intended chromium addition. These melt residues were spongy and semi-metallic in appearance and were usually saturated with oxide skins and flux inclusions. They oxidized rapidly on exposure to normal atmospheric conditions and gradually disintegrated leaving intact small particles of oxidation resistant, metallic constituents.

These metallic particles were examined and some were found to be relatively hard and brittle with an angular shape while others were found to be more ductile and nearly spherodial. In addition, there appeared to be many particles with hardness and shapes somewhere between these two extremes. Microstructural examination revealed intermetallic constituents similar to those found in the casting of the parent melt. However, in the residues they were usually found in much larger concentrations. In addition, several constituents not recognized in the parent casting were observed. In those alloys where chromium was added in the form of aluminum-chromium hardeners, structures similar to that of the hardener used were sometimes found, indicating that some of the hardener had settled to the crucible bottom.

Photomicrographs of structures representative of the constituents found in the crucible residues but not in the castings from the parent melt are shown in Figures 26 through 29. These structures were all believed to be associated with

Figure 24

Negative No: 707 Magnification: 500X
Specimen No: M-2554 Etch: 10 seconds in acetic picral

As extruded microstructure of alloy R-1235 (AZ31 - 0.3% manganese - 0.5% chromium, intended) showing a duplex structure of extremely fine, equi-axed grains mingled with a smaller amount of coarser grains.

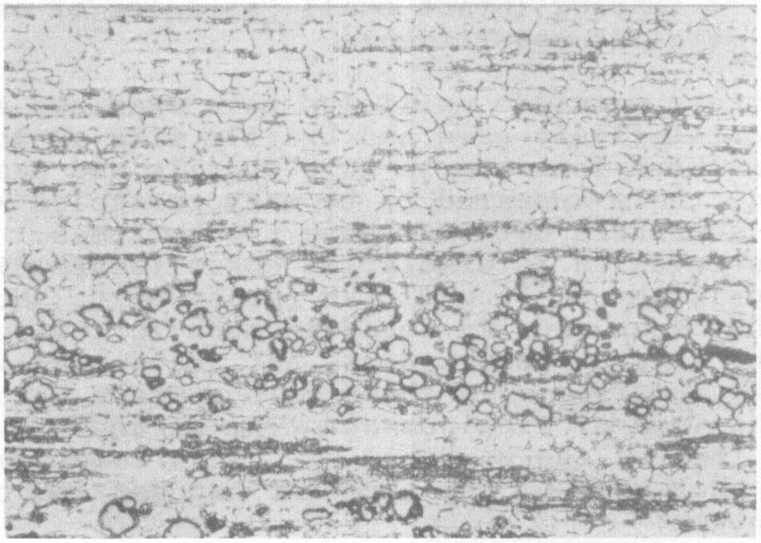

Figure 25

Negative No: 716 Magnification: 300X
Specimen No: M-2556 Etch: 20 seconds in acetic glycol

As extruded microstructure of hardener alloy R-1225 (AZ31 - 0.3% manganese - 16% chromium, intended).

chromium but positive identification of their composition and structure was not attempted.

The constituent shown in Figures 26 and 27 was creamy-white in color and consistently retained scratches from rough polishing throughout the final polishing operations, indicating that it was much harder than magnesium. It was similar in appearance to the predominant constituent in the aluminum - 56 chromium hardener, and, therefore, was believed to be either massive chromium or an aluminum-chromium intermediate phase. The former of these two tentative identifications was considered more reasonable in residues from alloys having no aluminum additions and in which chromium was added as a powder.

Figure 28 illustrates the appearance of another constituent observed in chromium bearing melt residues. This constituent was difficult to distinguish from the manganese constituent because of a similar shape and distribution. It had, however, a brownish-gray color when etched with glycol instead of the bluish-gray color characteristic of the manganese constituent. This color difference, although not a sharp contrast, was consistent. The smaller the particle size, the more difficult was the detection of the color difference, and, therefore, positive separation of the two constituents was not conclusive. This constituent was not found in all of the chromium bearing melts, possibly due to the ease of mistaking it for manganese, and no correlation between its presence or absence and the alloy components of the parent melt was observed. Its presence was, however, limited only to intended chromium bearing melts as far as the examination of crucible residues was conducted. The evidence which led to differentiating these particles from the nearly identical appearing manganese constituent is shown in Figure 29. This illustrates the rarely observed interface between chromium as derived from aluminum - 10 chromium hardener and AZ31 magnesium alloy, with 0.5 percent manganese. The residue containing this interface was recovered from the crucible of alloy R-1072 (AZ31 plus 0.014 Chromium plus 0.54 Manganese, analyzed) after pouring. This alloy was cast during previous work at Rensselaer[28]. The strikingly similar appearance of the chromium just at the interface to the generally observed appearance of massive manganese in magnesium is evident. Unfortunately, black and white reproduction does not show the slight color difference. The relatively sharp boundary line between the aluminum - 10 chromium hardener and the AZ31 alloy indicated a definite lack of either alloying or mechanical entrainment of chromium in magnesium. The aluminum rich areas of the aluminum-chromium hardener showed a continuous transition to the magnesium alloy wherever they were in contact with each other.

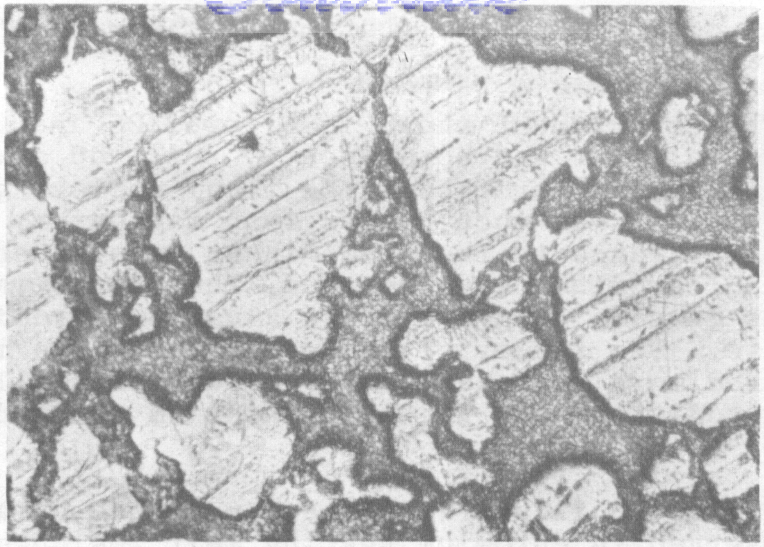

Figure 26

Negative No: 671 Magnification: 500X
Specimen No: 2587 Etch: As-polished

Microstructure of a residue recovered from the crucible bottom after pouring alloy R-1224 (high purity magnesium plus 50% chromium, intended). The scratches retained on the light colored constituent were due to its relative hardness compared to the magnesium rich matrix. The hard particles were believed to be either chromium or a magnesium-chromium phase.

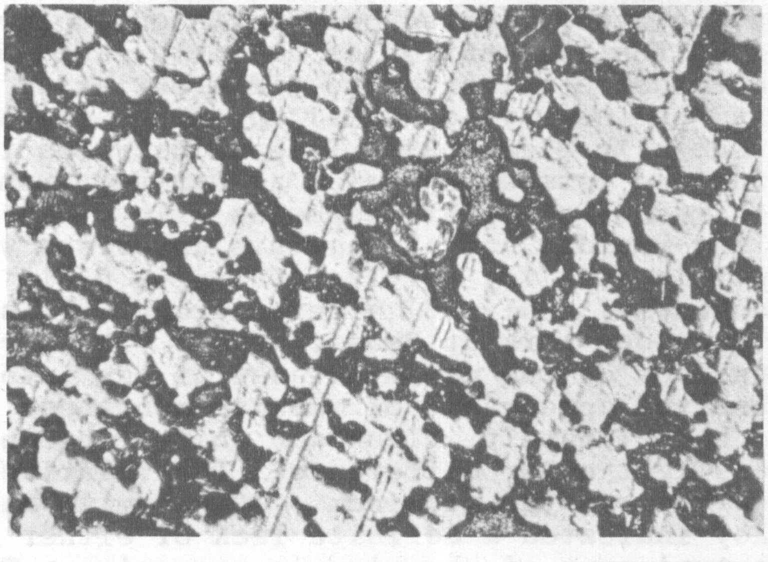

Figure 27

Negative No: 670 Magnification: 500X
Specimen No: 2588 Etch: As-polished

Microstructure of one type of residue recovered from the crucible bottom after pouring alloy R-1072 (AZ31 plus 0.54% manganese plus 0.014% chromium analyzed). This constituent was believed to be the same chromium or chromium-rich phase shown in Figure 26, but in this case it was broken up into finer particle sizes.

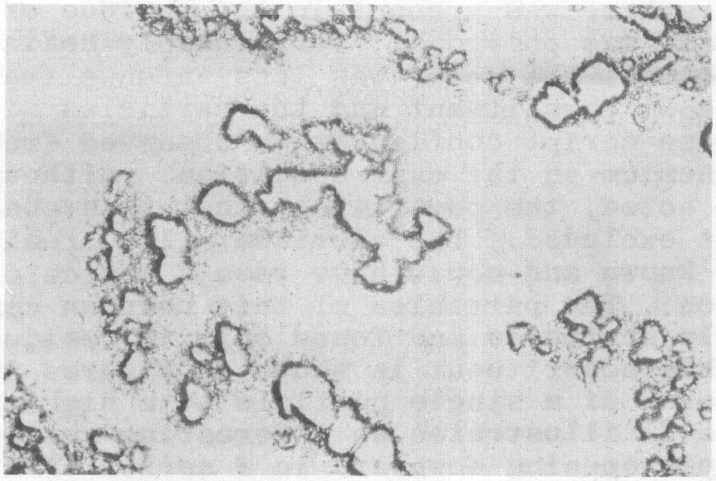

Figure 28

Negative No: 674 Magnification: 500X
Specimen No: 2586 Etch: As-polished

Appearance of a constituent believed to be a chromium segregate recovered from the crucible residue after pouring alloy R-1225 (AZ31 plus 0.3% manganese plus 16% chromium intended). This phase was similar in appearance to massive manganese but colored brownish gray after etching in glycol instead of bluish gray characteristic of manganese.

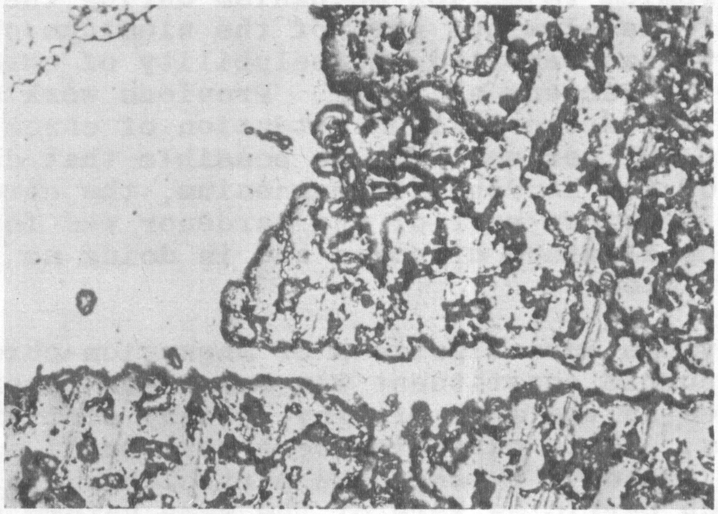

Figure 29

Negative No: 699 Magnification: 500X
Specimen No: 2589 Etch: Acetic glycol, 8 seconds

A section of the interface between AZ31 alloy (upper left) and a chromium rich constituent derived from the addition of aluminum-10% chromium hardener. This interface was found in a hard residue recovered from the crucible after pouring alloy R-1072 (AZ31 plus 0.54% manganese plus 0.014% chromium analyzed). Note the horizontal intrusion of AZ31 alloy into the chromium-rich constituent and the peculiar grain boundary condition in the upper left.

Another phase was present in the residue of alloy R-1072. This phase was polygonal, very sharply defined and bright blue in color. The color was less intense than that of watery-blue Mg_2Si constituent and the particles did not exhibit the Chinese script configuration observed frequently for Mg_2Si in magnesium in the cast condition. Although these differences were noted, the possibility that this constituent was Mg_2Si was not excluded. The aluminum - 10 chromium hardener analysis was not known and could have been a source of small amounts of silicon. The particles of this unknown constituent were small, widely scattered and found only in residues from alloy R-1072. This constituent is shown in Figures 30 and 31, the latter being of a single particle at a high magnification. Figure 31 illustrates an interesting surface configuration of a pit opening downward in a series of discrete steps to form a structure appearing to be built of stacked lamellae. This condition has been discussed by Buerger[39] for zinc and cadmium crystals grown by sublimation in vacuum. The step configuration in this crystal was believed to be evidence of the emergence of two dislocations of opposite sign on the crystal face as described by Cottrell[40].

These angular, blue particles were observed in a sectioned spheroid of metallic residue composed mainly of magnesium. The spheroid contained none of the other constituents mentioned above which were found mainly in brittle, angular pieces of residue. The blue particles might have been due to a chromium rejection mechanism during the alloying with magnesium of the aluminum part of the aluminum-chromium hardener. Sully[41] has reported the solubility of chromium in aluminum to be 0.07 percent at 752°F. Previous work at Rensselaer[28] estimated the maximum retention of chromium in magnesium to be 0.021 percent. It is possible that during the dissolution of the hardener in magnesium, the chromium dissolved in the aluminum part of the hardener was forced to precipitate as the aluminum dissoved and in doing so formed the observed particles.

In previous investigations of magnesium-chromium alloys[28] a deep purple constituent was sometimes observed in as-cast structures in the form of tiny, widely scattered angular particles. These particles were very small and were usually observed adjacent to manganese particles. The possibility that such particles were of the same nature as the blue particles discussed above is tenable. Tiny particles of the blue phase, trapped on a massive manganese particle, may not have easily settled to the crucible bottom prior to pouring and therefore might have been included in the as-cast structure. The fact that the color of the particles in the as-cast structure was purple compared to the blue color of the

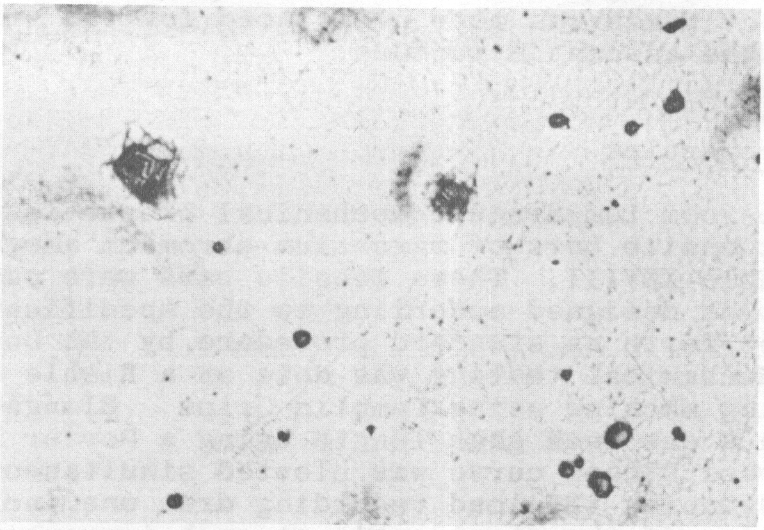

Figure 30

Negative No: 675 **Magnification:** 500X
Specimen No: 2588 **Etch:** Acetic Glycol, 10 seconds

Several small and one large particle of the bright blue constituent observed in the residue of alloy R-1072. This constituent was believed to be either Mg_2Si from silicon contamination, which was unlikely, or a complex chromium phase resulting from rejection of chromium from the aluminum dissolving in the AZ31 matrix.

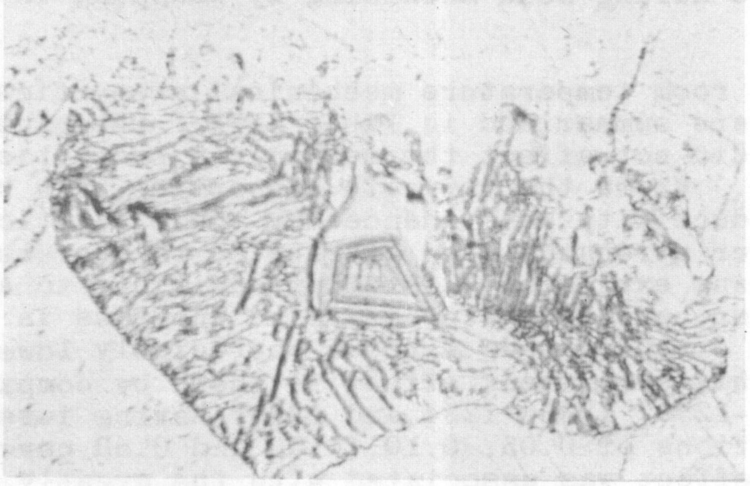

Figure 31

Negative No: 678 **Magnification:** 200X
Specimen No: 2588 **Etch:** Glycol, 5 seconds

One of the particles illustrated in Figure 30 at a higher magnification. The dissolution of this particle has taken place in discrete steps indicating the particle is composed of stacked lamellae.

residue particles might have been due to a shadowing of the staining effect which was more pronounced for the smaller particles in the as-cast structure.

Mechanical Properties

The room temperature mechanical properties of ½ inch diameter cast tensile bars of magnesium-chromium alloys are summarized in Table XXVIII. These tensile bars were cast in baked sand molds designed according to the specifications and dimensions set forth as standard procedure by the Dow Chemical Company[22]. Mechanical testing was done on a Riehle hydraulic tensile testing machine using Templin Grips. Elongations were determined on a one inch gage length using a Porter Lipp strain gauge. A stress strain curve was plotted simultaneously with loading by advancing the load recording drum one increment in the direction of the strain axis at each increment of strain read from the strain gauge. The drum was advanced by means of a manually actuated electrical impulse. No significant effects due to the addition of chromium were observed for the as-cast mechanical properties determined.

Room temperature mechanical properties of 0.150 inch diameter extruded rods were determined in a similar manner using the Porter-Lipp strain gauge over a one inch gauge length. As extruded, the rods were 0.175 inches in diameter but a two inch test section was reduced to 0.150 inches in diameter by acid machining in 25 percent nitric acid. The portions of the test specimens at each end of the reduced diameter test section were protected during acid machining by wrapping in electroplaters tape.

The room temperature mechanical properties of the extruded rod are summarized in Table XXIX. Chromium additions to magnesium did not affect the mechanical properties of extruded rods. Where the strength properties were higher than general, the ductility as evidenced by the elongation was low and the greater strengths were attributed to increased strain hardening during extrusion. Chromium additions to AZ31 base alloys, however, produced a progressive increase in the strength properties of extruded rods without appreciably lowering the ductility. This consistent effect is shown by comparing AZ31 base alloys R-1232, 1233, 1234 and 1235, having intended chromium additions of 0.05, 0.10, 0.30 and 0.50 percent, respectively. This effect was associated with the greatly refined microstructures of this series of alloys described above. It was considered significant that a 1.0 percent chromium addition produced lower mechanical properties, suggesting that the optimum chromium addition for strength increase of the extruded

TABLE XXVIII

ROOM TEMPERATURE MECHANICAL PROPERTIES OF SAND-CAST ONE-HALF INCH DIAMETER MAGNESIUM-CHROMIUM ALLOY TENSILE BARS

Alloy Number	Intended Addition Weight Percent		As-Cast Tensile Properties(b)		
	Chromium(a)	Other	Kips per sq.in. TYS	Kips per sq.in. UTS	Elongation % in 2 in.
Pure Mg(c)	-	-	3.0	12.0	6.0
R-1352(d)	-	-	3.1	13.8	6.5
R-1353(d)	0.10	-	4.3	13.0	5.5
R-1354(d)	0.50	-	3.5	13.2	5.0
R-1355(d)	1.00	-	3.4	12.2	6.3
R-1356(d)	0.10	0.20Zr	3.5	14.0	6.7
R-1358(d)	0.10	0.50Zr	3.7	13.8	5.5
R-1357(d)	0.50	0.20Zr	3.0	12.0	7.3
R-1359(d)	0.50	0.50Zr	4.6	13.1	5.7

(a) Chromium added as anhydrous chromium trichloride in all alloys listed.

(b) Mechanical properties reported are an average of two specimens.

(c) Data obtained from Metals Handbook, ASM, 1948, Edition, p.1014.

(d) Melt was chlorinated for five minutes at 1450°F prior to alloying.

TABLE XXIX

ROOM TEMPERATURE MECHANICAL PROPERTIES OF 0.150 INCH DIAMETER EXTRUDED RODS OF MAGNESIUM-CHROMIUM AND AZ31 CHROMIUM ALLOYS

Alloy Number	Intended Addition Weight Percent: Chromium(a)	Intended Addition Weight Percent: Other	As-Extruded Tensile Properties(b): Kips per sq.in. TYS	As-Extruded Tensile Properties(b): Kips per sq.in. UTS	As-Extruded Tensile Properties(b): Elongation % in 2 in.
FS1-F	Commercial Solid shapes (c)		22.0-26.0	35.0-37.0	10.0-12.0
R-1194	-	-	11.6	26.9	13.3
R-1227	0.05	-	9.4	24.3	15.5
R-1228	0.10	-	8.2	23.9	14.5
R-1229	0.30	-	16.0	29.2	9.8
R-1230	0.50	-	7.4	22.7	15.7
R-1231	1.00	-	12.9	27.1	15.0
R-1222	50.0(d)	-	8.3	23.4	18.3
R-1224	50.0(d)	-	20.1	30.2	11.2
R-1232	0.05	3.00Al 1.00Zn 0.30Mn	27.3	41.8	18.5
R-1233	0.10	3.00Al 1.00Zn 0.30Mn	27.2	41.9	16.8
R-1234	0.30	3.00Al 1.00Zn 0.30Mn	30.6	42.9	15.5
R-1235	0.50	3.00Al 1.00Zn 0.30Mn	35.2	43.4	15.0
R-1236	1.00	3.00Al 1.00Zn 0.30Mn	29.6	39.9	12.3
R-1225	16.0	3.00Al 1.00Zn 0.30Mn	23.7	37.3	6.8

(a) Notes are found on the next page.

Notes Continued

(a) Chromium was added in the form of anhydrous chromium trichloride unless otherwise stated.

(b) Properties reported are an average of three specimens extruded to 0.175 inch rods at 700°F using an extrusion ratio of 18 to 1. Two inch long, 0.150 inch diameter test sections were acid machined prior to testing.

(c) Data obtained from Dow Chemical Comapny Booklet, "Magnesium Alloys and Products", Copyright 1950, pp.24-25.

(d) Chromium was added as electrolytic chromium powder.

AZ31 base alloy was from 0.30 to 0.50 percent. Hardener alloy R-1225 (AZ31 - 0.3% Manganese - 16% Chromium, intended) exhibited reduced strength and ductility as was anticipated due to the relatively large amount of massive constituent in its microstructure.

The room temperature mechanical properties of hot rolled 0.064 inch magnesium-chromium alloy sheet, determined according to the standard procedures described in the Experimental Procedure section of this report, are summarized in Table XXX. No significant improvements in mechanical properties were noted for chromium additions to magnesium or to AZ31 base alloys. An exploratory evaluation of additions of chromium to magnesium-zirconium alloys, to magnesium-zinc-zirconium alloys and to magnesium-zinc-zirconium alloys with additions of rare earth chlorides or thorium did not produce significant changes in mechanical properties attributed to chromium in the range of compositions investigated.

Elevated temperature mechanical properties of 0.064 inch magnesium-chromium alloy sheet with additions of zinc, zirconium, rare earths and thorium were determined at 400°F and 500°F according to the method described in the Experimental Procedure section of this report. These properties summarized in Table XXXI, did not show any benefit due to the chromium additions.

Relative Resistance to Corrosion

Specimens for the magnesium-chromium alloy series were subjected to the standard static resistance to corrosion test described in the Experimental Procedure section of this report. The results of this test summarized in Table XXXII, did not show any marked increase or decrease in the relative resistance to corrosion of magnesium or magnesium base alloys due to additions of chromium in any of the three forms added.

Summary

The introduction of chromium as metallic powder and as chromium salts in magnesium and in selected magnesium-base alloys was studied. Three attempts to produce a mechanical mixture of chromium by stirring large quantities of chromium powder in molten magnesium were unsuccessful. The intended addition of 16% chromium as anhydrous chromium trichloride in AZ31 base alloy produced microstructural evidence interpreted as the retention of a small amount of chromium present as an undissolved, segregated microconstituent. As a general observation, however, it was believed that the recovery of chromium in all alloys studied was extremely small. A metallographic study of crucible residues recovered after attempted additions of chromium indicated that a large fraction of the addition settled to the bottom during the oxidation.

Chromium additions to magnesium and magnesium alloys did not produce significant grain refinement of primary structure. A consistent increase in the mechanical strength without sensible loss in ductility was associated with the presence of a relatively uniform, equiaxed microstructure of AZ31 base alloys with additions of chromium in the as-extruded condition. The effect was attributed to the addition of chromium and appeared to be optimum with an intended addition of approximately 0.3 to 0.5% chromium.

No significant change in microstructure or in the room and elevated temperature mechanical properties of magnesium or magnesium-base alloys with aluminum, zinc, manganese, zirconium, thorium and a mixture of rare earths was observed which could be attributed to the addition of chromium. The relative resistance to corrosion of these alloys was not influenced by the addition of chromium.

TABLE XXX

ROOM TEMPERATURE MECHANICAL PROPERTIES OF 0.064 INCH MAGNESIUM-CHROMIUM ALLOY SHEET IN THE HOT-ROLLED CONDITION

Alloy Number	Intended Addition Weight Percent		Longitudinal Mechanical Properties(b)			
	Chromium(a)	Other	Kips per sq. in.			Elongation % in 2 in.
			CYS	TYS	UTS	
Pure Mg(c)	-	-	-	14.0	27.0	16.0
Pure Mg(d)	-	-	-	27.0	37.0	9.0
R-1352(e)	-	-	10.2	17.7	26.6	6.0
R-1421	$0.05CrF_3 \cdot 3H_2O$	-	11.7	17.3	26.3	2.3
R-1422	$0.10CrF_3 \cdot 3H_2O$	-	11.7	18.8	26.6	3.2
R-1353(e)	0.10	-	10.9	17.7	27.1	6.0
R-1417	$0.10Cr_2O_3$	-	9.5	16.7	26.5	6.7
R-1354(e)	0.50	-	10.6	18.7	27.5	5.3
R-1418	$0.50Cr_2O_3$	-	11.6	18.4	27.8	3.8
R-1355(e)	1.00	-	10.7	18.2	27.3	5.5
R-1419	$1.00Cr_2O_3$	-	12.1	17.1	26.8	3.8
R-1356(e)	0.10	0.20Zr	10.1	18.1	27.8	5.0
R-1358(e)	0.10	0.50Zr	10.7	17.7	26.2	3.3
R-1357(e)	0.50	0.20Zr	11.0	17.9	27.0	3.3
R-1359(e)	0.50	0.50Zr	11.0	16.8	26.2	4.5
R-1360(e)	0.10	1.00Zn 0.20Zr	10.7	26.2	33.7	10.0
R-1361(e)	0.10	3.00Zn 0.60Zr	20.3	31.7	40.1	9.5
R-1397(e)	0.20	3.00Zn 0.50Zr 2.00R.E.	24.3	35.4	41.3	11.0
R-1398(e)	0.20	2.00Zn 0.70Zr 3.00Th	13.9	15.0	35.0	12.0
AZ31(c)	Commercial Sheet		16.0	22.0	37.0	21.0
AZ31(d)	Commercial Sheet		29.0	33.0	42.0	11.0

TABLE XXX (Continued)

ROOM TEMPERATURE MECHANICAL PROPERTIES OF 0.064 INCH MAGNESIUM-CHROMIUM ALLOY SHEET IN THE HOT-ROLLED CONDITION

Alloy Number	Intended Addition Weight Percent		Longitudinal Mechanical Properties(b)			
			Kips per sq. in.			Elongation
	Chromium(a)	Other	CYS	TYS	UTS	% in 2 in.
R-1364(e)	-	3.00Al 1.00Zn 0.50Mn	20.5	34.2	43.6	12.3
R-1362(e)	0.10	3.00Al 1.00Zn 0.50Mn	20.5	34.4	41.2	12.5
R-1363(e)	0.50	3.00Al 1.00Zn 0.50Mn	20.4	35.2	41.7	12.5
R-1420	$0.50Cr_2O_3$	3.00Al 1.00Zn 0.50Mn	17.4	19.0	40.5	12.3

(a) Chromium added in the form of anhydrous chromium trichloride unless otherwise stated.

(b) Properties reported are an average of two specimens unless otherwise stated.

(c) Properties in annealed condition. Data obtained from Metals Handbook, ASM, 1948 edition, pp.1014-1021.

(d) Properties in hard rolled condition. Data obtained from Metals Handbook, ASM, 1948 edition, pp.1014-1021.

(e) Melt was chlorinated for five minutes at 1450°F prior to alloying.

TABLE XXXI

ELEVATED TEMPERATURE MECHANICAL PROPERTIES OF 0.064 INCH MAGNESIUM-CHROMIUM ALLOY SHEET WITH ADDITIONS OF ZINC, ZIRCONIUM, RARE EARTHS AND THORIUM IN THE HOT-ROLLED CONDITION

Alloy Number	Intended Addition Weight Percent		Testing Temp., °F	Longitudinal Tensile Properties(a)	
	Chromium	Other		Kips/in² UTS	Elongation % in 2 in.
FS1-0	Commercial Sheet (b)		400	20.0	18.0
			500	18.0	46.0
FS1-H24	Commercial Sheet (b)		400	21.4	14.0
			500	17.3	43.5
R-1361(c)	$0.10CrCl_3$	3.00Zn	400	21.2	29.0
		0.60Zr	500	14.9	40.0
R-1397(c)	$0.20CrCl_3$	3.00Zn	400	22.2	26.5
		0.50Zr	498	15.5	39.0
		2.00R.E.			
R-1398(c)	$0.20CrCl_3$	2.00Zn	400	20.7	21.0
		0.70Zr	500	18.4	24.5
		3.00Th			

(a) Properties reported are from one test specimen.

(b) Commercial 0.064 inch thick supplied by the Dow Chemical Company.

(c) Melt was chlorinated for five minutes at 1450°F prior to alloying.

TABLE XXXII

RELATIVE RESISTANCE TO CORROSION OF 0.064 INCH HOT-ROLLED MAGNESIUM-CHROMIUM ALLOY SHEET COMPARED TO COMMERCIAL FS1-0 ALLOY SHEET

Alloy Number	Intended Additions Weight Percent		Relative Resistance to Corrosion(b)
	Chromium(a)	Other	
R-1352(c)	-	-	1
R-1421	$0.05CrF_3 \cdot 3H_2O$	-	3
R-1422	$0.10CrF_3 \cdot 3H_2O$	-	3
R-1353(c)	0.10	-	2
R-1417	0.10 Cr_2O_3	-	2
R-1354(c)	0.50	-	2
R-1418	0.50 Cr_2O_3	-	2
R-1355(c)	1.00	-	3
R-1419	1.00 Cr_2O_3	-	3
R-1356(c)	0.10	0.20Zr	2
R-1358(c)	0.10	0.50Zr	2
R-1357(c)	0.50	0.20Zr	2
R-1359(c)	0.50	0.50Zr	2
R-1360(c)	0.10	1.0Zn, 0.2Zr	2
R-1361(c)	0.10	3.0Zn, 0.6Zr	3
R-1397(c)	0.20	3.0Zn, 0.5Zr, 2.0R.E.	2
R-1398	0.20	2.0Zn, 0.7Zr, 3.0Th	4
R-1426	-	3.0Al, 1.0Zn, 0.3Mn	2
R-1364(c)	-	3.0Al, 1.0Zn, 0.5Mn	4
R-1362(c)	0.10	3.0Al, 1.0Zn, 0.5Mn	3
R-1363(c)	0.50	3.0Al, 1.0Zn, 0.5Mn	3
R-1420	0.50 Cr_2O_3	3.0Al, 1.0Zn, 0.5Mn	3

(a) Chromium added in the form of anhydrous chromium trichloride unless otherwise stated.

(b) The relative resistance to corrosion was determined according to the procedure and rating scheme described in the Experimental Procedure section of this report.

(c) Melt was chlorinated for five minutes at 1450°F prior to alloying.

MAGNESIUM - YTTRIUM ALLOYS

Review of Literature

As summarized by Carapella[4], the possibility exists for some solid solubility of yttrium in magnesium due to its hexagonal close-packed space lattice and border-line atomic size factor. It would be expected that the extent of solid solubility would be limited, however, because of an apparent alloying valence of zero and an electronegative position with respect to magnesium.

Sauerwald and Eisenreich[42] claimed that the addition of small amounts of yttrium to magnesium produced a strong grain refining effect and increased the mechanical strength and percentage elongation of magnesium. Their invention covered magnesium alloys with additions of yttrium in the range 0.1 to 10% by weight and with additions of manganese between 0.1 to 2% by weight, although it was indicated that yttrium additions in excess of about 4% were not beneficial. The following tensile mechanical properties of alloys in the sand-cast condition were claimed:

Alloy	Kips per square inch TYS	Kips per square inch UTS	Elongation, Percent in Two inches
Magnesium, unalloyed	4.25	12.8 - 18.4	5 - 6
Magnesium with 0.3% yttrium	7.1	22.5	16
Magnesium with 2.5% yttrium	9.6	24.2	15.6

Kroll[43] reported the successful preparation of an aluminum-yttrium alloy by the calcium reduction of yttrium fluoride in the presence of molten aluminum. This alloy was stated to be a calcium-free binary containing 16.35% yttrium. The alloy was fine grained, stable in air, exhibited an extensive interdendritic network of a pale-violet microconstituent and was slightly harder than the commercially pure aluminum. This investigator also suggested the possibility of an improvement in mechanical properties of magnesium-base alloys with additions of yttrium.

Leontis[44] described the influence of cerium, lanthanum, didymium, praseodymium and cerium-free misch-metal on the elevated temperature properties of sand-cast magnesium alloys. All of the rare earth elements improved the mechanical properties, particularly the resistance to creep. Leontis[45] later extended the study to investigate the influence of these elements, except praseodymium, on the elevated temperature mechanical properties of extruded magnesium alloys. Similar improvements were obtained.

Spedding and his co-workers[46,47] conducted extensive work to develop procedures for isolation of high-purity rare earth salts by ion exchange techniques and to produce metallic rare earths of exceptional purity. Daane and Spedding[48] produced yttrium metal by the calcium reduction of anhydrous yttrium fluoride at 1550°C in a tantalum crucible under an argon atmosphere. The melting point of this high-purity yttrium was estimated to be approximately 1500°C.

Due to the expense of yttrium and yttrium salts attention was directed to a consideration of methods and procedures for the preparation of small-size magnesium alloy melts. Hanawalt and his co-workers[18] described the preparation of small melts of high purity magnesium-base alloys using graphite crucibles, molds and melt handling tools. Marande[49] emphasized the importance and benefit of using a magnesium chloride-free flux, Dow 220, during the preparation of magnesium-base alloys with additions of cerium. As a general procedure, the use of Dow 220 flux was considered advisable when adding any of the rare-earth elements to magnesium to minimize the loss of these elements in the flux phase.

Preparation of Alloys

Alloys were prepared according to the general practice of Melt Procedure II discussed in the Experimental Procedure section of this report. Melt sizes ranged from 100 to 200 grams and Dow 220 flux was used exclusively for refining and protection.

Dow Pure grade of magnesium was used in approximately one-half of the experimental alloys prepared; redistilled magnesium was used in the remainder. Yttrium was introduced as yttrium chloride, yttrium fluoride and metallic yttrium. The salts[a] were specified to be at least 99% pure. Metallic yttrium(b) was a calcium-reduced product and was stated to be greater than 98% yttrium.

(a) Supplied by Lindsay Chemical Company, West Chicago, Illinois.

(b) Supplied by Institute For Atomic Research, Iowa State College, Ames, Iowa.

The scope of this investigation was limited to a study of the influence of additions of yttrium chloride yttrium fluoride and metallic yttrium to magnesium on the mechanical properties of hot rolled sheet. Original plans for experimental work included the preparation of an aluminum-yttrium master alloy for later addition to magnesium,the addition of various forms of yttrium to molten magnesium previously treated with chlorine and zirconium and the addition of yttrium to selected magnesium alloys containing aluminum, zinc and manganese. The aluminum-yttrium master alloy was prepared successfully but was not added to magnesium nor were the other portions of the contemplated work carried out due to a decision to devote more experimental effort to other phases of the general problem of study.

A summary of the intended compositions, conditions of preparation and as-cast grain sizes of the binary magnesium-yttrium alloys investigated is given in Table XXXIII.

As indicated in Table XXXIII, a large proportion of the alloys were made in Dixon Number 4/0 clay-graphite crucibles(a). Initial microscopic examination of magnesium and magnesium-yttrium alloy primary structure indicated that this was a suitable procedure. Later examination, made to observe micro-structural conditions associated with consistently low values of percentage elongation in hot rolled sheet, disclosed the presence of an interdendritic network of unidentified micro-constituents of a variable degree of severity in primary structure of some of the alloys. As was learned in a more detailed investigation, discussed in Appendix I, this condition was attributed to a reaction between the molten magnesium and the clay-graphite crucible. Failure to recognize this condition in earlier microscopic examination was considered reasonable since it did not occur in all melts made in clay-graphite crucibles. Alloys R-1321 through R-1326 were made in crucibles machined from Acheson Grade CS(b) graphite. No distinct evidence of the interdendritic condition was observed in primary microstructure.

During the preparation of alloys R-1142 through R-1145, where yttrium chloride was seated in a magnesium capsule and stirred into the melt, a deep-red color was observed on the melt surface and also in the flux phase. This condition increased with an increased amount of yttrium chloride. Mellor[50] stated that yttrium oxide becomes milk-white upon ignition and turns deep-red below 1000°C. On the basis of this description the condition was believed to be yttrium oxide. The condition was not observed during preparation of alloys R-1146 through R-1176 or in any of the other alloys in which the

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(a) Supplied by F. B. Stevens, Inc., Detroit, Michigan.

(b) Supplied by National Carbon Company, Inc., Niagara Falls, N.Y.

TABLE XXXIII

SUMMARY OF INTENDED COMPOSITIONS, CONDITIONS OF PREPARATION AND AS-CAST GRAIN SIZES OF BINARY MAGNESIUM-YTTRIUM ALLOYS

	Yttrium Addition		Alloying Conditions			Superheat Conditions		Average
Alloy Number(a)	Form	Amount Wt. %	Method (c)	Alloying Temp, °F	Stir Time, Min.	Temp, °F	Time, Min.	As-Cast Grain Size, In.
R-1119	-	None	-	-	-	-	-	0.015
R-1142	YCl_3	0.1	A	1400	1	1645-1700	7	0.005
R-1143	YCl_3	0.1	A	1400	1	1630-1700	10	0.005
R-1144	YCl_3	0.5	A	1400	1	1600-1650	10	0.005
R-1145	YCl_3	1.0	A	1400	1	1700-1735	10	0.005
R-1146	YCl_3	0.1	B	1600	4	1600-1650	5	0.005
R-1147(b)	YCl_3	0.1	B	1600	4	1600-1650	5	0.015
R-1148	YCl_3	0.5	B	1600	4	1600-1650	5	0.004
R-1149	YCl_3	1.0	B	1600	4	1600-1650	5	0.003
R-1176(b)	YCl_3	5.0	B	1600	5	1600-1650	10	0.003
R-1177	-	None	-	-	-	1700-1760	10	0.004-0.012
R-1178	YF_3	0.05	B	1700	7	1700-1750	10	0.004-0.015
R-1179	YF_3	0.1	B	1700	7	1700-1830	10	0.010-0.015
R-1180	YF_3	0.5	B	1700	7	1700-1730	10	0.002
R-1181	YF_3	1.0	B	1700	7	1700-1740	10	0.004-0.012
R-1187	Y	1.0	B	1700	7	1700-1770	10	0.003

TABLE XXXIII (Continued)

SUMMARY OF INTENDED COMPOSITIONS, CONDITIONS OF PREPARATION AND AS-CAST GRAIN SIZES OF BINARY MAGNESIUM-YTTRIUM ALLOYS

	Yttrium Addition		Alloying Conditions			Superheat Conditions		Average
Alloy Number(a)	Form	Amount Wt. %	Method (c)	Alloying Temp, °F	Stir Time, Min.	Temp, °F	Time, Min.	As-Cast Grain Size, In.
R-1321(b)	-	None	-	-	-	1650-1700	5	(d)
R-1323(b)	YF_3	0.2	B	1700	1	1700-1750	10	(d)
R-1324(b)	YF_3	1.0	B	1700	1	1700-1750	10	(d)
R-1325(b)	YCl_3(e)	0.2	B	1650	2	1700-1750	10	(d)
R-1326(b)	YCl_3(e)	1.0	B	1650	2	1700-1725	10	(d)

Notes

(a) All alloys prepared as 100 to 200 gram melts using Dixon #4/0 clay-graphite crucibles (except as noted), using Dow 220 flux exclusively Alloys R-1119 through R-1176 were prepared with Dow Pure grade of magnesium. All other alloys were prepared with redistilled magnesium.

(b) Alloy prepared in a crucible machined from graphite.

(c) Methods of introducing the yttrium additions were:

Method A- dried yttrium salt was loaded into a magnesium cartridge and the end was closed with a magnesium plug. This assembly was stirred into liquid magnesium.

Method B- dried yttrium salt was placed in a porous phosphorizing tool machined from graphite and stirred into the melt.

Method C- metallic yttrium was placed in a small graphite basket and moved gently through the melt.

(d) Structure was relatively coarse-grained, transcolumnar.

(e) When the yttrium chloride was introduced a vigorous reaction occurred, causing melt activity and a thick surface skin. It was believed possible that some of the chloride was entrained in this skin and was removed mechanically from the melt.

yttrium salt was held beneath the melt surface by means of a graphite phosphorizing tool.

As-Cast Grain Size

Primary grain structure of magnesium-yttrium alloys prepared in clay-graphite crucibles was generally equiaxed and fine grained. The specific contribution of the yttrium addition to this condition was uncertain due to the presence of a variable degree of contamination from the crucibles. Comparing the primary structures of alloys R-1321 through R-1326 in which the contamination was not observed, however, all alloys exhibited coarse transcolumnar grain structure which decreased in grain size with increased intended addition of yttrium. The finest grain structure of the group was exhibited by R-1324 (magnesium - 1.0% yttrium, intended as yttrium fluoride), which approached a coarse grained, equiaxed structure. On the basis of these observations, the intended addition of 1.0% yttrium to redistilled magnesium produced only a moderate refinement of primary grain structure.

Aluminum-Yttrium Master Alloy

Two attempts to prepare an aluminum-yttrium master alloy for eventual introduction in magnesium were successful. The general procedures described by Kroll[43] were followed.

One aluminum-yttrium alloy was prepared having an intended yttrium addition of 8% using yttrium chloride instead of the fluoride as used by Kroll. The reaction was carried out at 1700°F and the calcium was added cautiously in small amounts. Despite this precaution a relatively violent reaction followed each calcium addition. The alloy was solidified in the crucible, producing a dull-grey metallic pellet weighing 42 grams. A second aluminum-yttrium alloy was made with an intended addition of 16% yttrium, using yttrium fluoride and following the Kroll procedure as closely as possible. As observed before, the introduction of calcium was accompanied by a violent melt reaction. Solidification in the crucible produced a similar button weighing 38 grams.

Microscopic examination of these two alloys revealed an extensive amount of a massive, pale-pink microconstituent in a solid solution matrix. This condition was more extensive in the alloy with an intended 16% yttrium addition and it was believed that the microconstituents were associated with the yttrium additions.

Considerable difficulty was encountered in the determination of yttrium in these two alloys. Several analytical procedures were tried unsuccessfully before a method was developed which was considered adequate for this purpose. The method used is described in Appendix II. Results of the determination are listed in Table XXXIV.

TABLE XXXIV

DETERMINATION OF YTTRIUM IN ALUMINUM-YTTRIUM MASTER ALLOYS

Alloy Number	Form of Yttrium Addition	Intended Yttrium Addition Weight %	Yttrium Analysis,(a) Weight %
A-1	YCl_3	8.0	4.8
			3.9
			4.4 average
A-2	YF_3	16.0	10.0
			8.9
			9.5 average

Notes:

(a) See Appendix II for method used.

Chemical Analyses

A summary of chemical analyses of magnesium yttrium alloys is given in Table XXXV. It was believed that a determination of yttrium in sheet structure would be a more reliable indication than when determined in cast structure due to the opportunity for a greater degree of homogenization and for a more representative sampling. Results for alloy R-1149 apparently confirmed this belief.

Comparing the analyses for sheet specimens of alloys R-1149, R-1181 and R-1187, an intended addition of 1% yttrium as yttrium fluoride and as metallic yttrium produced an 80% recovery, whereas the addition as yttrium chloride was approximately 60%. An intended addition of 5% yttrium as the chloride, R-1176, produced an yttrium analysis of 1.7%, or approximately 34% recovery. No explanation was found in a review of the preparation or microstructure of alloys R-1179

TABLE XXXV

DETERMINATION OF YTTRIUM IN BINARY MAGNESIUM-YTTRIUM ALLOYS

	Yttrium Addition				
Alloy Number(a)	Form of Addition	Alloying Temp., $^{\circ}$F	Intended Addition Weight %	Condition of Specimen for Analysis(c)	Yttrium Analysis Weight %(d)
R-1142	YCl_3	1400	0.1	As-Cast	0.15
R-1143	YCl_3	1400	0.1	As-Cast	0.085
R-1144	YCl_3	1400	0.5	As-Cast	0.26
R-1145	YCl_3	1400	1.0	As-Cast	0.24
R-1147(b)	YCl_3	1600	0.1	As-Cast	0.064
R-1148	YCl_3	1600	0.5	As-Cast	0.12
R-1149	YCl_3	1600	1.0	As-Cast	0.20
R-1149	YCl_3	1600	1.0	Sheet	0.63
R-1176(b)	YCl_3	1600	5.0	Sheet	1.70
R-1179	YF_3	1700	0.1	Sheet	0.028
R-1180	YF_3	1700	0.5	Sheet	0.096
R-1181	YF_3	1700	1.0	Sheet	0.79
R-1187	Metallic Yttrium	1700	1.0	Sheet	0.81

Notes:

(a) Alloys prepared as 100 to 200 gram melts in clay-graphite crucibles except as noted.

(b) Alloy prepared in a graphite crucible.

(c) Samples for chemical analysis were either from the chill cast bottom of the as-cast ingot or were from 0.064 inch sheet in the hot rolled condition.

(d) Detailed procedures for chemical analysis given in Appendix II.

and R-1180 for a relatively lower recovery of yttrium.

Mechanical Properties

Ingots were hot rolled to 0.064 inch sheet and tensile mechanical properties were determined at room temperature according to methods described in the Experimental Procedure section of this report. No difficulty was encountered in the hot rolling of these alloys. A summary of the mechanical properties is given in Table XXXVI.

The influence of using Dow Pure grade of magnesium compared to the use of redistilled magnesium was indicated clearly in increased tensile yield strengths. In both groups of alloys prepared in clay-graphite crucibles strength values exhibited no significant change but percentage elongations were consistently constant and low, regardless of the intended addition of yttrium. As discussed under "Alloy Preparation" in this section and in Appendix I, a general condition of an unpredictable degree of melt contamination was associated with alloys prepared in clay-graphite crucibles. This made the evaluation of the contribution of the yttrium addition to mechanical properties uncertain.

Mechanical properties of alloys R-1321 through R-1326, prepared in graphite crucibles, indicate a definite influence of the yttrium addition. A significant increase in yield and ultimate strengths was observed for alloys R-1323 and R-1324 with intended additions of 0.2 and 1.0% yttrium, respectively, as yttrium fluoride compared with R-1321 (unalloyed magnesium having same conditions of fabrication). Similar intended additions as yttrium chloride produced a smaller increase in these properties. No distinct evidence of melt contamination was observed in these alloys. Secondary microconstituents were not recognized and it was believed, tentatively, that the alloys were solid solutions.

Summary

The influence of additions of yttrium as yttrium chloride, yttrium fluoride and metallic yttrium on mechanical properties of hot rolled sheet was studied. Additions of yttrium fluoride and metallic yttrium produced higher recovery of yttrium than yttrium chloride. Tentative evidence indicated that the solid solubility of yttrium in magnesium is at least 0.5 to 0.8%. The addition of 1% yttrium to redistilled magnesium produced a mild refinement of primary macrostructure and a significant increase in tensile yield and ultimate strength of 0.064 hot rolled sheet.

TABLE XXXVI

MECHANICAL PROPERTIES OF MAGNESIUM-YTTRIUM ALLOYS AS 0.064 INCH SHEET IN THE HOT-ROLLED CONDITION

Alloy Number	Crucible Type	Form of Magnesium(a)	Yttrium Addition Weight Percent		Longitudinal Properties(b)		
			Intended	Analysis	Kips/in^2 TYS	Kips/in^2 UTS	Elong. % in 2 in.
R-1119	clay-graphite	A	None	-	15.7	25.4	3.7
R-1142	clay-graphite	A	0.1	0.15	16.6	24.0	3.0
R-1143	clay-graphite	A	0.1	0.085	14.3	24.4	3.8
R-1144	clay-graphite	A	0.5	0.26	16.6	25.8	3.8
R-1145	clay-graphite	A	1.0	0.24	16.1	24.2	3.3
R-1146	clay-graphite	A	0.1	-	16.4	25.4	4.0
R-1147(c)	graphite	A	0.1	0.064	14.0	21.3	2.8
R-1148(c)	clay-graphite	A	0.5	0.12	16.0	24.0	3.8
R-1149(c)	clay-graphite	A	1.0	0.63	13.8	24.6	3.3
R-1176(c)	graphite	A	5.0	1.70	13.6	25.7	2.8
R-1177	clay-graphite	B	None	-	8.0	21.7	4.8
R-1178	clay-graphite	B	0.05	-	8.7	22.0	5.7
R-1179	clay-graphite	B	0.1	0.028	8.2	21.7	5.0
R-1180	clay-graphite	B	0.5	0.096	10.1	22.8	3.7
R-1181	clay-graphite	B	1.0	0.79	8.6	20.3	6.5
R-1187	clay-graphite	B	1.0	0.81	11.6	26.0	4.7
R-1321	graphite	B	None	-	11.8	22.0	6.5

TABLE XXXVI (Continued)

MECHANICAL PROPERTIES OF MAGNESIUM-YTTRIUM ALLOYS AS 0.064 INCH SHEET IN THE HOT-ROLLED CONDITION

Alloy Number	Crucible Type	Form of Magnesium(a)	Yttrium Addition Weight Percent		Longitudinal Properties(b)		
					Kips/in^2		Elong. %
			Intended	Analysis	TYS	UTS	in 2 in.
R-1323	graphite	B	0.2	-	14.8	24.2	6.0
R-1324	graphite	B	1.0	-	18.5	27.8	6.5
R-1325	graphite	B	0.2	-	12.1	22.2	6.5
R-1326	graphite	B	1.0	-	14.9	23.8	7.0

Notes

(a) A Magnesium used was Dow Pure grade.

B Magnesium used was redistilled grade.

(b) Average of three specimens unless specified otherwise.

(c) Average of two test specimens.

MAGNESIUM - RHENIUM ALLOYS

Review of Literature

Rhenium is a Group VII transition metal existing in all valence states from minus 1 to plus 7 and is chemically similar to manganese. This similarity to manganese and, therefore, the possibility that, like manganese, it would have a beneficial effect as an alloy addition to magnesium was the major reason for its inclusion in this investigation. Rhenium has a hexagonal close packed space lattice and a borderline atomic size factor indicating the possibility of limited solubility in magnesium. Compared to magnesium it is strongly electronegative and would be expected to form stable intermetallic compounds. The melting point of rhenium has been reported[26] to be 5732 + 90°F and its density is about 21. Both its melting point and density, therefore, are much higher than those of any alloying elements commonly used in magnesium.

No references dealing specifically with alloying of rhenium with magnesium were found in the available literature. No references were found on the subject of rhenium as an impurity in magnesium.

Sims and Wyler[51] prepared a complete bibliography of the available literature on rhenium through 1952. This literature survey summarized the occurrence, history, preparation, properties and chemistry of rhenium, rhenium compounds and rhenium alloys. Druce[52] has written a book on rhenium and in it is included a complete bibliography to 1946. Kates[53] recently summarized the present status of rhenium as a commercial metal.

Exploratory Studies

Early in the investigation of magnesium rhenium alloys three diffusion couple experiments were attempted to determine the presence or absence of solid state diffusion across a magnesium-rhenium interface. The diffusion couples were made by preparing a metallographic polish on one end of a section of swaged rhenium rod(a) and on a like section of high purity redistilled extruded magnesium rod and then pressing these two polished surfaces into intimate contact with each other. The sections were pressed together and held tightly by placing them midway between two opposing bolts in an internally threaded steel

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(a) Donated by the Chase Copper and Brass Company, Waterburry, Connecticut, for this investigation.

cylinder and tightening the bolts with about 20 foot-pounds of applied torque. The whole assembly was then sealed in a Pyrex tube with an inert gas atmosphere and heated for a prolonged period at the desired test temperature. During sealing of the Pyrex tube the pressure of inert gas was attempted to be fixed at 5 psi so as to minimize volatilization of magnesium during the experiment.

The first diffusion experiment was run at 1000 ± 10°F for 14 days in an argon gas atmosphere. When the couple was examined the magnesium was found to have been badly volatilized. Metallographic study of the rhenium side of the couple revealed no evidence of diffusion in that direction. The second diffusion experiment was run at 900 ± 10°F for 10 days in an argon atmosphere and the results of this experiment were lost due to an imperfect seal in the Pyrex tube and resulting oxidation of the magnesium. The third diffusion experiment was run at 864 ± 10°F for 10 days in a dried helium gas atmosphere and was successful. Visual examination of the couple following the 10 day heat treatment showed no evidence of either evaporation or oxidation. Microscopic examination of the interface and base metal on both sides of the interface showed no evidence of alloying in either the magnesium or rhenium. Further experimental work on this phase of the investigation was abandoned.

Preparation of Experimental Alloys

A total of 36 experimental alloys with additions of rhenium were melted and cast during this investigation. All were prepared according to the general method designated in Melt Procedure II in the Experimental Procedure section of this report. Modifications of this general procedure were used in certain cases and these are described below.

Rhenium was added to the experimental alloys in three different forms: massive rhenium metal, rhenium metal powders and potassium perrhenate. The massive rhenium metal was in the form of about ¼ inch diameter swaged rod. An analysis of the rhenium used reported the following impurities, weight percent:

Copper	0.0005	Silicon	0.007	Hydrogen	0.00014
Iron	0.08	Magnesium	0.01		
Aluminum	0.015	Oxygen	0.0009		
Manganese	0.003	Nitrogen	<0.0008		

It was added to magnesium by cutting off a short piece and immersing this piece in the melt for a prolonged soaking at the alloying temperature. The buttons cut from the swaged rod were weighed prior to the addition, recovered from the bottom of the crucible after pouring, cleaned by immersion in a 5 percent aqueous solution of hydrochloric acid and reweighed so as to detect any weight loss due to alloying. The weighings were made on an analytical balance and were considered accurate to 0.001 gram.

The surface of the rhenium button after recovery from the melt was in every case coated with magnesium indicating that magnesium wetted the rhenium. However, only in alloys R-1193 and R-1372 was the button found to have any measureable weight loss. The weight losses determined on the button recovered from these melts were 0.0002 grams and 0.0006 grams, respectively. These weight losses were considered insignificant and the unattacked condition of the recovered rhenium button allowed it to be reused for succeeding melts.

The rhenium metal powder(a) was reported as 99.5 percent pure and a sieve test indicated that all the particles were -270 mesh and all but a small fraction were -325 mesh. The powder was added to the melt by placing it in a hole drilled in a solid piece of magnesium, plugging the hole with magnesium and submerging the whole assembly into the previously melted balance of the charge. Additions of rhenium metal powder caused a black scum to rise to the melt surface immediately following the addition. Subsequent stirring deposited this material on the crucible wall at the outside perimeter of the melt surface but its cause was not determined.

The potassium perrhenate(b) was specified to be 99.91 percent pure as determined by the Nitron method. Introduction of the perrhenate salt was attempted both before and after melting the main charge of magnesium by inserting the perrhenate addition in a drilled block of magnesium similar to the method described for addition of rhenium metal powder. In the case of alloy R-1215 (Magnesium - 1.10% Rhenium, intended) the block containing the perrhenate addition was included with the initial charge. In alloys R-1220 and 1221 (Magnesium - 0.70% and 1.0% Rhenium, intended, respectively) the block containing the perrhenate addition was added to the molten balance of the charge after meltdown. The melting point of potassium perrhenate salt is about 662°F and, therefore, it was probably liquid by the time it came into contact with molten magnesium. No reactions causing disturbance of the melt were noted for these two methods of adding potassium perrhenate.

(a) Supplied by A. D. Mackay, Inc., 198 Broadway, New York 38, New York.

(b) Supplied by the Chase Copper and Brass Company, Waterbury, Connecticut.

Attempts were made to add potassium perrhenate to molten magnesium by wrapping it in paper, alloys R-1216 and 1217 (Magnesium - 0.30% and 0.50% Rhenium, intended, respectively) and in aluminum foil, alloys R-1218 and 1219 (Both Magnesium - 0.7% Rhenium, intended). The paper wrapped additions did not cause a reaction when introduced. The aluminum foil wrapped additions caused violent reactions, however, and in the case of alloy R-1218 totally destroyed the melt. Whether the reaction was caused by the aluminum foil in contact with the molten potassium perrhenate or by trapped moisture was not determined. The former condition was thought more tenable in view of the 10 to 15 second time lapse between introduction of the addition and occurrence of the reaction.

Additions of zinc, manganese, aluminum, zirconium, thorium and rare earths were made similar to methods used in preparing magnesium-chromium alloys previously described. The alloying and superheating temperature for all magnesium-rhenium alloys was in the range of 1450 to 1550°F. Several minutes of stirring with a graphite rod followed alloying and was continued intermittently throughout the prolonged superheating.

The melting and casting conditions and as-cast grain size of all experimental magnesium alloys with rhenium additions are summarized in Table XXXVII.

As-Cast Grain Size

Alloys R-1193 and R-1214, magnesium with additions of a rhenium button, were observed to have a refined equiaxed grain size. Alloy R-1194, however, which was a pure magnesium control casting prepared in the same manner had large transcolumnar grains. All three alloys were contaminated with the interdendritic network believed to be due to impurities in the crucible binder and described in detail in Appendix I.

Initially, the grain refinement observed was believed to be due to the rhenium button addition but later preparation of alloy R-1368, R-1372 and R-1394 (Magnesium with rhenium button addition) in Acheson graphite crucibles resulted in castings with no significant grain refinement. The grain refining effect observed in alloys R-1193 and R-1214 was, therefore, believed to be due to melt contamination.

In all other melts cast in the magnesium-rhenium alloy system no grain refinement due to rhenium additions was observed.

TABLE XXXVII

MELTING AND CASTING CONDITIONS AND AS-CAST GRAIN SIZE FOR EXPERIMENTAL MAGNESIUM-BASE ALLOYS WITH ADDITIONS OF RHENIUM

Alloy Number	Intended Addition Weight Percent		Melt Procedure (a)	Superheat Time, Hrs.	Average Grain Diameter, Inches
	Rhenium	Other			
R-1194(b)	-	-	A	6.5	large,columnar
R-1371	-	-	B	7	large,columnar
R-1368	2.523 gram button	-	B	1	large,columnar
R-1394	2.523 gram button	-	B	4	large,columnar
R-1193(b)	2.523 gram button	-	A	6.5	0.006
R-1372	2.523 gram button	-	B	6.5	large,columnar
R-1214(b)	5.320 gram button	-	A	6.5	0.0015
R-1215	0.10 $KReO_4$	-	A	10 min.	0.015 x 0.125
R-1197	0.10 powder	-	A	4	large,columnar
R-1216(b)	0.30 $KReO_4$	-	A	1	0.005
R-1198(b)	0.30 powder	-	A	4	0.015
R-1217	0.50 $KReO_4$	-	A	1	large,columnar
R-1331	0.50 powder	-	A	3	0.036
R-1218	0.70 $KReO_4$	-	A	-	-
R-1219(b)	0.70 $KReO_4$	-	A	15 min.	0.040
R-1220(b)	0.70 $KReO_4$	-	A	1	0.025
R-1221	1.0 $KReO_4$	-	A	1	0.060
R-1369	1.0 powder	-	B	1	0.030 x 0.070
R-1332	1.0 powder	-	A	3.5	large,columnar
R-1395	1.0 powder	-	B	4	large,columnar
R-1370	2.0 powder	-	B	8	large,columnar

TABLE XXXVII (Continued)

MELTING AND CASTING CONDITIONS AND AS-CAST GRAIN SIZE FOR EXPERIMENTAL MAGNESIUM-BASE ALLOYS WITH ADDITIONS OF RHENIUM

Alloy Number	Intended Addition Weight Percent		Melt Procedure (a)	Superheat Time, Hrs.	Average Grain Diameter, Inches
	Rhenium	Other			
R-1408	2.523 gram button	2.0Zn	B	6	0.010
R-1196	0.1 $KReO_4$	2.0Zn	A	1	0.055
R-1327	0.1 powder	2.0Zn	A	3	0.080
R-1195	0.3 $KReO_4$	2.0Zn	A	1	0.070
R-1328	0.3 powder	2.0Zn	A	3	0.040 x 0.075
R-1329	0.5 powder	2.0Zn	A	3	0.060
R-1401	0.5 powder	1.0Zn	B	1	0.015
R-1402	0.5 powder	2.0Zn	B	1	0.030
R-1403	0.5 powder	5.0Zn	B	1	0.008
R-1330	1.0 powder	2.0Zn	A	4	0.050
R-1404	0.5 powder	0.1Mn	B	1	0.040 x 0.115
R-1405	0.5 powder	0.3Mn	B	1	0.055 x 0.175
R-1406	0.5 powder	1.0Al	B	1	0.035
R-1407	0.5 powder	3.0Al	B	1	0.005
R-1409	2.523 gram button	3.0Zn 1.0Zr	B	6	0.005
R-1399	0.5 powder	2.0Zn 0.5Zr 3.0Th	B	1	0.005
R-1400	0.5 powder	3.0Zn 0.5Zr 3.0R.E.	B	1	0.007

(a) Notes are found on the next page.

(a) Melt procedures are given in the Experimental Procedure section of this report.

A means Melt Procedure II using a Dixon Number 4/0 clay-graphite crucible, 100 gram melt size, and a three inch long, 3/4 inch diameter cylindrical graphite ingot mold.

B means Melt Procedure II.

(b) Melt contaminated by unknown substance from Dixon crucible. See Appendix I.

(c) Melt was lost due to violent reaction following addition of potassium perrhenate.

Metallographic Observations

Metallographic examination of as-cast microstructures of magnesium alloys with rhenium additions did not show any positively identified evidence of the presence of rhenium. Evidence of a eutectic structure found in alloy R-1216 (Magnesium - 0.3% Rhenium, intended) was first thought to be due to Rhenium but found by chemical analysis to be primarily contamination due to silicon, iron and copper.

A few tiny, angular particles, soft violet in color and located primarily at grain boundaries were noted in several of the alloys with additions of rhenium as rhenium metal powder and potassium perrhenate. Several of these particles are shown in Figure 32, a photomicrograph of as-cast alloy R-1215 (Magnesium - 0.1% Rhenium, intended). They exhibited a strong tendency to retard grain boundary migration.

Of interest also was the marked tendency for formation of subgrain structure in magnesium-rhenium alloys. This condition illustrated in Figure 33 and also present in the upper left of Figure 32 was found in varying degrees in nearly all of the pure magnesium base alloys containing single additions of rhenium. Whether or not it was primarily due to rhenium was not determined.

Analysis for Rhenium in Magnesium

Attempts were made to analyze the most promising alloys, selected on the basis of microstructure, for rhenium content. Spectrographic analysis was attempted as a qualitative test for rhenium and for contaminating elements such as iron, silicon, aluminum, zinc, copper and manganese.

Three alloys were investigated; R-1216 (Mg plus 0.3 rhenium, intended), R-1220 (Mg plus 0.7 rhenium, intended), and, as a control, R-1226 (High Purity Magnesium). The spectra were obtained on a Bausch and Lomb 1.5 meter spectrograph utilizing an A. C. spark. Rhenium lines could not be identified positively in any of the samples. This was not considered a conclusive test, however, because of the possibility of the large magnesium content depressing the spectral lines of rhenium. This effect of large amounts of other elements depressing the rhenium spectrum was reported by Hillebrand and Lundell[54].

Alloy R-1216 was found to contain silicon, iron and copper. The 2881.6, 2528.5, 2524 and 2516.2 silicon lines were identified. Very strong copper lines at 3273.9 and 3247.6

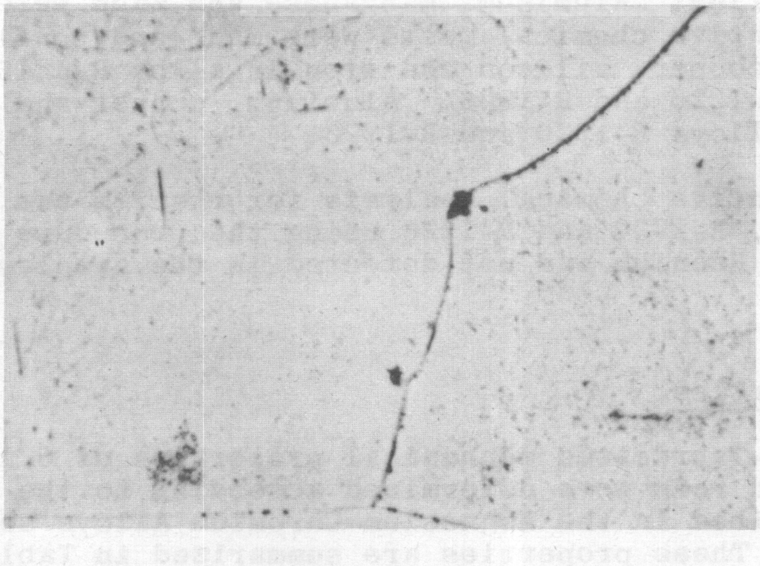

Figure 32

Negative No: 587 Magnification: 500X
Specimen No: M-2341 Etch: 10 seconds in glycol

As-cast microstructure of alloy R-1215 (magnesium - 0.1% rhenium, intended) showing soft violet colored particles of a constituent located in a grain boundary.

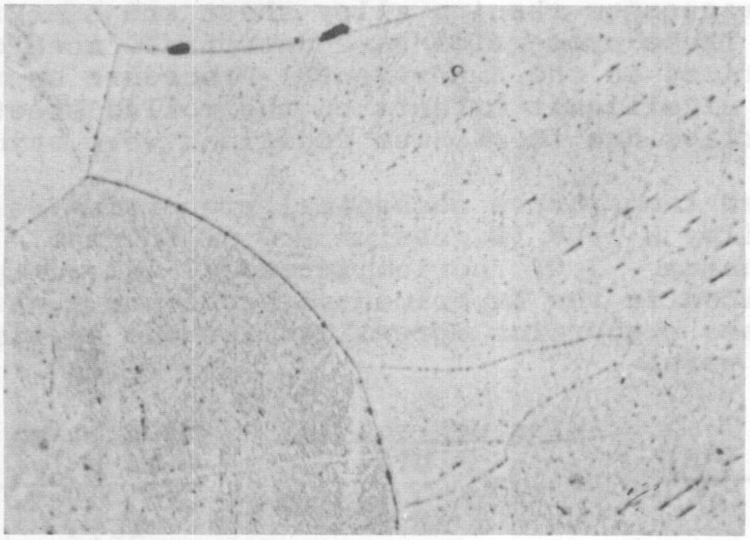

Figure 33

Negative No: 584 Magnification: 500X
Specimen No: M-2341 Etch: 20 seconds in glycol

As-cast microstructure of alloy R-1215 (magnesium - 0.10% rhenium, intended) showing prominent subgrain structure.

were also identified. Aluminum, manganese and zinc were not present. Qualitative chemical tests were made and confirmed the presence of copper, silicon and iron in alloy R-1216 and iron in alloys R-1220 and R-1226. Aluminum, copper and zinc were absent in alloys R-1220 and R-1226.

Qualitative chemical analysis for rhenium was attempted on alloys R-1216, R-1220 and R-1226 using the procedure described in Appendix II. Rhenium was not detected in the samples by this test.

Mechanical Properties

The as-fabricated mechanical properties of 0.150 inch diameter extruded rods were determined according to the same procedures described in the Magnesium-Chromium Alloys section of this report. These properties are summarized in Table XXXVIII. No improvements on the mechanical properties of extruded rods due to the rhenium additions were observed. Of significance was the marked reduction in both yield and ultimate strength by the prolonged superheating. The comparatively high yield and tensile strength of alloys R-1214 (Magnesium-Rhenium button) and R-1216 (Magnesium-0.3% Rhenium, as potassium perrhenate) was attributed to the fine grain size imparted by the impurities present in these alloys.

The room temperature mechanical properties of 0.064 inch hot rolled magnesium-rhenium alloy sheet are summarized in Table XXXIX. These properties were determined according to the methods described in the Experimental Procedure section of this report. No significant effects on the rolled sheet mechanical properties due to rhenium additions were evident.

Elevated temperature mechanical properties were determined for alloy R-1399 (Magnesium - 0.5% Rhenium - 2.0% Zinc - 0.5% Zirconium - 3.0% Thorium, intended) according to procedures described in the Experimental Procedure section of this report. These properties determined for one specimen at each temperature were:

Test Temperature (°F)	Kips per sq. in. UTS	Elongation % in 2 in.
402	21.1	25.0
500	15.7	27.5

The results were not considered significant.

were also identified. Aluminum, manganese and zinc were not present. Qualitative chemical tests were made and confirmed the presence of copper, silicon and iron in alloy R-1216 and iron in alloys R-1220 and R-1226. Aluminum, copper and zinc were absent in alloys R-1220 and R-1226.

Qualitative chemical analysis for rhenium was attempted on alloys R-1216, R-1220 and R-1226 using the procedure described in Appendix II. Rhenium was not detected in the samples by this test.

Mechanical Properties

The as-fabricated mechanical properties of 0.150 inch diameter extruded rods were determined according to the same procedures described in the Magnesium-Chromium Alloys section of this report. These properties are summarized in Table XXXVIII. No improvements on the mechanical properties of extruded rods due to the rhenium additions were observed. Of significance was the marked reduction in both yield and ultimate strength by the prolonged superheating. The comparatively high yield and tensile strength of alloys R-1214 (Magnesium-Rhenium button) and R-1216 (Magnesium-0.3% Rhenium, as potassium perrhenate) was attributed to the fine grain size imparted by the impurities present in these alloys.

The room temperature mechanical properties of 0.064 inch hot rolled magnesium-rhenium alloy sheet are summarized in Table XXXIX. These properties were determined according to the methods described in the Experimental Procedure section of this report. No significant effects on the rolled sheet mechanical properties due to rhenium additions were evident.

Elevated temperature mechanical properties were determined for alloy R-1399 (Magnesium - 0.5% Rhenium - 2.0% Zinc - 0.5% Zirconium - 3.0% Thorium,intended) according to procedures described in the Experimental Procedure section of this report. These properties determined for one specimen at each temperature were:

Test Temperature (^oF)	Kips per sq. in. UTS	Elongation % in 2 in.
402	21.1	25.0
500	15.7	27.5

The results were not considered significant.

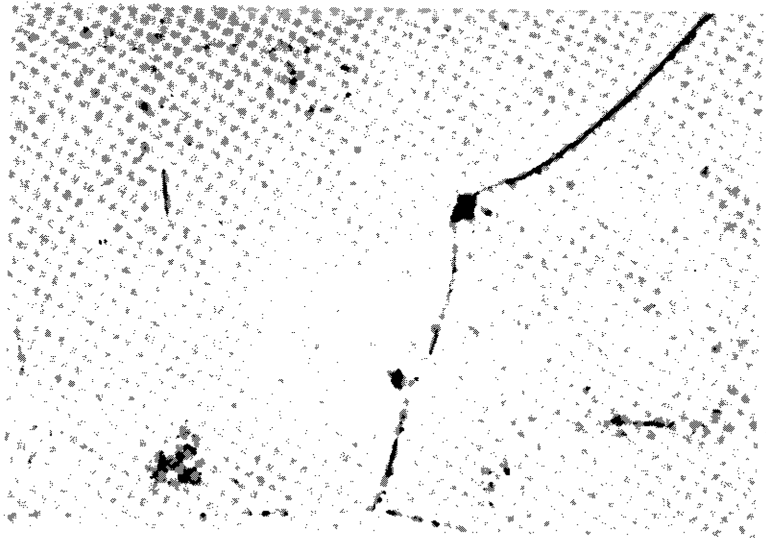

Figure 32

Negative No: 587
Specimen No: M-2341

Magnification: 500X
Etch: 10 seconds in glycol

As-cast microstructure of alloy R-1215 (magnesium - 0.1% rhenium, intended) showing soft violet colored particles of a constituent located in a grain boundary.

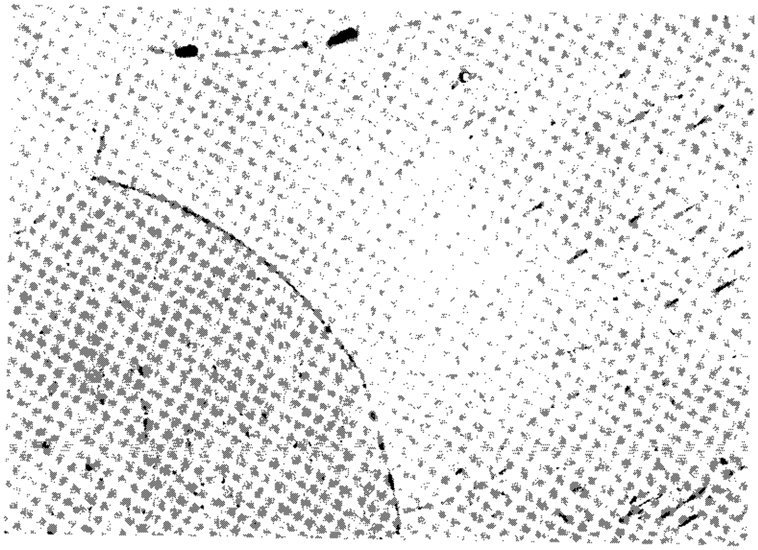

Figure 33

Negative No: 584
Specimen No: M-2341

Magnification: 500X
Etch: 20 seconds in glycol

As-cast microstructure of alloy R-1215 (magnesium - 0.10% rhenium, intended) showing prominent subgrain structure.

TABLE XXXVIII

ROOM TEMPERATURE MECHANICAL PROPERTIES OF 0.150 INCH DIAMETER EXTRUDED RODS OF MAGNESIUM-RHENIUM ALLOYS

	Intended Addition Weight Percent		As-extruded Mechanical Properties(a)		
Alloy Number	Rhenium	Other	Kips per sq. in. TYS	Kips per sq. in. UTS	Elongation % in 2 in.
FS1-F	Commercial Solid Shapes(b)		22.0-26.0	35.0-37.0	10.0-12.0
R-1194(c)	-	-	11.6	26.9	13.3
R-1193(c)	button	-	10.8	23.6	11.8
R-1214(c)	button	-	34.8	38.9	9.8
R-1215	0.10 $KReO_4$	-	19.9	30.4	10.0
R-1197	0.10 powder	-	7.2	23.5	15.7
R-1216(c)	0.30 $KReO_4$	-	30.4	38.0	4.3
R-1198(c)	0.30 powder	-	11.5	26.2	16.7
R-1217	0.50 $KReO_4$	-	17.8	30.5	11.5
R-1331	0.50 powder	-	10.1	24.5	16.5
R-1219(c)	0.70 $KReO_4$	-	12.8	27.1	13.0
R-1220(c)	0.70 $KReO_4$	-	7.0	21.7	17.3
R-1221	1.0 $KReO_4$	-	5.9	21.9	17.7
R-1332	1.0 powder	-	7.4	23.1	13.2
R-1196	0.1 $KReO_4$	2.0Zn	14.7	30.3	13.8
R-1327	0.1 powder	2.0Zn	15.0	29.8	9.2
R-1195	0.3 $KReO_4$	2.0Zn	15.4	30.0	15.0
R-1328	0.3 powder	2.0Zn	14.3	30.1	16.7
R-1329	0.5 powder	2.0Zn	16.0	30.3	15.3
R-1330	1.0 powder	2.0Zn	16.9	31.7	16.7

(a) Notes are found on the next page.

(a) Properties reported are an average of three specimens extruded to 0.175 diameter rod with an acid machined test section 0.150 inches in diameter.

(b) Data obtained from Dow Chemical Company Booklet "Magnesium Alloys and Products", 1950, pp.24-25.

(c) Melt was contaminated by crucible. See Appendix I.

TABLE XXXIX

ROOM TEMPERATURE MECHANICAL PROPERTIES OF 0.064 INCH MAGNESIUM-RHENIUM ALLOY SHEET IN THE HOT-ROLLED CONDITION

Alloy Number	Intended Addition Weight Percent		Longitudinal Mechanical Properties(a)			
			Kips per sq.in.			Elongation % in 2 in.
	Rhenium	Other	CYS	TYS	UTS	
Pure Mg(b)	-	-	-	14.0	27.0	16.0
Pure Mg(c)	-	-	-	27.0	37.0	9.0
R-1371	-	-	7.5	12.0	20.7	5.5
R-1368	button	-	8.0	10.3	21.1	5.0
R-1394	button	-	6.8	11.5	22.2	3.3
R-1372	button	-	6.1	9.8	22.0	4.3
R-1369	1.0 powder	-	12.4	14.4	22.8	9.7
R-1395	1.0 powder	-	8.3	13.1	23.4	4.3
R-1370	2.0 powder	-	6.7	10.8	20.5	5.5
R-1408	button	2.0Zn	13.2	23.9	32.5	6.0
R-1401	0.5 powder	1.0Zn	14.8	25.5	34.7	10.3
R-1402	0.5 powder	2.0Zn	14.3	26.4	34.6	12.0
R-1403	0.5 powder	5.0Zn	19.7	32.8	39.2	15.3
R-1404	0.5 powder	0.1Mn	12.9	18.7	27.6	10.5
R-1405	0.5 powder	0.3Mn	16.5	15.9	26.1	4.3
R-1406	0.5 powder	1.0Al	21.4	24.1	31.5	12.5
R-1407	0.5 powder	3.0Al	17.9	15.2	26.0	10.7
R-1409	button	3.0Zn,1.0Zr	24.9	36.8	43.3	11.0
R-1399	0.5 powder	2.0Zn 0.5Zr 3.0Th	20.4	31.2	38.3	12.3
R-1400(d)	0.5 powder	3.0Zn 0.5Zr 3.0R.E.	-	-	-	-

(a) Notes are found on next page.

(a) Properties reported are an average of two specimens.

(b) Properties in annealed condition. Data obtained from Metals Handbook, ASM, 198 edition, pp.1014-1021.

(c) Properties in hard rolled condition. Data obtained from same source as in (b) above.

(d) Sheet destroyed by transverse shear cracking during rolling.

Relative Resistance to Corrosion

The relative resistance to corrosion of specimens from the magnesium-rhenium alloy series subjected to the standard, static resistance to corrosion test described in the Experimental Procedure section of this report is summarized in Table XL.

Alloys R-1394 (Magnesium-Rhenium button) and R-1395 (Magnesium - 1.0% Rhenium metal powder) both exhibited unusually high relative resistance to corrosion. They both were melted in Acheson graphite crucibles and were both superheated four hours. Other alloys with similar additions, also melted in Acheson graphite crucibles but superheated at a lower temperature for only one hour or for much longer than four hours, did not have the high resistance to corrosion of these two alloys. The appearance of this effect is shown in Figure 34 which is a photograph of the corroded specimens of the pure magnesium series. In comparison, the unalloyed magnesium control specimen, alloy R-1371, prepared under identical conditions except for time of superheating, was destroyed completely.

A review of experimental conditions of alloy preparation did not furnish a satisfactory explanation for the remarkable resistance to corrosion exhibited by alloys R-1394 and R-1395. Experimental time was not available to establish the relative contribution to the effect of the time and temperature of superheating and the chemical analyses of the samples. A similar degree of excellent resistance to corrosion was observed for an alloy with the addition of tantalum, as indicated in the Magnesium-Tantalum section of this report.

Summary

Additions of rhenium as massive metal, metallic powder and potassium perrhenate were made to 36 experimental magnesium alloys. No significant effects which could be traced specifically to the rhenium additions were observed in the mechanical property, as-cast grain size and metallographic data resulting from these alloys. Rhenium additions were thought to be the possible cause of pronounced substructure formation and very small soft violet colored particles observed in the microstructure. Two alloys with intended rhenium addition in the form of a massive rhenium button in one case and 1.0% metallic rhenium powder in the other case exhibited exceptional resistance to corrosion. This behavior was believed to be significant but the specific reason for the beneficial action was not found in the limited experimental work completed.

TABLE XL

RELATIVE RESISTANCE TO CORROSION OF 0.064 INCH HOT-ROLLED MAGNESIUM-RHENIUM ALLOY SHEET COMPARED TO COMMERCIAL FS1-0 ALLOY SHEET

Alloy Number	Intended Addition Weight Percent		Relative Resistance to Corrosion(a)
	Rhenium	Other	
R-1371	-	-	5
R-1368	button	-	4
R-1394	button	-	1(b)
R-1372	button	-	4
R-1369	1.0 powder	-	4
R-1395	1.0 powder	-	1(b)
R-1370	1.0 powder	-	4
R-1408	button	2.0Zn	2
R-1401	0.5 powder	1.0Zn	3
R-1402	0.5 powder	2.0Zn	3
R-1403	0.5 powder	5.0Zn	4
R-1404	0.5 powder	0.1Mn	3
R-1405	0.5 powder	0.3Mn	2
R-1406	0.5 powder	1.0Al	2
R-1407	0.5 powder	3.0Al	4
R-1409	button	3.0Zn, 1.0Zr	4
R-1399	0.5 powder	2.0Zn, 0.5Zr, 3.0Th	4

(a) The relative resistance to corrosion was determined according to the procedure and rating scheme described in the Experimental Procedure section of the report.

(b) No visible evidence of corrosion attack after the test. Specimen surfaces appeared identical to their condition prior to the test.

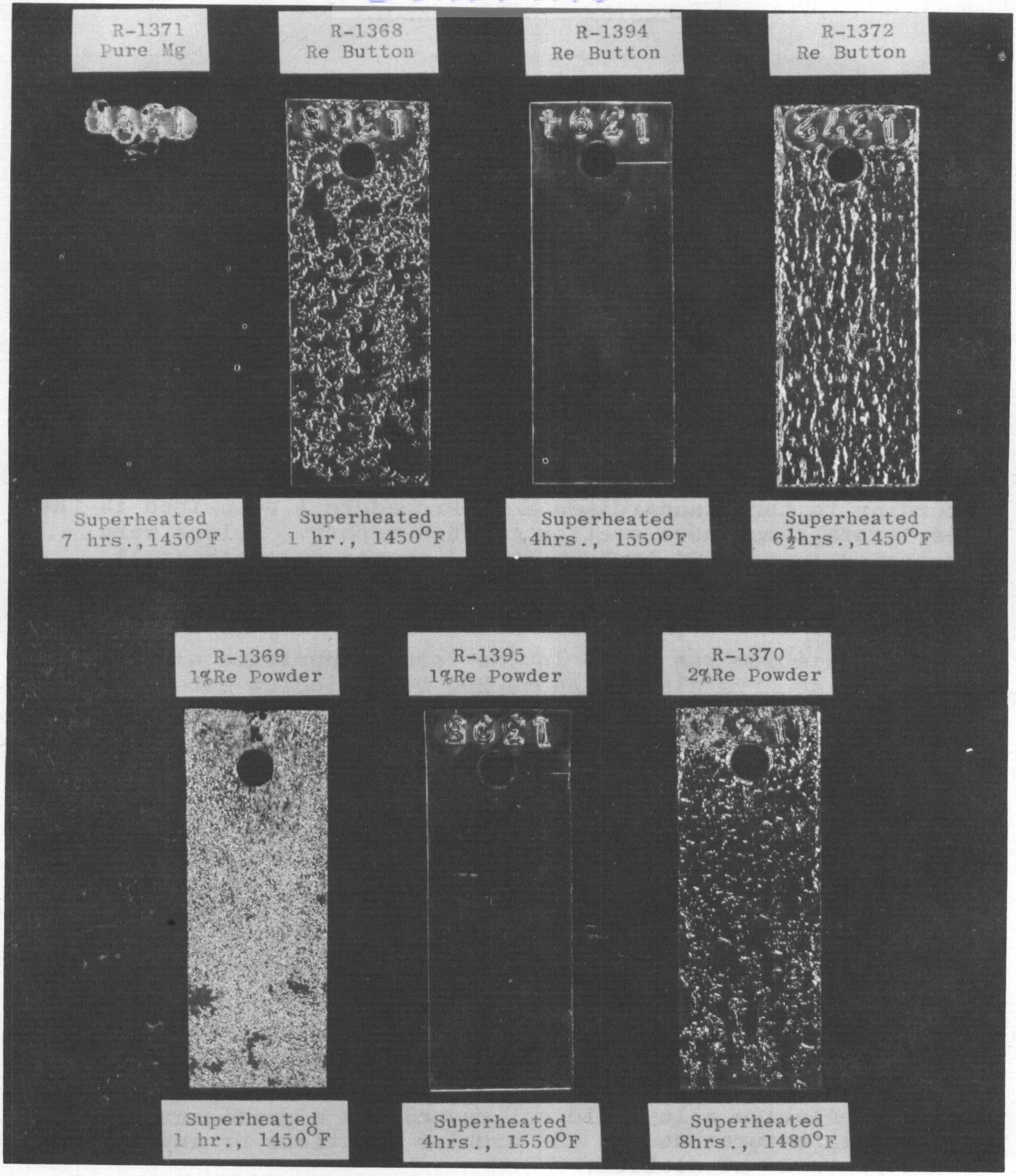

Figure 34. Effect of rhenium addition and superheat time on the relative resistance to corrosion of magnesium.

The specific cause of the superior resistance to corrosion exhibited by alloys R-1394 and R-1395 was not learned. No appreciable differences between these and the other alloys shown were observed in the as-rolled microstructures.

MAGNESIUM-NIOBIUM ALLOYS

Review of Literature

Niobium is a Group V transition metal with a body centered cubic space lattice. Its atomic size differs from that of magnesium by only seven percent according to Carapella[4] and therefore has an atomic size factor favorable for solubility in magnesium. It is, however, electronegative with respect to magnesium and from this standpoint would be expected to form stable intermetallic compounds. Magnesium base alloys with additions of niobium have been reported in the literature[25] but the effect of the niobium additions was not discussed.

Preparation of Experimental Alloys

Four experimental alloys were cast containing additions of niobium from 0.30 to 1.0 percent. All alloys were prepared according to the standardized Melt Procedure I described in the Experimental Procedure section of this report. Alloys were fabricated into 0.064 inch sheet and tested for mechanical properties and resistance to corrosion according to procedures described in the Experimental Procedure section of this report.

Niobium was added in the form of purified niobium pentachloride crystals(a) and as 200 mesh niobium metal powder(a). These additions were wrapped in paper and stirred into the melt at 1450°F using an iron ladle.

The pentachloride additions gave off large quantities of black smoke as they were introduced into the melt. This was accompanied by violent bubbling. Similar bubbling but without the evolution of smoke was noted for the niobium metal powder additions.

A summary of the alloys prepared and their melting and casting conditions and as-cast grain size is given in Table XLI.

Metallographic Observations

Examination of as-cast and wrought microstructures of magnesium-niobium alloys did not reveal any significant microstructural features due to the niobium additions or any evidence of the presence of niobium.

(a) Supplied by A. D. Mackay, Inc., 198 Broadway, New York 38, New York.

TABLE XLI

MELTING AND CASTING CONDITIONS AND AS-CAST GRAIN SIZE FOR EXPERIMENTAL MAGNESIUM-NIOBIUM ALLOYS

Alloy Number	Intended Addition Weight Percent Niobium	Intended Addition Weight Percent Other	Form of Addition	Melt Procedure(a)	Average Grain Diameter, Inches
R-1352	-	-	-	A	Large,columnar
R-1388	0.30	-	$NbCl_5$	B	0.078(b)
R-1386	0.50	-	Powder	B	Large,columnar
R-1387	1.00	-	Powder	B	0.055(b)
R-1392	0.30	3.0Al 1.0Zn 0.3Mn	$NbCl_5$	B	0.005

(a) Melt procedures are given in the Experimental Procedure section of this report.

A means Melt Procedure I with chlorination for five minutes prior to alloying.

B means Melt Procedure I.

(b) Grain size determined on equiaxed grains in center of casting cross section. Grains at edges predominantly large and columnar.

As-Cast Grain Size

Niobium additions to alloys R-1388 (Magnesium - 0.3% Niobium, intended) and R-1387 (Magnesium - 1.0% Niobium, intended) reduced the extent of the columnar grain structure, producing large but equiaxed grains in the center of the casting. This effect was not noticed in alloy R-1386 (Magnesium - 0.5% Niobium, intended). The grain refining effect of niobium in magnesium was considered relatively mild.

Mechanical Properties

Longitudinal tension and compression blanks were sheared from 0.064 inch sheet, flattened, machined to the proper size for test specimens and tested according to the standard procedure described in the Experimental Procedure section of this report. The mechanical properties of magnesium-niobium alloys and one AZ31-niobium alloy are summarized in Table XLII. These results indicated that niobium had no significant effect on the mechanical properties of the magnesium base and AZ31 base alloys in this investigation.

Resistance to Corrosion

Specimens for the magnesium-niobium alloy series were subjected to the standard static resistance to corrosion test described in the Experimental Procedure section of this report. The results of this test are summarized in Table XLIII and show that niobium additions had no significant effect on the resistance to corrosion of either pure magnesium or AZ31 alloy.

Summary

Four experimental magnesium alloys containing niobium were cast. Niobium was added as niobium metal powder and as niobium pentachloride. No significant effects on the as-cast grain size, cast and wrought microstructures, mechanical properties and relative resistance to corrosion due to the niobium additions were observed.

TABLE XLII

ROOM TEMPERATURE MECHANICAL PROPERTIES OF 0.064 INCH MAGNESIUM-NIOBIUM ALLOY SHEET IN THE HOT-ROLLED CONDITION

Alloy Number	Intended Addition Weight Percent		Longitudinal Mechanical Properties(a)			
			Kips per Square Inch			Elongation % in 2 in.
	Niobium	Other	CYS	TYS	UTS	
Pure Mg(b)	-	-	-	14.0	27.0	16.0
Pure Mg(c)	-	-	-	27.0	37.0	9.0
R-1352(d)	-	-	10.2	17.7	26.6	6.0
R-1388	0.30NbCl$_5$	-	9.9	17.9	27.0	5.8
R-1386	0.50 Powder	-	10.4	17.9	27.2	5.5
R-1387	0.00 Powder	-	9.8	17.5	26.0	5.3
AZ31	Commercial Alloy(b)		16.0	22.0	37.0	21.0
AZ31	Commercial Alloy(c)		29.0	33.0	42.0	11.0
R-1392	0.30NbCl$_5$	3.0Al 1.0Zn 0.3Mn	16.9	29.3	39.7	12.2

(a) Properties reported are an average of two specimens.

(b) Properties in annealed condition. Data obtained from Metals Handbook, ASM, 1948 Edition, pp.1014-1021.

(c) Properties in hard rolled condition. Data obtained from same source as (b) above.

(d) Melt was chlorinated for five minutes at 1450°F prior to alloying.

TABLE XLIII

RELATIVE RESISTANCE TO CORROSION OF 0.064 INCH HOT-ROLLED MAGNESIUM-NIOBIUM ALLOY SHEET COMPARED TO COMMERCIAL FS1-0 ALLOY SHEET

Alloy Number	Intended Addition Weight Percent		Relative Resistance to Corrosion(a)
	Niobium	Other	
R-1352(b)	-	-	1
R-1388	0.30 $NbCl_5$	-	3
R-1386	0.50 Powder	-	2
R-1387	1.00 Powder	-	3
R-1392	0.30 $NbCl_5$	3.0Al 1.0Zn 0.3Mn	3

(a) The relative resistance to corrosion was determined according to the procedure and rating scheme described in the Experimental Procedure section of this report.

(b) Melt was chlorinated for five minutes at 1450°F prior to alloying.

MAGNESIUM - TUNGSTEN ALLOYS

Review of Literature

Tungsten is a Group VI transition element with normally a body centered cubic space lattice, a borderline atomic size factor and a highly electronegative nature compared to magnesium. It would not, therefore, be expected to be highly soluble in magnesium but would tend to form stable intermetallic compounds. It has the highest melting point of any metal, 6152°F, and a density of 19.3. Magnesium alloys with additions of tungsten have been reported in the literature[25] but no data were given.

Preparation of Experimental Alloys

Two experimental alloys were cast containing additions of tungsten. Both were prepared according to the standard Melt Procedure I described in the Experimental Procedure section of this report. The tungsten addition in both cases was made by introducing purified tungsten hexachloride crystals(a) wrapped in paper into the melt with an iron ladle. Alloying was done at 1450°F. Extremely violent bubbling and splattering of the molten charge was encountered immediately after the tungsten hexachloride addition was immersed. No burning occurred, however, even though molten magnesium was thrown from the crucible out onto the floor. Several seconds after the initial reaction had subsided a dense gray smoke rose from the melt causing a slight disturbance but no burning or splattering. The reactors were probably due to the evolution of chlorine gas formed by reduction of the hexachloride. The fact that no burning occurred even during the most violent stages of the reaction was attributed to melt protection furnished by the chlorine gas being formed.

A summary of the alloys prepared and their melting and casting conditions and as-cast grain size is given in Table XLIV.

Metallographic Observations

Examination of as-cast and wrought microstructures of magnesium-tungsten alloys did not reveal significant microstructural evidence attributed to the presence of tungsten.

(a) Supplied by A. D. Mackay, Inc., 198 Broadway, New York 38, New York.

TABLE XLIV

MELTING AND CASTING CONDITIONS AND AS-CAST GRAIN SIZE FOR EXPERIMENTAL MAGNESIUM-TUNGSTEN ALLOYS

Alloy Number	Intended Addition Weight Percent		Form of Addition	Melt Procedure(a)	Average Grain Diameter, Inches
	Tungsten	Other			
R-1352	-	-	-	A	Large, columnar
R-1389	0.50	-	WCl_6	B	0.040(b)
R-1390	0.20	3.0Al 1.0Zn 0.3Mn	WCl_6	B	0.010

(a) Melt Procedures are given in the Experimental Procedure section of this report.

A means Melt Procedure I with chlorination for five minutes at 1450°F prior to alloying.

B means Melt Procedure I.

(b) Grain size determined on experimental grains in center of casting cross section. Grains at edges were predominantly large and columnar.

As-Cast Grain Size

The tungsten addition to alloy R-1389 (Magnesium - 0.50% Tungsten, intended) reduced the extent of the columnar grain structure to about the same degree as noted previously for additions of niobium. However, this one case was not considered sufficient evidence to determine whether or not the effect was due to the tungsten addition.

Mechanical Properties

Longitudinal tension and compression blanks were sheared from the hot rolled 0.064 inch sheet, flattened machined into test specimens and tested according to the standard procedures described in the Experimental Procedure section of this report. The mechanical properties of the magnesium-tungsten and AZ31 tungsten alloys are summarized in Table XLV. These results indicated that tungsten addition had no significant effect on the machined properties of the alloys tested.

Resistance to Corrosion

Specimens of the magnesium-tungsten alloy series were subject to the standard static resistance to corrosion test described in the Experimental Procedure section of this report. The results of this test are summarized in Table XLVI and show that tungsten additions reduced the resistance to corrosion of the two alloys investigated.

Summary

Two experimental magnesium alloys containing tungsten additions as tungsten hexachloride were cast. No significant effects on the as-cast grain size, cast and wrought microstructures, mechanical properties and relative resistance to corrosion due to the tungsten additions were observed.

TABLE XLV

ROOM TEMPERATURE MECHANICAL PROPERTIES OF 0.064 INCH MAGNESIUM-TUNGSTEN ALLOY SHEET IN THE HOT-ROLLED CONDITION

	Intended Addition Weight Percent		Longitudinal Mechanical Properties(a)			
			Kips per sq. in.			Elongation
Alloy Number	Tungsten	Other	CYS	TYS	UTS	% in 2 in.
Pure Mg(b)	-	-	-	14.0	27.0	16.0
Pure Mg(c)	-	-	-	27.0	37.0	9.0
R-1352(d)	-	-	10.2	17.7	26.6	6.0
R-1389	0.5	-	11.2	17.6	26.9	5.0
AZ31	Commercial Alloy(b)		16.0	22.0	37.0	21.0
AZ31	Commercial Alloy(c)		29.0	33.0	42.0	11.0
R-1390	0.20	3.0Al 1.0Zn 0.3Mn	18.9	32.9	41.0	9.8

(a) Properties reported are an average of two specimens.

(b) Properties in annealed condition. Data obtained from Metals Handbook, ASM, 1948 Edition, pp. 1014-1021.

(c) Properties in hard rolled condition. Data obtained from same source as in (b) above.

(d) Melt was chlorinated for five minutes at 1450°F prior to alloying.

TABLE XLVI

RELATIVE RESISTANCE TO CORROSION OF 0.064 INCH HOT-ROLLED MAGNESIUM-TUNGSTEN ALLOY SHEET COMPARED TO COMMERCIAL FS1-O ALLOY SHEET

Alloy Number	Intended Addition Weight Percent		Relative Resistance to Corrosion (a)
	Tungsten	Other	
R-1352(b)	-	-	1
R-1389	0.50	-	3
R-1390	0.20	3.0Al 1.0Zn 0.3Mn	4

(a) The relative resistance to corrosion was determined according to the procedure and rating scheme described in the Experimental Procedure section of this report.

(b) Melt was chlorinated for five minutes at 1450°F prior to alloying.

MAGNESIUM-MOLYBDENUM ALLOY

Review of Literature

Molybdenum is a Group VI transition metal with a body centered cubic space lattice, a borderline atomic size factor and a relatively electronegative nature compared to magnesium. It, therefore, would not be expected to be soluble in magnesium to any extent and would more likely form stable intermetallic compounds. Magnesium alloys with molybdenum additions have been reported in the literature[25].

Preparation of Experimental Alloy

Only one magnesium-molybdenum alloy, R-1391, was cast. It was prepared according to the standardized Melt Procedure I described in the Experimental Procedure section of this report. The molybdenum addition of 0.54 percent was added in the form of purified molybdenum pentachloride crystals(a) wrapped in paper and stirred into the melt at 1450°F with an iron ladle.

The ingot was scalped, homogenized and rolled to 0.064 inch sheet from which mechanical properties and resistance to corrosion data were obtained according to procedures described in the Experimental Procedure section of this report.

Metallographic Observations and As-Cast Grain Size

No significant microstructural condition or reduction in as-cast grain size due to the molybdenum in alloy R-1391 was observed. The transcolumnar grain structure of this alloy extended into the center of the casting.

Mechanical Properties

The average longitudinal mechanical properties in the hot rolled condition of alloy R-1391 were:

Kips per Square Inch			Elongation
CYS	TYS	UTS	% in 2 in.
11.7	18.4	28.2	5.8

(a) Supplied by A. D. Mackay, Inc., 198 Broadway, New York 38, New York.

These properties were not significantly different from those of unalloyed magnesium, R-1352, indicating that the molybdenum addition had little effect on the mechanical properties.

Relative Resistance to Corrosion

The relative resistance to corrosion of alloy R-1391 was comparable to the relative resistance to corrosion of commercial FS1-0 alloy sheet.

Summary

One alloy was prepared with an addition of 0.54 molybdenum as molybdenum pentachloride. No significant effect on the as-cast and wrought microstructure, as-cast grain size, mechanical properties and relative resistance to corrosion due to the molybdenum addition was observed.

CONCLUSIONS

1. The intended addition of titanium up to 4.2% to magnesium and to magnesium-base alloys as titanium sponge, halides of titanium, potassium fluotitanate and a manganese - 35% titanium caused no improvement in mechanical properties of the alloys in the form of hot rolled sheet.

    a. The retention of titanium in these alloys was believed to be extremely small.

2. A pronounced refinement of as-cast grain structure resulted from the addition of approximately 0.10 to 0.15% titanium dioxide to magnesium and to magnesium-base alloys.

    a. The addition to unalloyed magnesium produced a marked reduction in the extent and grain size of the columnar zone. This behavior was related to the particle size of the titanium dioxide and was much more pronounced for an addition having minus 200 mesh size than for coarser fractions.

    b. The addition was particularly effective when made to magnesium alloys with soluble components as evidenced by the results for additions to base compositions Z3, AZ31 and AZM331.

    c. Manganese reduced the effectiveness of the grain refining action of titanium dioxide.

    d. A distinct improvement in hot working characteristics of all alloys and a significant increase in tensile mechanical properties of AZM331 was associated with additions of titanium dioxide, compared with the same base compositions without this addition.

3. Intended additions of hafnium up to 1.0% to magnesium and to Z3 base composition as metallic hafnium and hafnium tetrachloride produced no significant effect on the mechanical properties or resistance to corrosion of hot rolled sheet. It was believed that the retention of hafnium in these alloys was small.

    a. Hafnium additions to Z3 base composition reduced the as-cast grain size to the same range as obtained by the addition of saturation zirconium to the same base composition.

4. Intended tantalum additions up to 1.0% to magnesium and to Z3, ZM30, ZM31 and ZK30 base compositions as metallic powder, tantalum chloride and tantalum potassium fluoride produced no

significant change in mechanical properties of hot rolled sheet.

a. Experimental evidence indicated that metallic tantalum was wet by molten magnesium. Although chemical analyses for tantalum were not made it was believed that the amount of tantalum retained in the alloys was small.

b. Exceptionally good resistance to corrosion was exhibited by one alloy with an intended addition of 1.0% tantalum as metallic powder and by two alloys with intended additions of 0.1% tantalum as tantalum potassium fluoride, compared with commercial FS1-0 sheet. This result was considered significant but no explanation for its occurrence was observed.

5. The intended addition of nickel up to 2.2% to magnesium and to selected magnesium alloys with addition of manganese, zinc and zirconium produced these results:

a. Six micron nickel powder added to magnesium produced the greatest recovery of this element, approximately 90%, compared with 70% nickel - 30% magnesium hardener and nickelous chloride forms of addition.

b. Nickel additions produced a small to moderate refinement of as-cast grain structure of experimental alloys.

c. A moderate increase in room temperature mechanical properties of hot rolled sheet was associated with an intended addition of 2.2% nickel to magnesium and an intended addition of 0.1% nickel to ZM30 and ZK30 base compositions.

d. A small improvement in the ultimate tensile strength of hot rolled sheet at 400°F was obtained with additions of nickel to magnesium and to magnesium alloys containing manganese, zinc and zirconium but decreased this property for alloys containing zinc and zirconium.

e. The relative resistance to corrosion was decreased sharply by nickel additions to experimental alloys.

6. Intended additions of cobalt up to 1.0% to magnesium and to selected magnesium alloys with additions of manganese, zinc and zirconium produced these results:

a. The highest recovery of cobalt in magnesium, approximately 40%, resulted from the addition as a fine metallic powder, compared to the cobaltous chloride form of addition.

b. As-cast grain sizes were not influenced significantly by cobalt additions.

c. The addition of 1% cobalt powder to magnesium and to ZM31 produced a small increase in as-cast tensile ultimate strengths and percentage elongations at room temperature.

d. Cobalt additions did not produce a consistent improvement in the mechanical properties of hot rolled sheet at room and elevated temperatures.

e. The relative resistance to corrosion was lowered by the cobalt additions.

7. Intended vanadium additions up to 1% to magnesium and to AZ31 composition as metallic powder, divanadyl tetrachloride and an 85 vanadium - 15% aluminum hardener produced no significant improvement in room temperature mechanical properties or resistance to corrosion of hot rolled sheet.

   a. Microstructural observations of an undissolved constituent in these alloys were interpreted as tentative evidence of the presence of vanadium.

8. Vanadium additions to magnesium and to AZ31 composition produced extensive refinement of as-cast grain structure, similar in effect to the results for titanium dioxide additions.

9. Intended chromium additions up to 1% to magnesium and to AZ31 composition as chromium trichloride, chromium fluoride and chromium sesquioxide indicated:

   a. A pronounced tendency for the chromium addition to settle to the crucible bottom. Retention of chromium in experimental alloys was believed to be extremely small.

   b. No significant grain refinement of primary structure that could be attributed distinctly to the chromium addition.

   c. A consistent increase in tensile yield and ultimate strengths without loss in ductility associated with increased chromium additions to AZ31 composition in the as-extruded condition, reaching an optimum at 0.3 to 0.5% chromium, intended addition.

d. No significant change in microstructure, in the room and elevated temperature mechanical properties or in the relative resistance to corrosion which could be related distinctly to the intended chromium addition.

10. Additions of yttrium up to 1% to magnesium as yttrium chloride, yttrium fluoride and massive metallic yttrium gave these results:

a. Metallic yttrium and yttrium fluoride form of addition produced higher recovery of yttrium, approximately 80%, than the addition as yttrium chloride, approximately 60%.

b. Microscopic observations indicated that the solid solubility of yttrium in magnesium is at least 0.5 to 0.8%.

c. Moderate refinement of as-cast grain size was obtained but not complete elimination of the transcolumnar pattern of structure.

d. The intended addition of 1% yttrium as yttrium fluoride to magnesium was associated with a significant increase in tensile yield and ultimate strengths (36 and 26.5%, respectively). A similar but slightly smaller increase was obtained for the same addition as yttrium chloride.

11. Intended rhenium additions up to 1% to magnesium and to selected magnesium alloys with additions of zinc, aluminum, manganese zirconium and thorium as massive metallic rhenium, rhenium powder or potassium perrhenate did not produce significant changes in as-cast grain size, microstructures or mechanical properties of hot rolled sheet which could be attributed distinctly to the presence of rhenium.

a. The general resistance to corrosion of these alloys was less than commercial FS1-O sheet.

b. Exceptionally good resistance to corrosion was exhibited by two alloys with intended additions of 1% rhenium as massive metallic and as powdered rhenium to magnesium. The appearance of the sheet after the corrosion test closely resembled the magnesium tantalum sheet which exhibited a similar effect. The behavior was believed significant but the exact cause of the excellent protection was not found.

12. A limited, exploratory evaluation of intended additions of niobium as a metallic powder and a niobium pentachloride, tungsten as tungsten hexachloride and boron as calcium boride, boron nitride and manganese boride disclosed no significant influence on as-cast grain size, resistance to corrosion and room temperature mechanical properties.

RECOMMENDATIONS

1. A potentially attractive method for a powerful grain refinement of primary structure of magnesium alloys by means of small additions of titanium dioxide and vanadium was demonstrated. This behavior occurred in the intended absence of aluminum. It is presumed that, unlike the well established methods of grain refinement by superheating and carbon innoculation, aluminum was not a necessary requirement for operation. The method, would be especially useful, therefore, in magnesium alloys without aluminum. A more complete study of this method is recommended to establish its operating mechanism and the limits of methods, procedures and compositions for optimum effectiveness in order to provide a new means for obtaining improved mechanical working characteristics and improved mechanical properties. It is believed that other materials may be equally or even more effective than titanium dioxide and vanadium.

2. Excellent relative resistance to corrosion was exhibited by two magnesium-rhenium and two magnesium-tantalum alloys in the form of hot rolled sheet. The cause of this desirable behavior was not clear from the limited experimental evidence at hand. A search for the conditions necessary to provide this protection is recommended in order to establish the reproducibility of the effect and to examine the possibility of extending the behavior to other magnesium-base alloys.

3. Yttrium additions to magnesium produced a significant increase in room temperature mechanical properties and microstructural observations indicated that the solid solubility was at least 0.5% to 0.8%. Continued study is recommended to determine elevated temperature mechanical properties, particularly resistance to creep, and the influence of other addition elements in combination with yttrium on these properties.

4. Further study of the additions of titanium, hafnium, rhenium, nickel, cobalt, chromium,niobium, boron, tungsten and molybdenum to magnesium is not recommended.

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APPENDIX I

AUXILIARY INVESTIGATION OF MELT CONTAMINATION

An extensive interdendritic network was observed in some of the alloys prepared in small melts (200 gms. or less). This network was not peculiar to any alloy system but was found in melts containing either rhenium, yttrium, hafnium, nickel, or tantalum, and even in supposedly pure redistilled magnesium control melts. The network, however, was not found in all melts made, and for these reasons was not considered an effect of any intended alloying addition. It was believed that the interdendritic network observed was due to a decomposition of the binder of the Dixon number 1 clay-graphite crucibles used. The decomposition would result in contamination of the melts by either the binder or the clay-graphite base.

Seven small melts of pure redistilled magnesium were made to test this theory. Two melt procedures were used in this investigation. Procedure A was a normal melting and casting cycle used in previous work in which the charge was melted under flux, refined, heated to approximately 1700°F and poured at approximately 1400°F under Dow 181 agent. Procedure B was the same as procedure A except that an additional flux refining treatment was given at 1700°F for one to two minutes just prior to pouring. Three types of crucibles were used; new clay-graphite, reused clay-graphite, and "Acheson" Grade CS graphite. Dow 310 flux was substituted for Dow 220 in two melts. The melting conditions used are summarized in Table XLVII.

A microscopic examination of the as-cast structure from the bottom of each slab casting was made. Extensive evidence of an interdendritic network was observed in alloys R-1298 and R-1313, indicating that the condition was produced when using a new clay-graphite crucible and that an extra flux refining treatment was not effective in removing the contamination. Figure 35 illustrates the appearance of the interdendritic network in alloy R-1298. The network was not obtained in alloy R-1302 as shown in Figure 36 with a re-used clay-graphite crucible. The absence of the network was also observed in alloy R-1301 which was also melted in a re-used clay-graphite crucible. It was believed that the network was eliminated by the use of a clay-graphite crucible exposed previously to molten magnesium. No recognizable interdendritic network was observed in alloys R-1310, R-1311, and R-1312 when using a graphite crucible. A typical example is shown in Figure 37. The absence of the interdendritic network in Figures 36 and 37 is accentuated by the coarse grain size and the extreme difficulty in removing surface distortion during mechanical polishing of these specimens.

TABLE XLVII

MELTING CONDITIONS FOR PREPARING 200 GRAM INGOTS OF REDISTILLED MAGNESIUM

Alloy Number	Melting Procedure(a)	Type of Crucible	Flux Used
R-1298	A	new clay-graphite(b)	220
R-1301	B	re-used clay-graphite(b)	220
R-1302	A	re-used clay-graphite(b)	310
R-1310	A	graphite (c)	220
R-1311	B	graphite (c)	220
R-1312	A	graphite (c)	310
R-1313	B	new clay-graphite(b)	220

(a) See text for melting procedures.

(b) Dixon number 1 crucible, supplied by F. B. Stevens, Company, Detroit, Michigan.

(c) Acheson Grade CS graphite, supplied by National Carbon Company, Niagra Falls, New York.

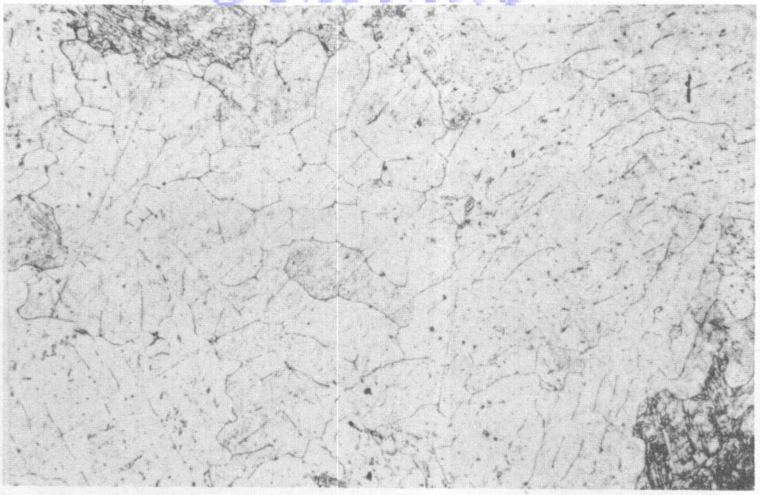

Figure 35

Negative No: 663 Magnification: 100X
Specimen No: 2472 Etch: 3 seconds in
10% acetic acid

As-cast microstructure of alloy R-1298 (re-distilled magnesium, intended) melted in a new clay-graphite and cast into a cast-iron mold. Dow 220 flux was used for protection. A large extent of an interdendritic constituent network is evident and was believed to be the evidence of a reaction between molten magnesium and the salts in the crucible binder to cause reduction and solution of these materials.

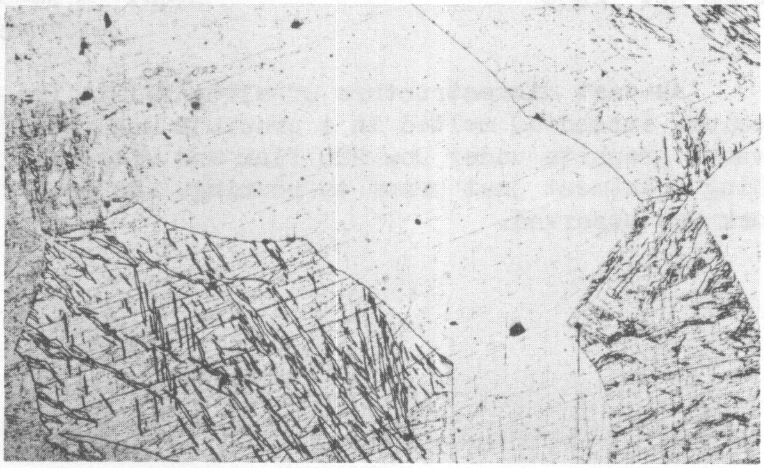

Figure 36

Negative No: 666 Magnification: 100X
Specimen No: 2497 Etch: 3 seconds in
10% acetic acid

No interdendritic network or microconstituents was observed in alloy R-1302 (re-distilled magnesium, intended) melted in a re-used clay-graphite crucible under Dow 310 flux.

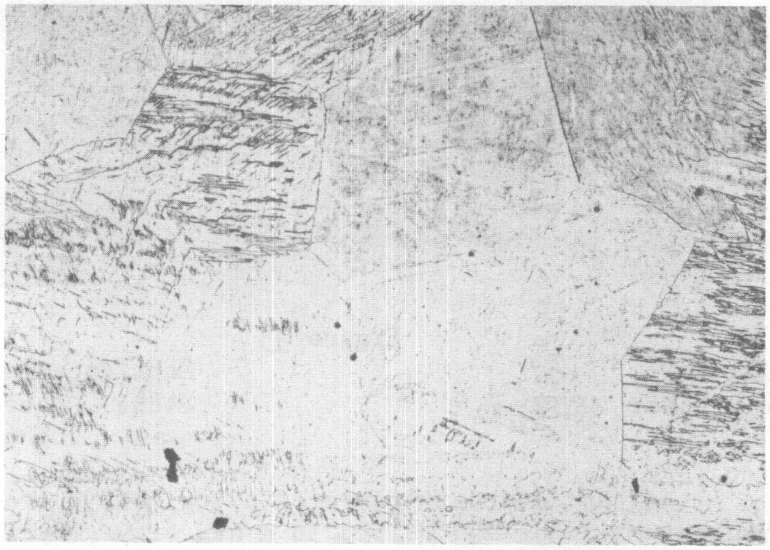

Figure 37

Negative No: 667
Specimen No: 2498

Magnification: 100X
Etch: 3 seconds in 10% acetic acid

As-cast microstructure of alloy R-1311 (re-distilled magnesium, intended) melted in a crucible machines from "Acheson" graphite under Dow 220 flux and with an extra flux refining treatment just prior to pouring. No interdendritic network was observed.

The influence of the interdendritic network on mechanical properties of hot-rolled sheet is given in the results for the seven alloys summarized in Table XLVIII.

TABLE XLVIII

INFLUENCE OF INTERDENDRITIC NETWORK OF MICROCONSTITUENTS ON THE MECHANICAL PROPERTIES OF 0.064 INCH REDISTILLED MAGNESIUM SHEET IN THE HOT-ROLLED CONDITION

Alloy Number	Crucible Type	Evidence of Interdendritic Network	Longitudinal Mechanical Properties		
			Kips per sq. in.		Elongation % in 2 in.
			TYS	UTS	
R-1298	New c.-g.	Extensive	12.4	23.1	4.5
R-1391	Re-used c.-g.	None	11.0	20.9	5.2
R-1302	Re-used c.-g.	None	11.6	21.0	6.3
R-1310	Graphite	None	11.6	21.5	5.5
R-1311	Graphite	None	11.4	21.3	7.0
R-1312	Graphite	None	11.5	21.8	6.3
R-1313	New c.-g.	Extensive	12.8	22.1	4.3

These data show a small but significant increase in tensile yield and ultimate strength and a lower percentage elongation for the two alloys in which the network was observed.

The results of this investigation indicated clearly that the use of new clay-graphite crucibles was the source of the melt contamination. A relative lack of contamination when using clay-graphite crucibles after several melts had been made in them was interpreted as evidence of the formation of a protective or "aged" layer on the crucible wall that minimized further attack of the crucible. Although no significant melt contamination was obtained in this limited study when re-used clay-graphite crucibles were employed, it was considered best not to use them due to the uncertainty of the mechanism and degree of protection obtained. The principal recommendation from this study was to prepare all small melts in graphite crucibles.

APPENDIX II

PROCEDURES FOR CHEMICAL ANALYSIS OF EXPERIMENTAL ALLOYS

Determination of Titanium

Qualitative spectrographic analysis was used for detection of the presence of titanium in a limited number of experimental alloys. A Baird Three-Meter Spectrograph was used in this work. The persistent lines of titanium (3349, 3383.8, 3372.8 and 3361) were identified in the spark spectra in several alloys.

The procedure used for the spectrophotometric determination of titanium in magnesium alloys was based on a method described by Eisenreich[7]. This procedure reported both dissolved titanium and total titanium (only dissolved titanium is soluble in sulfuric acid while total titanium is determined by dissolution in nitric acid). Deposited titanium was designated as the difference between these results. For total titanium, four gms. of metal chips were placed in 150-200 ml. water and concentrated nitric acid was added dropwise. The water white solution was reduced to 90 ml. and mixed with 10 ml. of 30% hydrogen peroxide. This solution was compared with standard titanium sulfate solutions on a Beckman Spectrophotometer, Model B. Because of the low percentages, the determinations were made in the 0.00 to 0.05 absorbance range of the instrument. Soluble titanium was determined by substitution of the correct amount of sulfuric acid for the nitric acid.

Determination of Nickel

Nickel was determined by a gravimetric method recommended by the Dow Chemical Company[22].

Determination of Cobalt

The method used was based on a procedure described by McNaught[23]. Samples were dissolved in hydrochloric acid and appropriate aliquots were taken. Sodium acetate and phenolphthalein were added and the solution was neutralized with potassium hydroxide. The reagent,0.1% Nitroso-R-Salt, was then added and produced a red-brown color in the presence of cobalt. Concentrated nitric acid was added to the boiling solution to destroy any color other than that due to the cobalt complex. Standards were prepared in the same way using standard cobalt chloride and dissolved high purity magnesium. The cobalt solution was standardized by electroplating from a strongly ammoniacal solution. Measurements were made on a Beckman Spectrophotometer, Model B.

Determination of Rhenium

Qualitative detection of rhenium in several alloys was attempted by spectrographic methods. Rhenium lines were not identified positively in any of the samples. Study of the problem disclosed that spectrographic determination of rhenium is not recommended due to interference from other elements.

Quantitative determination of rhenium was attempted for three experimental alloys. The samples were dissolved in nitric acid and placed in 50 ml. volumetric flasks. Ammonium persulfate was added and the solutions were boiled to oxidize rhenium to the plus seven valence state. Then a two percent solution of potassium thiocyanate in 12 normal hydrochloric acid diluted to 250 ml. was added followed by a one percent solution of stannous chloride in the same hydrochloric acid solution. The solution was then diluted to volume and measured on a Beckman Spectrophotometer, Model B. Standards were prepared in the same way by adding potassium perrhenate to a nitric acid solution of redistilled, high purity magnesium.

Determination of Yttrium

A gravimetric procedure was developed for the determination of yttrium in magnesium alloys. Samples ranging from 5 to 10 gms., depending on the relative amount of the intended addition of yttrium, were dissolved in hydrochloric acid. Ten gms. of ammonium chloride were added and the pH was adjusted to 7.5 to 8.5. The solution was heated and ammonium sebacate was added. The precipitate was filtered, dried and ignited to yttrium oxide. In some cases a second precipitation was necessary and the procedure was the same as for the first.

The determination of yttrium in an aluminum-yttrium master alloy was more difficult but a satisfactory procedure was obtained. Evidence indicated that aluminum complexed the oxalate of yttrium and prevented complete precipitation of yttrium. This difficulty was avoided in the following procedure. The sample, containing 10 to 100 mg. of yttrium was placed in a 400 ml. beaker with 50 ml. water. Concentrated hydrochloric acid was added drop by drop until dissolution was complete. The solution was evaporated to dryness by gentle heating, dissolved in a minimum amount of concentrated hydrochloric acid and diluted to 100 ml. volume.

The solution was nearly neutralized (bromothymol blue) with 10% sodium hydroxide, heated to boiling and poured slowly with constant stirring into 100 ml. of hot, fresh 10% sodium hydroxide solution. After boiling two to three minutes with gentle stirring, the solution was allowed to settle and was filtered through number 40 paper previously washed with hot 5% sodium hydroxide until 50 ml. of filtrate was water white. The precipitate was washed in hot 5% sodium hydroxide. The paper was ignited, care being used to avoid spatter and ignition of the precipitate. The precipitate was re-dissolved in hot, dilute sulfuric acid and the precipitation was repeated. The precipitate was dissolved in a minimum amount of concentrated hydrochloric acid, diluted to 50 ml. volume with water, adjusted to pH of 0.75 and heated to boiling. Fifty ml. saturated oxalic acid solution (150 gm. of oxalic acid dihydrate in one liter of warm distilled water) were added slowly with stirring, the solution was boiled gently for 1 hour and then allowed to stand overnight. After filtering on number 42 paper, the paper was ignited. The precipitate was re-dissolved in a minimum amount of concentrated hydrochloric acid and the oxalate precipitation was repeated. The precipitate was finally ignited to constant weight at 950°C.