

FOREWORD

This report was prepared by the General Electric Research Laboratory under USAF Contract No. AF 33(616)-7714. This contract was initiated under Project No. 7350, "Refractory Inorganic Non-Metallic Materials," and Task No. 735001, "Ceramic and Cermet Materials Development." The work was administered under the direction of the Directorate of Materials and Processes, Deputy for Technology, Aeronautical Systems Division, with Lt. T. E. Lippart acting as project engineer.

This report covers work conducted from December 1960 to December 1961.

The authors are pleased to acknowledge the very capable assistance of A. J. Peat who made the hundreds of hardness measurements required during the course of this study. They are also grateful to D. J. Conley for electron microprobe measurements, and to A. U. Seybolt, J. R. Low, and D. Turnbull for critical reading of the manuscript.

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ABSTRACT

An increased hardness of grain boundary regions above that of the bulk material is found to exist generally in intermetallic compounds having a stoichiometric excess of active metal component. This hardening is shown to be associated with the anomalously high brittle-ductile transition temperature in these materials, and to be related to the "pest" phenomenon. The presence of adsorbed oxygen and/or nitrogen in grain boundary regions is found to be responsible for the increased hardness in these areas; the precise manner in which the resistance to plastic deformation is increased in this phenomenon is not clear. The effect can be modified, however, by ternary solute additions and to some extent by appropriate annealing treatments.

This technical documentary report has been reviewed and is approved.



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EFFECT OF BASIC PHYSICAL PARAMETERS ON ENGINEERING PROPERTIES OF INTERMETALLICS

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GENERAL INTRODUCTION

The class of materials termed intermetallic compounds includes materials of high hardness and materials of excellent oxidation resistance at elevated temperature; they are, thus, materials of great potential as high-temperature structural materials. Because of their brittleness at ordinary temperatures and the difficulty with which they are prepared as pure single-phase materials, few studies of their mechanical properties have been made.

The program under this contract is directed toward establishment of correlations of structural, compositional, and physical parameters of intermetallic compounds with their mechanical properties. It is hoped that such correlations will lead to an elucidation of the factors affecting the flow process in such materials, and particularly to a better understanding of the source of brittleness in polycrystalline intermetallics.

From December 1958 to December 1960 techniques were developed for producing suitable test specimens of both AgMg and NiAl, methods for testing were devised, and the tensile behavior of the CsCl structure compound AgMg was extensively documented in terms of strain, strain rate, temperature, grain size, composition, and metallurgical processing treatment. These results are summarized in WADD Technical Report 60-184--Part I, March 1960, and Part II, September 1961.

An extensive and detailed evaluation of these results have enabled a selection of particular areas of work for attention during future work periods.

The following items were among those which seemed most needful of immediate attention.

1. An improved understanding of low-temperature brittleness from a detailed study of the mechanical behavior and the chemical nature of grain boundaries and adjacent regions.

Manuscript released by the authors May 1962 for publication as a WADD Technical Documentary Report.

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2. Establishment of the generality with respect to other types of inter-metallic compounds of the principles and effects found for the mechanical behavior of AgMg. It is desirable not only to establish those characteristics of mechanical behavior that are common to intermetallics, but also to identify those that are peculiar to intermetallics and that would serve to distinguish them as a material class.

3. Certain types of fundamental concepts not yet clear, e. g. , the strengthening mechanism, must also be evaluated further.

During the current work period a detailed study of grain boundaries in AgMg, NiAl and other intermetallics has been accomplished. It is planned that work of the immediate future will be directed primarily toward further fundamental studies of the mechanical behavior of intermetallics.

GRAIN BOUNDARY STUDIES

I. INTRODUCTION

It has been long recognized that brittleness in intermetallics is generally associated with grain boundaries--not only in that fracture almost always occurs along grain boundaries, but also in the fact that single crystals themselves are often quite ductile. Little attention has been given, however, to the nature of the grain boundary regions and to the manner in which such brittleness may arise. In addition, the possibility has not been seriously considered that the spontaneous disintegration of many intermetallics in certain regimes of temperature (the so-called "pest" phenomenon) might still be the usual intergranular mode of failure only with the stress acting internally rather than externally.

Grain boundaries in crystalline solids differ from the bulk material within a grain in several respects, each of which constitutes a potential source of intergranular embrittlement. Some of these are:

(a) The boundary is an internal surface and is therefore a likely site for nucleation of second phases whether by precipitation or other solid state transformation.

(b) The grain boundary is by definition a demarcation of a geometric transition from one crystallographic orientation to another.

(c) The grain boundary is a high-energy region, i. e., individual atoms do not have the normal complement and arrangement of neighbors.

(d) [Corollary to (c)] as a result of both the unusual structure and the high energy of the grain boundary region, chemical segregation may occur in systems containing more than a single component.

Examples might be adduced of established mechanisms for grain boundary embrittlement of ordinary metals and alloys under each of these headings. However, for many intermetallics the cause of their intergranular failure over wide ranges of temperature and strain rate remains obscure. No second phases can be found at grain boundaries, no geometric impediment to the propagation of slip into the adjoining grains is apparent, and no significant impurities appear in their analyses.

Direct investigations of the structure, composition, and mechanical properties of grain boundaries in any polycrystalline solid are hampered by the fact that the grain boundary region proper is estimated to extend over only a few atom distances. Effects arising from the presence of the boundary, such as that of chemical segregation, may, however, extend over much larger distances than can be ascribed to the grain boundary proper. In any instance where such segregation does occur it will surely have an influence on the mechanical properties.

The ordinary microhardness test appears to offer one means of sampling a mechanical property from a region of a few microns dimension. If loads of 50 grams or less are used, sufficiently small indentations result (10μ to 30μ for most metals) that it is possible to compare, on a properly prepared sample, the hardness of the material at or very near grain boundaries with the hardness of the grain bulk remote from grain boundaries. It might be expected, even in the absence of any chemical effect or presence of discrete phases, that due to the misorientation of adjacent grains and the resulting local distortion a hardness gradient could exist over very small distances. Mott⁽¹⁾ reports studies by Harman et al. of high purity molybdenum where the hardness at grain boundaries was found to differ from that of the bulk only by 1/2 per cent on the average. Hundy⁽²⁾ found a 7 per cent increase in both copper and mild steel. An effect of unstated magnitude has been reported by Chalmers⁽³⁾ in tin. In the present investigation, examination of both pure silver and pure chromium showed that the hardness of the boundaries was the same as that of the bulk within the data scatter band width of ± 4 per cent. Insofar as is known, however, microhardness measurements have never been employed in cases where grain boundary segregation was suspected.

A recent extensive study by the authors^(4, 5) of the microstructure and mechanical behaviors of the CsCl structure compound AgMg disclosed no unusual features of grain boundaries in this material. Fracture was found to occur generally along grain boundaries, although in brittle polycrystalline material, individual grains showed considerable ductility. AgMg exhibits typical ductile-brittle transition temperature curves but without a change in fracture mode at the ductile transition. Most importantly, however, as is shown in the schematic curves of Fig. 1, the tensile test transition temperatures were found to be about 400°C lower for compounds containing excess Ag than for those with excess Mg, even though the deviation from the stoichiometric composition in some instances was only a few tenths of a per cent. This striking dependence of deformability on

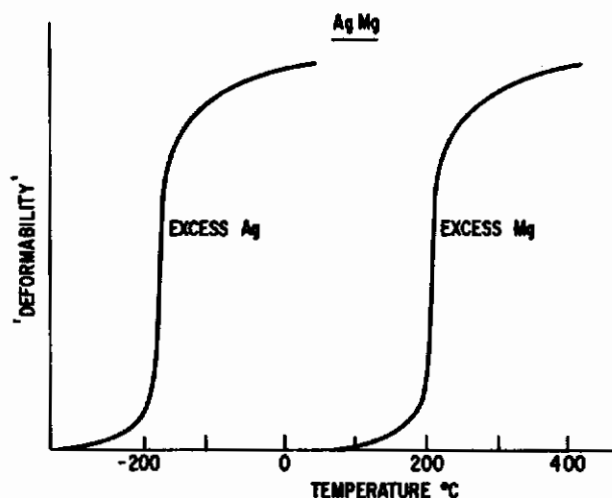


Fig. 1 Schematic representation of the effect of composition on the transition temperature of AgMg compounds. (5)

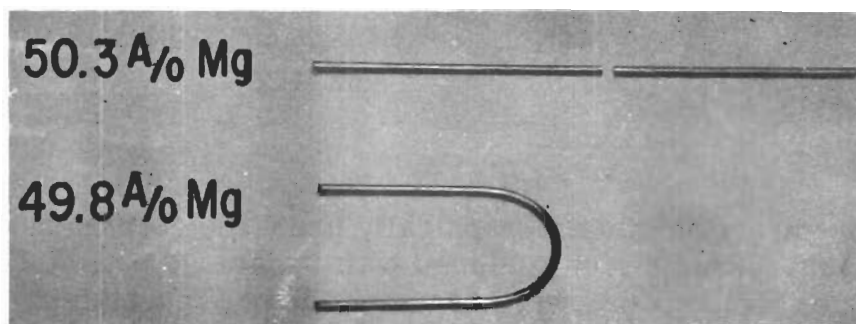


Fig. 2 The extent to which Ag-rich and Mg-rich AgMg wires can be bent by hand at room temperature. (5)

composition is further demonstrated in Fig. 2 which shows the extent to which extruded wires of 49.8 and 50.3 A/o Mg can be bent by hand without fracture at room temperature.

Because of the typical fracture behavior of AgMg, the pronounced effect of composition on ductility, and the accumulation of information on this compound, it was proposed to compare the micro-hardness of grain boundaries and bulk material in both Ag-rich and Mg-rich AgMg over a range of temperatures in an attempt to identify the impediment to slip propagation from one grain to the next. Significant grain boundary hardening was found under certain conditions and the studies were therefore extended to other intermetallic materials. This report describes these observations of grain boundary hardening, describes the apparent relations of this increased grain boundary hardness to brittleness in the several materials studied, and examines possible sources of this hardening. In addition evidence is brought out which suggests that, at least in some cases, the "pest" type of disintegration is also a consequence of grain boundary hardening.

II. EXPERIMENTAL PROCEDURES

A. Materials

Samples of AgMg and NiAl in the as-cast condition and in the form of extruded rod were available from previous investigations. (4,5) These compounds had been prepared by induction melting a mixture of the component elements under argon, and, following appropriate homogenization anneals in argon, the ingots were extruded to rod. Further details of the processing procedures may be found in Ref. 4. Certain ternary AgMg based compositions utilized in the present study as well as specimens of γ MgAl were prepared in similar fashion but were studied only in the cast and homogenized condition.

Samples of NiTi, AgTi, CoAl, Ir₃Cr, MoSi₂, and Ni₃Al, which had been arc melted and homogenized with argon anneals, were available from previous studies by one of the authors (JHW).

Samples of ZrBe₁₃, Zr₂Be₁₇, and TaBe₁₂ prepared by hot-pressing techniques were obtained from Dr. E. Aitken of the General Electric Aircraft Nuclear Propulsion Department.

B. Testing Procedures

1. Microhardness Tests

Microhardness measurements on metallographically prepared specimens were made with a Kentron microhardness tester equipped with a diamond pyramid indenter. Tests at liquid nitrogen temperature were accomplished by indenting the sample while it was submerged in liquid nitrogen; tests above room temperature up to 250°C were carried out with the specimen in a silicone oil bath. Tests at temperatures above 250°C were done in an argon atmosphere in a hot microhardness tester of special design. (6)

2. Impact Tests

The drop weight impact test, after Soxman et al., (7) was used in this study. However, since cylindrical rods 1/4 inch in diameter were used as specimens rather than specimens of standard size and shape, the measured impact strengths are qualitative. In these tests, test temperatures above room temperature were obtained by electrical resistance heating of the specimens.

III. RESULTS

A. Grain Boundary Hardening in AgMg

As indicated above, abnormally high grain boundary hardening was first observed in the current study in the compound AgMg. It was found that for all samples which contained Mg in excess of the stoichiometric composition of 50 A/o, considerable grain boundary hardening (from 20 to 50 per cent increase over the bulk hardness) occurred in material tested in the as-cast condition. None of the compounds, however, whose compositions contained Ag in excess of the stoichiometric composition exhibited any grain boundary hardening. Figure 3 shows typical results of hardness traverses from one grain into an adjacent grain across the boundary for both an Ag-rich compound and a Mg-rich compound. It is noteworthy that the Mg deficit and excess referred to in Fig. 3 are of the order of 0.2 A/o. The hardening is shown to extend over a region of the order of 20 μ on either side of the boundary. The hardness values in Fig. 3 were obtained using a 10-gram load, about the minimum load with which load-independent hardness values may be measured. Indentations were separated from each other by about 3 diameters along a traverse making a very small angle with the grain boundary, but distances for plotting were measured perpendicular to the boundary. It was thus possible to define a relatively narrow profile even with a moderately large indentation. Decreasing the load to 1 gram resulted in smaller indentations (though not proportionately so because of vibration and inertia effects) which reveal hardness profiles as in Fig. 4, comparable to those obtained with the more reliable load of 10 grams. A sufficient number of grain boundary hardness profiles were

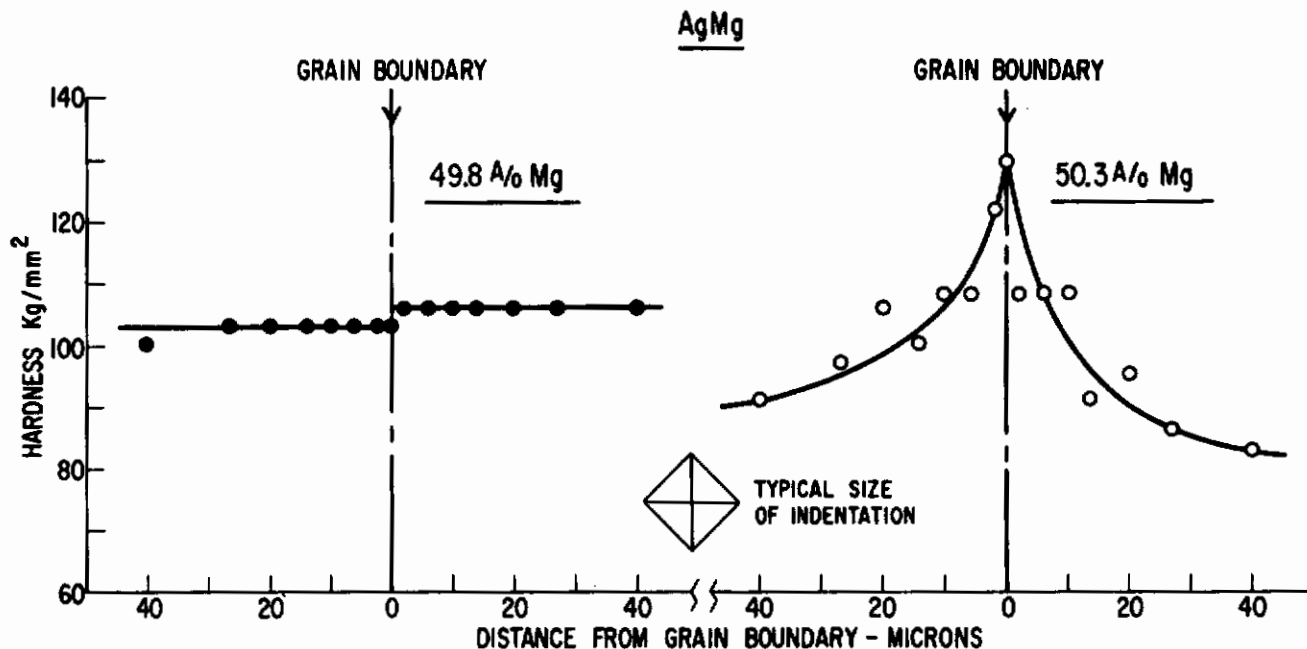


Fig. 3 Microhardness traverses, using a 10-gram load, across grain boundaries in Ag-rich and Mg-rich AgMg compounds.

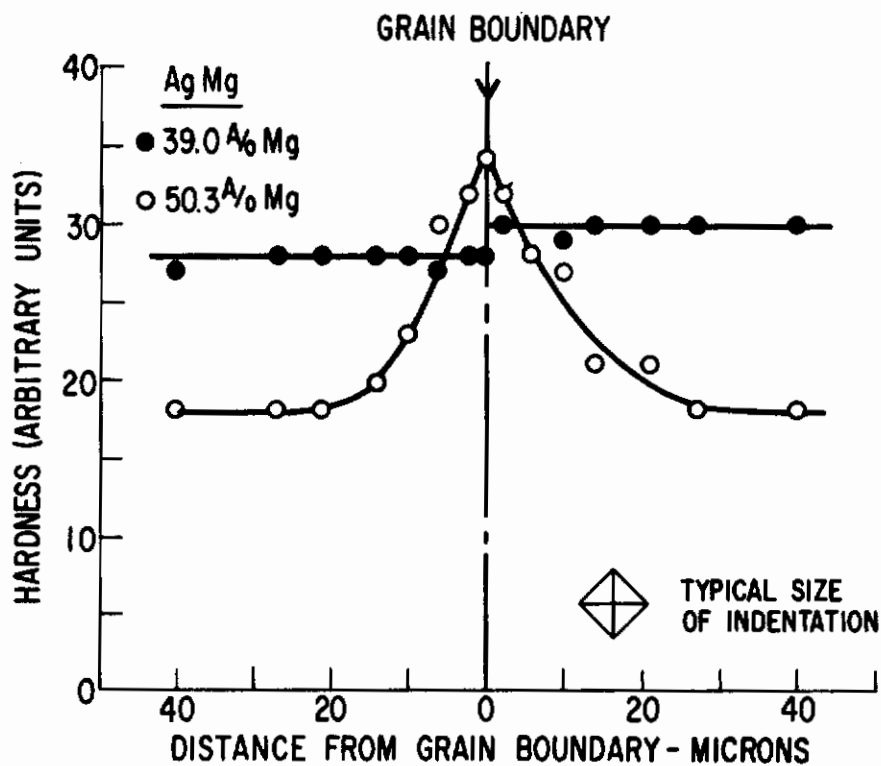


Fig. 4 Microhardness traverses, using a 1-gram load, across grain boundaries in Ag-rich and Mg-rich AgMg compounds.

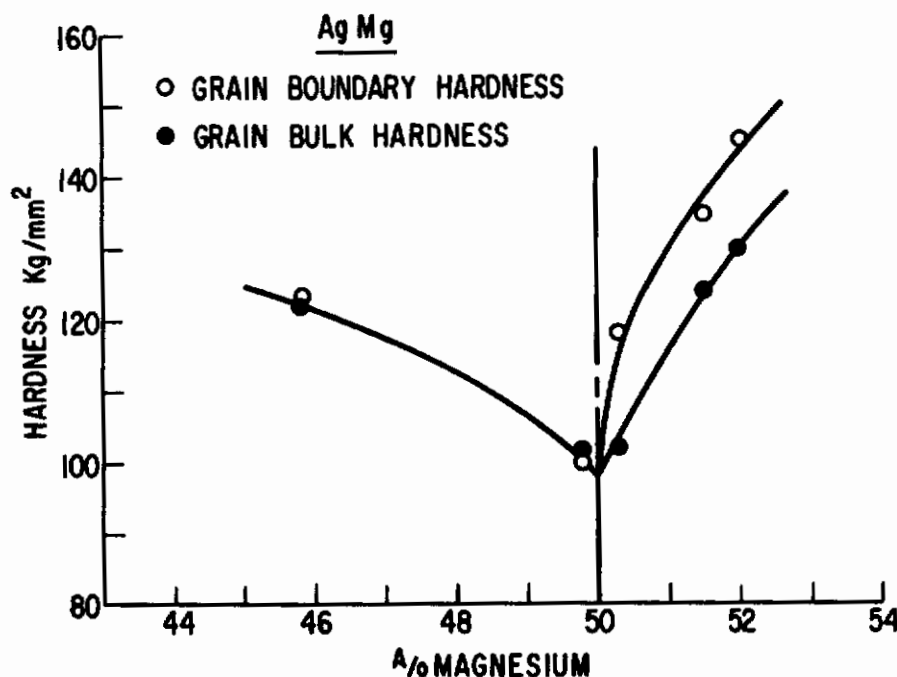


Fig. 5 Bulk and grain boundary hardness of AgMg as a function of composition.

run on randomly oriented grains to establish that the magnitude of the effect and the distance over which it occurs are not strongly affected by the relative orientations of adjoining grains. Similar effects were found for the as-cast, extruded, and annealed conditions. The composition dependencies of grain boundary and bulk hardness of AgMg are shown in Fig. 5, in which each plotted point is the average of 10 independent readings in randomly selected grains.

B. Generality of Grain Boundary Hardening in Intermetallics

In an attempt to establish the generality of grain boundary hardening in intermetallics, several compounds differing in crystal structure from the CsCl type AgMg, and compounds with active components other than magnesium were examined. In all instances, as is shown in Table I, those compounds having an active element in excess of the stoichiometric composition exhibited grain boundary hardening while those with a concentration of the active element less than the stoichiometric composition showed no boundary hardening. Little significance can be attached to the relative values of the degree of hardening as shown in the table, however, since, these are strongly dependent on metallurgical treatment. Some more detailed measurements were made on the compound NiAl, which is isomorphous with AgMg. Figure 6, which plots the variation with composition of grain bulk and of grain boundary hardness for NiAl, is quite similar in all respects to the AgMg curves in Fig. 5.

TABLE I

**Approximate Grain Boundary Hardening, ΔH , at Room Temperature
in Several Intermetallic Compounds**

$$\Delta H (\%) = \left(\frac{H_{\text{boundary}} - H_{\text{bulk}}}{H_{\text{bulk}}} \right) \times 100$$

Compound (A_mB_n)	Crystal Structure	$\sim \Delta H(\%)$	
		Excess A	Excess B
AgMg	CsCl	0	20-50
NiAl	CsCl	0	25-60
NiTi	CsCl	0	~25
CoAl	CsCl	0	~20
Ni ₃ Al	Cu ₃ Au	0	~15
Ir ₃ Cr	Cu ₃ Au		~20*
AgTi	CuAu	0	~20
TiAl	CuAu		~20*
Zr ₃ Be ₁₇	Complex hexagonal		~35*
TaBe ₁₂	Complex tetragonal		~60*
ZrBe ₁₃	NaZn ₁₃ (f. c. c.)		25-50*
γ MgAl	α -Mn (b. c. c.)		~15*
MoSi ₂	Body-centered tetragonal		~33*

*Exact composition not known.

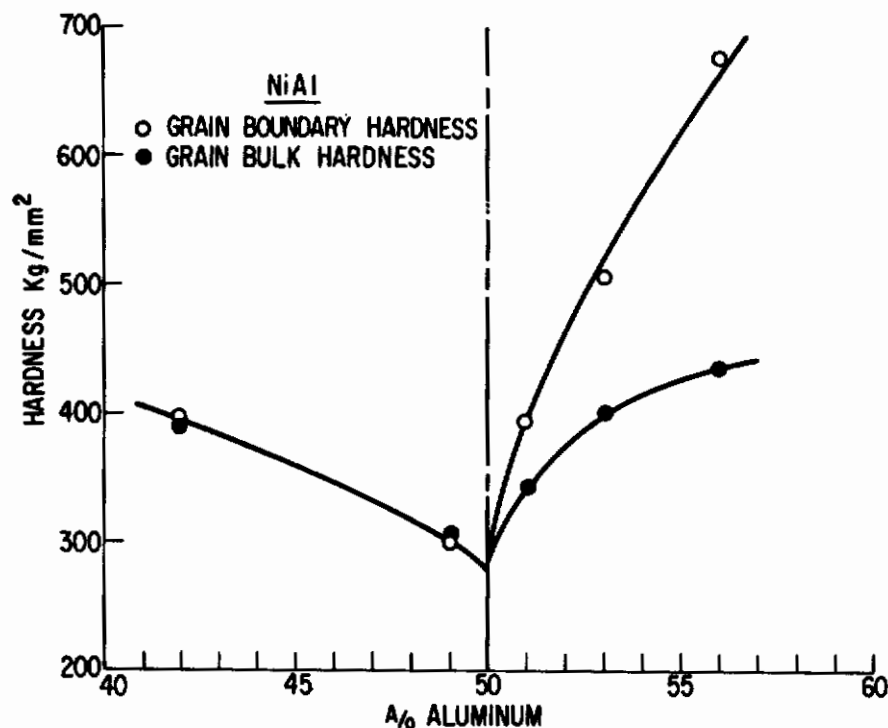


Fig. 6 Bulk and grain boundary hardness of NiAl as a function of composition.

C. Relation of Grain Boundary Hardening to Brittle Behavior

With the generality of grain boundary hardening among several inter-metallics established, it was of interest to determine if any relation exists between this hardening and the brittle behavior of these materials. As was indicated in Fig. 1, it was found in the previous tensile study that Mg-rich compounds could be made to undergo plastic deformation only at temperatures above about 200°C. Hardness measurements made at a series of increasing temperatures on such a Mg-rich compound indicated, as shown in Fig. 7, that the temperature at which plastic deformation could be accomplished corresponds to the temperature at which the grain boundaries cease to be harder than the bulk material. Such a correlation strongly suggests that the increased transition temperature of the Mg-rich compounds over that of the Ag-rich compounds is due at least in part to the presence of grain boundary hardening. The brittle behavior of Ag-rich compounds which occurs at nitrogen temperatures, however, is apparently a different phenomenon and is not due to boundary hardening since no grain boundary hardening was found to exist in these compounds at -196°C.

Since Mg-rich AgMg is both ductile and free from abnormal grain boundary hardening above about 200°C, an experiment was designed to determine if this state

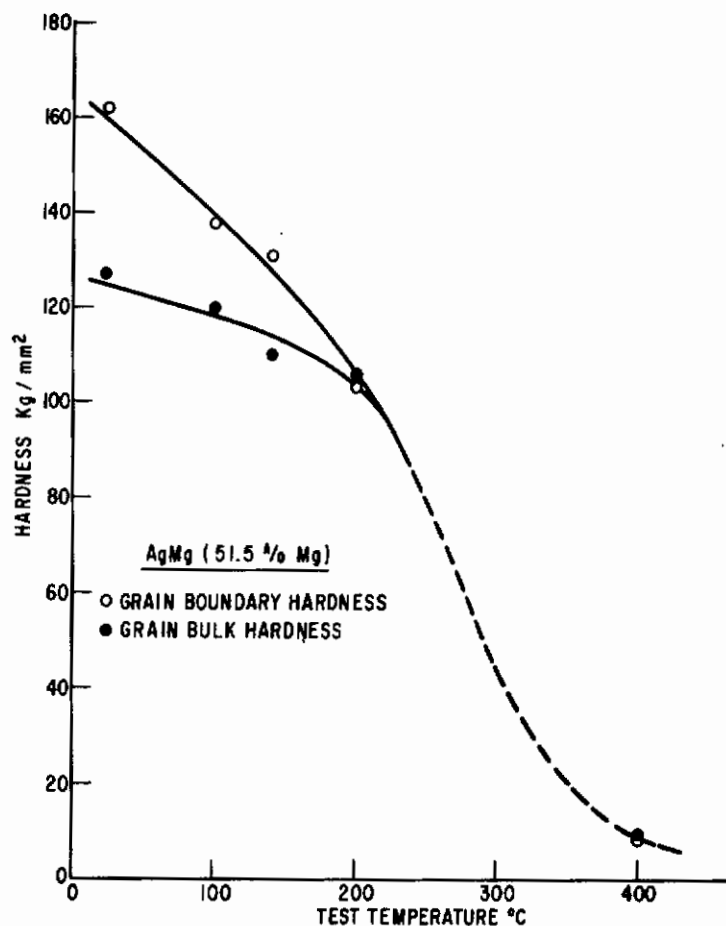
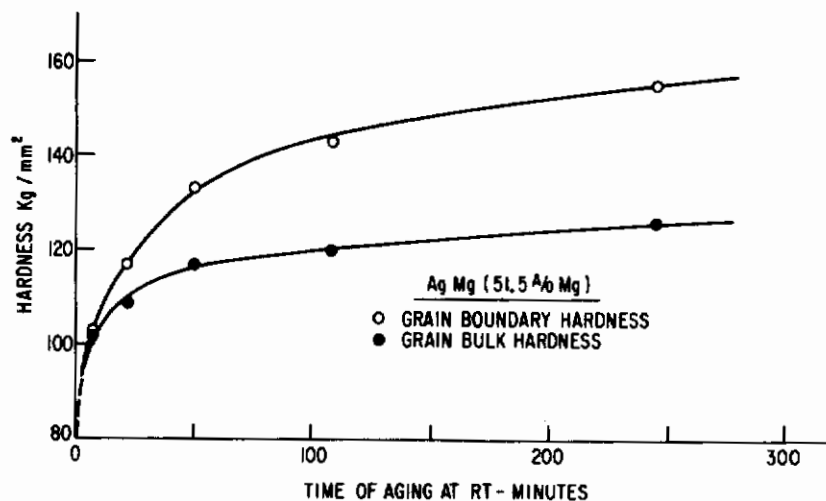


Fig. 7 Variation in bulk and grain boundary hardness of AgMg with temperature.

Fig. 8 The increase of bulk and grain boundary hardness in AgMg with time at room temperature after quenching in liquid N₂ from 225°C.



can be preserved by quenching to a low temperature. Specimens were annealed in a silicone oil bath at 225°C, quenched into liquid N₂, up-quenched to room temperature, and hardness measurements of both grain boundary and bulk made as a function of time. The N₂ quenching procedure was used to ensure a rapid cooling rate in the vicinity of room temperature. Figure 8 shows that the curves for boundary and

bulk hardness extrapolate to a common value at zero time. The hardening of the bulk material was unexpected and no explanation is obvious. No marked changes in microstructure were observable either after quenching or after aging. The saturation hardness levels for both bulk and boundary were comparable with those obtained for the same sample in the as-cast condition. Attempts were made, without success, to demonstrate retention of ductility immediately after quenching from a temperature above the transition temperature.

Experiments similar in purpose to those just described were carried out on other compounds. Samples of Al-rich NiAl were annealed in air at a series of temperatures and quenched in liquid N₂. Hardness values measured immediately after quenching remained stable over periods of at least 48 hours. Because of the high melting point of NiAl, 1650°C, there is apparently sufficient lack of atomic mobility at room temperature that the high temperature state can be maintained indefinitely. Room temperature hardness measurements showed, Fig. 9, that above a temperature of about 1000°C, grain boundaries were no longer harder than the bulk. Confirmation of the temperature coincidence of the observed loss of grain boundary hardening and the onset of ductile behavior was sought from impact tests on extruded specimens at a series of temperatures. Figure 10 shows the results of measurements made on three sets of specimens: (a) annealed at 1200°C and slowly cooled; (b) quenched from 1000°C; and (c) quenched from 790°C. The slowly cooled material evidently has a transition temperature of the order of 985°C, a temperature quite close to the observed disappearance of grain boundary hardening. The room temperature impact strength of the material quenched from 1000°C is approximately doubled, but the data are inadequate to determine a possible shift in transition temperature. Quenching from a temperature such as 790°C, where grain boundary hardening still exists, gives some impairment in room temperature toughness.

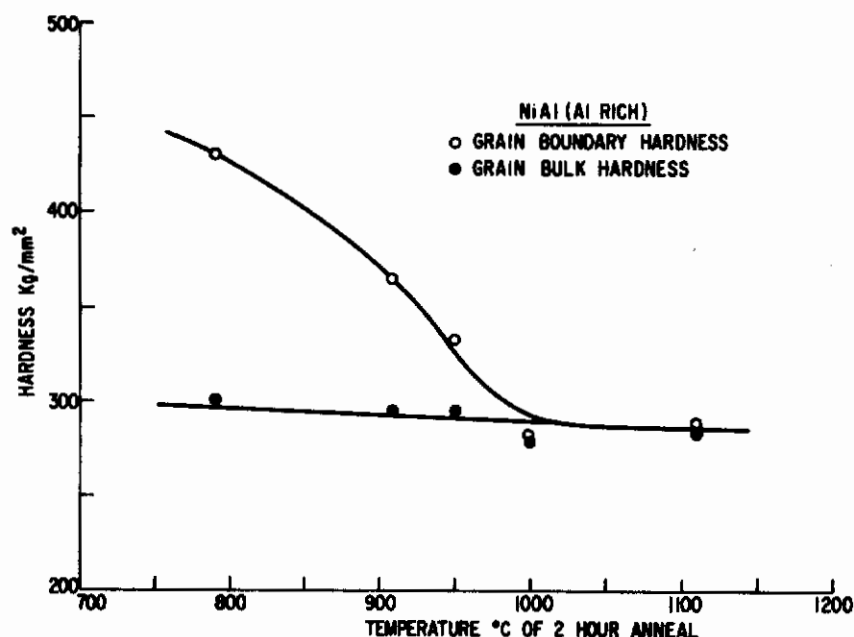


Fig. 9 Bulk and grain boundary hardness at room temperature for NiAl quenched in liquid N₂ from a series of annealing temperatures.

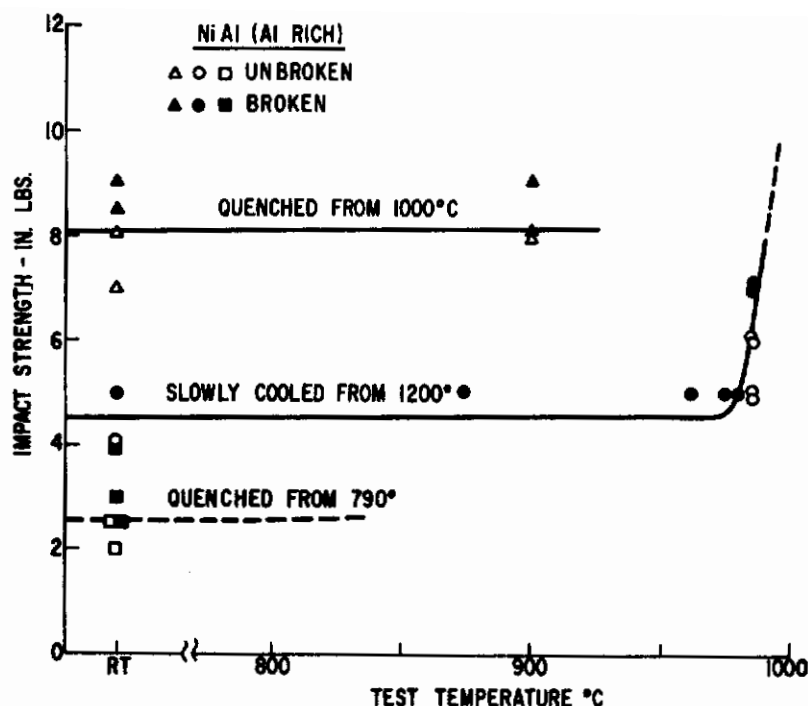
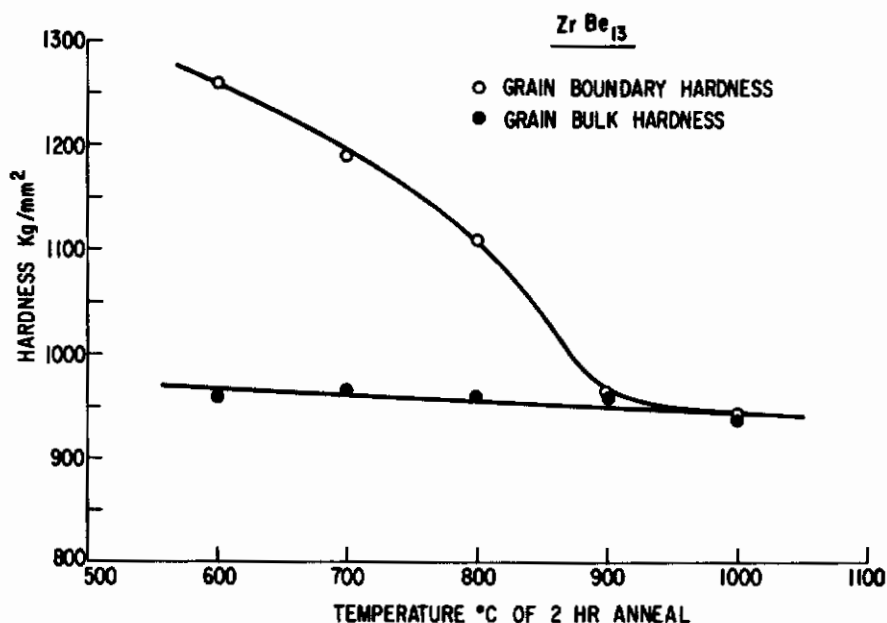


Fig. 10 Impact strength at various temperatures for NiAl specimens of different thermal treatment.

Fig. 11 Bulk and grain boundary hardness at room temperature for $ZrBe_{13}$ quenched in liquid nitrogen from a series of annealing temperatures.



Tests on $ZrBe_{13}$ gave results exactly analogous to those obtained for NiAl. Samples quenched from above 900°C show no grain boundary hardening, as can be seen in Fig. 11. This temperature corresponds approximately to the upper limit of the "pest" range as reported for this compound by Lewis. (8)

Thus, it seems clear that the grain boundary hardening phenomenon which exists generally in intermetallics containing an active element in excess of stoichiometry, and which disappears at some elevated temperature, is in large part

responsible for the extreme brittleness common to these compositions at ordinary temperatures. It remains to examine the nature of this hardening and to explore the possibilities of the manner in which it arises.

D. Origin of Grain Boundary Hardening

In seeking an origin for the grain boundary hardening in ordered intermetallics, magnesium-rich AgMg was chosen for detailed study. This selection was made because considerable auxiliary information was at hand for this material and because the foregoing experiments had demonstrated that its behavior with respect to the intergranular embrittlement problem is typical. Furthermore, the finding of a previous study⁽⁵⁾ that a multiplicity of slip systems is available in AgMg eliminates the possibility of a simple geometric impediment to slip. Local distortion at grain boundaries can at most account for only a few per cent increase in hardness as is shown by the results obtained for pure metals and simple alloys reviewed above. Hardening near grain boundaries can result from dislocation pile-up during cold work,⁽⁹⁾ but this cannot be invoked in the case of the present experiments because large boundary hardening is found in fully annealed material. There remain then but two possible ways in which the hardness of AgMg in regions at or very near grain boundaries might be significantly increased above the general hardness of the bulk:

- (a) Preferential grain boundary precipitation of a second phase from solid solution.
- (b) Segregation of solute or impurity atoms to the boundary region.

Experiments were carried out which were intended to clarify which, if either, of these mechanisms is responsible for the observed hardening.

1. Structural and Analytical Studies

A study was made to identify any microstructural or chemical anomalies which might exist at grain boundaries in ordered intermetallics. Optical and electron microscopic studies on both normal sections and fractographs failed to give any evidence of a precipitated second phase in the grain boundary regions. However, it is recognized that even particles some tens of angstrom units in size can be effective hardeners, and these observations therefore are not conclusive. X-ray microprobe analyses, capable of detecting composition changes of 0.1 A/o, showed no boundary segregation of either Ag or Mg in the several AgMg compounds examined. Similar analyses also showed that iron, a common impurity in Mg, was not segregated in these materials.

2. Atmosphere Studies

Since gaseous impurities are not detected by x-ray microprobe techniques, it was thought advisable to give consideration to the possibility that some gaseous impurity had segregated to the grain boundary regions during the casting process. The AgMg material used in all of the experiments described in this report had been cast and thermally treated under a positive pressure of inert gas as is common practice for alloys containing an active, volatile element. Since it was found that the tank argon normally used in these processes contained significant amounts of both nitrogen and oxygen, an experiment was carried out to determine if further contact of the cast material with tank argon would produce greater grain boundary hardening. Figure 12 shows the results of annealing, in argon, material which exhibited relatively little grain boundary hardening in the as-cast condition. The degree of boundary hardening existing in the cast material was unchanged by annealing temperatures below about 500°C. At higher temperatures although the bulk hardness remained unchanged, a considerable increase occurred in the hardness of the grain boundary regions. Samples annealed for various times at a constant temperature exhibited a square root time dependence of the hardening, as shown in Fig. 13, an indication that the hardening process is diffusion dependent. These experiments, although strongly suggestive that impurities are entering the material from the argon, are not conclusive in this respect since similar results might be expected if a normal age hardening phenomenon with grain boundary precipitation had occurred.

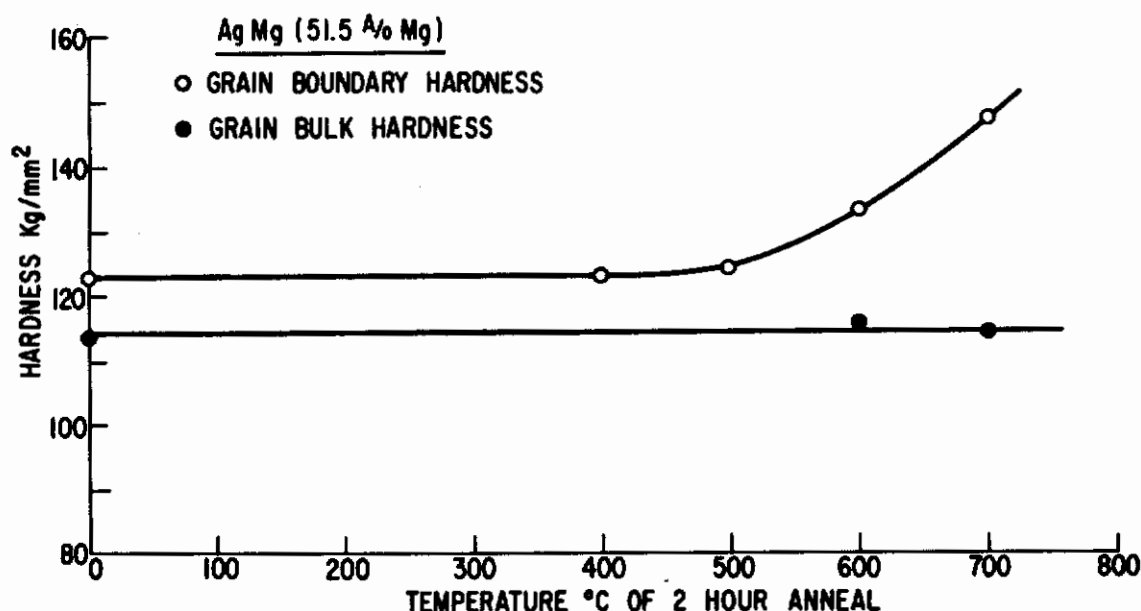


Fig. 12 Bulk and grain boundary hardness at room temperature for AgMg annealed at various temperatures.

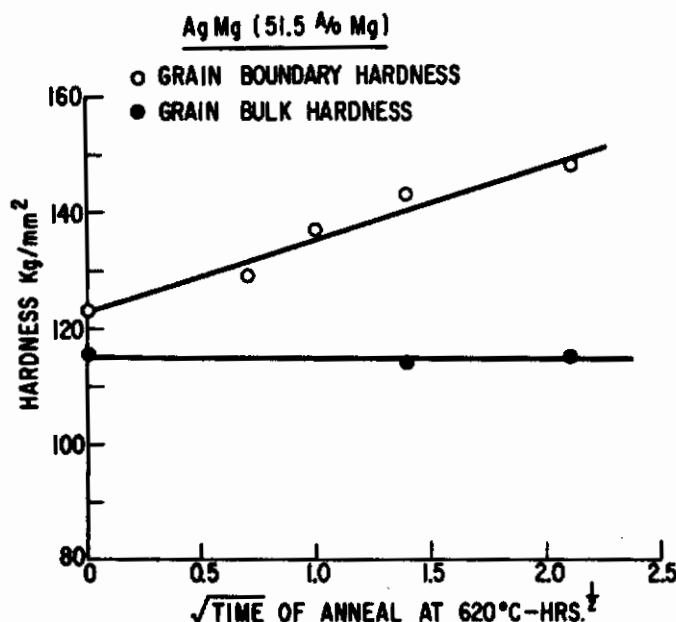
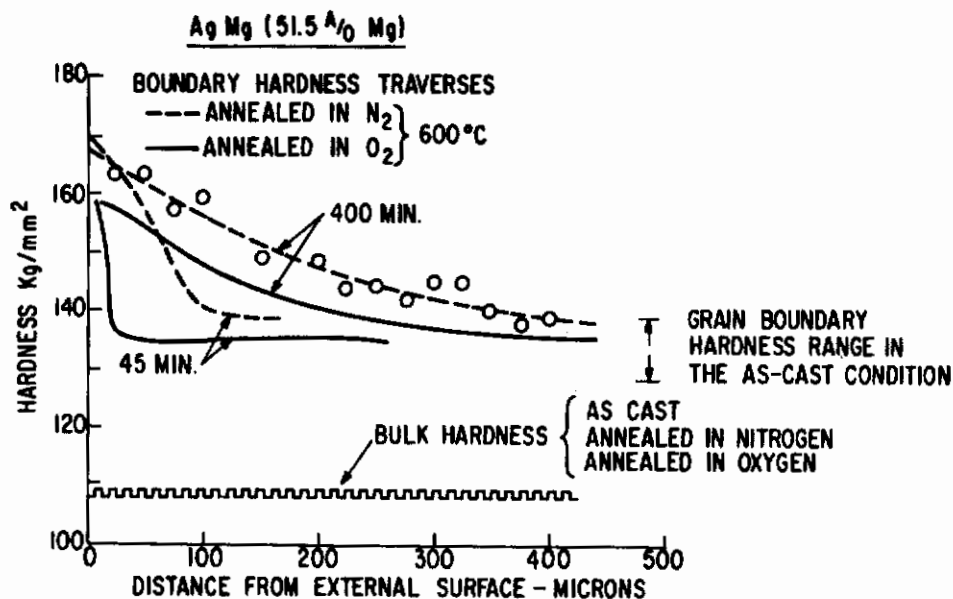


Fig. 13 Bulk and grain boundary hardness at room temperature for AgMg as a function of the square root of time of anneal at 620°C.

Fig. 14 Hardness values for AgMg as a function of distance from external surface for specimens exposed at 600°C to either oxygen or nitrogen.



A more conclusive demonstration that impurities are being absorbed is gained from an experiment in which some AgMg specimens were annealed in nitrogen and others annealed in oxygen. Cylindrical specimens, annealed at 700°C and slowly cooled, were sectioned and measurement made of the variation in hardness as a function of distance inward from the cylindrical surface which had been exposed to the gas during the anneal. Approximately radial traverses were made along both grain boundary and bulk paths, with impressions made every few microns. The scatter in the raw data for boundary hardness was rather large because the path followed was that of a boundary of unknown orientation intersecting the sample section. The curves of Fig. 14 are smooth curves drawn through points which are

rolling averages of 50 μ samplings of the raw data plotted on 25 μ centers; typical points are shown on one curve. It will be observed from Fig. 14 that grain boundary hardening is greatest near the external surface, and decreases with distance from the external surface toward the center of the sample, whereas the bulk hardness is constant along a similar traverse. The hardness profiles move toward the center of the sample with continued annealing. It may also be noted that the hardness of the boundaries near the center of the sample remained unchanged from that of the untreated, as-cast material. Since the inner portions of the sample underwent the same thermal treatment as did the outer portions, but showed no increase in boundary hardening, it must be concluded that in this material the increased hardness of the grain boundary region is due to the absorption of oxygen and/or nitrogen rather than to an ordinary age hardening process. The curves also indicate that, at the temperature investigated, grain boundary diffusion of nitrogen is faster than that of oxygen.

E. Effects of Ternary Solute Additions to AgMg

Some studies were made of the effects of small ternary solute additions on grain boundary hardening in AgMg. A wide variety of solutes were included so as to consider noble and active elements, large and small atoms, and substituents for Ag as well as for Mg. Additions were made to AgMg bases with Mg/Ag ratios both greater than and less than one. The compositions studied are noted in Table II which also lists the incidence of grain boundary hardening. Inspection of Table II

TABLE II

Effect of Ternary Solute Additions to Both Ag-Rich
and Mg-Rich AgMg on Grain Boundary Hardening

<u>Mg/Ag</u>	<u>A/o Mg in Ternary Compound</u>	<u>A/o Ternary Solute</u>	<u>Grain Boundary Hardening</u>
1	49.5	1.0 Sn	Present
<1	48.9	1.0 Sn	Present
<1	48.5	2.3 Sn	Present
<1	49.4	1.0 Zn	Not present
>1		1.0 Si	Present
>1	50.2	1.0 Zn	Not present
>1	50.0	2.0 Zn	Not present
>1	50.1	0.3 Cu	Not present
>1	50.0	1.0 Cu	Not present
>1	50.0	0.2 Al	Present
>1	50.0	1.1 Al	Present
>1	50.6	0.03 La	Not present
>1	50.6	0.05 Ce	Not present
>1		0.5 Au	Not present

reveals that grain boundary hardening is extremely sensitive to ternary solute additions. Instances are observed of grain boundary hardening imparted to a base originally free from this effect as well as elimination of such hardening from magnesium-rich bases which once had it.

F. Nitrogen Analysis of Grain Boundary Regions

An experiment has been designed which enables a quantitative measure of the degree of grain boundary segregation of nitrogen. Slugs of Ag + 52 A/o Mg 3/8 inch in diameter and 1/2 inch long were annealed in purified argon for 3 hours at 770°C to provide a large grain size within the sample. The average grain diameter after such treatment was found to be 0.45 millimeter. The sample was then annealed in pure nitrogen at 600°C for about 90 hours. (Removal of an external layer of heavily nitrated material provided a sound, bright core which was used as the sample.) Such treatment so embrittled the inner core material that it was easily separated by mechanical shock into individual grains. Precaution was taken that the separated grains were not contaminated by exposure to the atmosphere. A carefully weighed sample (of the order of 1 gram) of the individual grains was subjected to chemical analysis in the following manner. Reaction with an appropriate acid was allowed to occur for a time sufficient for the dissolution of the grains to proceed a short distance inward. The reaction was stopped, the amount of material dissolved determined, and the nitrogen content of the dissolved material measured. This process was repeated through several dissolution steps on the same sample. Knowing the average diameter of the grains, and assuming a spherical shape, the actual width of the layer dissolved at each stage could be computed. A measurement of the nitrogen content (in ppm) of each successive layer enabled the nitrogen content as a function of the distance from the grain boundary to be tabulated, as is shown in Table III.

TABLE III

Nitrogen Content at Various Distances from the Grain Boundary
in Ag + 52 A/o Mg Annealed in Nitrogen for 90 Hours at 600°C.

Original Weight of Analysis Sample = 1.28 Grams;

Average Grain Diameter = 0.45 mm

Dissolution Step	% of Original Sample Dissolved	Thickness of Layer Removed (microns)	Nitrogen Found in Dissolved Layer (ppm)	Cumulative Depth of Dissolution (microns)	Mean Distance from Grain Boundary (microns)
1	5.4	5	180	5	2.5
2	4.6	4	26	9	7.0
3	3.1	2	0	11	10.0
4	4.1	3	0	13	12.0

IV. DISCUSSION

The experiments have demonstrated that pronounced grain boundary hardening exists in many intermetallic compounds having a stoichiometric excess of an active metal component. This hardening has been shown to result from a concentration of oxygen and/or nitrogen at the grain boundaries. Mechanisms are now discussed which seek to interpret grain boundary embrittlement in intermetallics in terms of these observations.

Two generalized types of models are imagined. In the first of these it is assumed that the extent of the segregation of oxygen and/or nitrogen is essentially independent of temperature and composition. The existence of intergranular brittleness would then depend on the ease with which this constant barrier is penetrated by dislocations whose properties are a function of other parameters. Although this constant barrier model cannot be explicitly ruled out on the basis of any experiment reported or yet conceived, it seems highly unlikely since it requires the implausible assumption that the penetrating power of the dislocations is both temperature and composition dependent.

The second class of model assumes a composition and temperature dependent segregation of oxygen and/or nitrogen which thus constitutes a variable barrier to a constant type of dislocations. In studying such a model, consideration must be given to the following questions:

Why is segregation affected by

- (a) Temperature ?
- (b) Presence of an active metal ?
- (c) Stoichiometry ?
- (d) Ternary solutes ?

Why does segregation harden and embrittle ?

Before these questions are treated in detail, the initial introduction of the embrittling agent, i. e. , the gaseous impurities, will be discussed.

A. Introduction of Gaseous Impurities

Gaseous contaminants may be present in melt stock, they may be adsorbed into a molten material from the casting atmosphere, or into a solid material from an annealing atmosphere. The observed frequent occurrence of grain boundary hardening in as-cast intermetallics, together with a consideration of the highly reactive nature of either one of or both of the components of many intermetallics, indicates that both the purity of melt stock and processing atmosphere are of vital importance in the preparation of such materials. Experiments, such as that described in Fig. 12, indicate that relatively uncontaminated materials are subject to rapid

contamination during annealing even in ordinarily pure argon. Such observations are of considerable pertinence to any practical application of intermetallics for high temperature service.

B. The Segregation Process

In the absorption of gaseous contaminants into a solid material, it is clear that the grain boundary affords a rapid diffusion path. Over most temperatures diffusion will be more rapid along grain boundaries than laterally from them into the bulk. Therefore, with a continuing source of gas, grain boundary regions will tend to have an unusually high content of the gaseous element. In addition, even if the gas content of the whole piece remains constant, the evidence shows that non-uniform distribution of gaseous elements is not merely a transient condition, but that equilibrium grain boundary segregation of oxygen and/or nitrogen can occur under some combinations of temperature and base composition.

The theory of equilibrium adsorption of solute at grain boundaries* pictures the grain boundary as offering solute atoms, disparate in size relative to the solvent atoms, sites of lower strain energy than are available in the bulk lattice. Oxygen and nitrogen atoms differ in size from metallic atoms and hence can give rise to appreciable strain whether accommodated in the lattice substitutionally or interstitially. It is therefore not unlikely that they segregate to grain boundaries under favorable circumstances. Explicit analytical proof that these elements are indeed concentrated at grain boundaries will be difficult to obtain. In fact, although equilibrium adsorption of solute elements at grain boundaries in metals is well accepted as a concept, it is thus far unequivocally demonstrated in but few cases. Perhaps the best evidence is that for sulfur in alpha-Fe by Ainslie et al., (11,12) who also review the evidence in other systems. The problem is more acute in the present case in that there are no suitable radioactive tracers for oxygen and nitrogen.

1. Temperature Effects

One of the most prominent observations to be accounted for is the marked effect of temperature on the segregation process, i. e., at a sufficiently high temperature, grain boundary hardening disappears. Although more complicated mechanisms of a temperature dependent segregation have been suggested in certain instances, (13) a simple presumption is that temperature acts through affecting the relative solubilities of grain boundary and bulk for the segregant. Since solid solubilities are known generally to decrease considerably with decreasing temperature, it is conceivable that as the temperature is lowered, a driving force is built up causing the gaseous impurities to migrate to the grain boundaries with a

*For a review see McLean. (10)

consequent concentration buildup in those regions. On the other hand, sufficiently rapid quenching from a temperature where solute is evenly distributed between bulk and boundary to a low homologous temperature where diffusion is very slow could effectively prevent such segregation even where the distribution ratio might be very high at the lower temperature. Establishment of such a metastable equilibrium is believed to have been achieved in the experiments on NiAl and ZrBe₁₃ reported here. It may also account for the results observed in Fe-S alloys by Leymonie et al. (14) although Ainslie et al. (12) suggest another explanation.

In AgMg, however, even with an ideally rapid quench, room temperature is high enough for solute migration to occur from bulk to boundary as demonstrated by the return of grain boundary hardening with time in Fig. 8. McLean, (10) in discussing the equilibrium concentration of solutes at grain boundaries, considers the rate at which the grain boundary concentration builds up after a specimen has been cooled suddenly from a high to a low temperature. Measuring the grain boundary concentration $f(C)$ by $(C_{gbt} - C_{gb0}) / (C_{gb\infty} - C_{gb0})$ he finds:

$$f(C) = 1 - e^{-x^2} (1 - \operatorname{erf} x) \quad (1)$$

where the argument $x = \frac{2\sqrt{Dt}}{\alpha_2 d}$

with D the diffusion coefficient of solute
t the time
 α_2 the ratio of equilibrium grain boundary concentration to the grain interior concentration, and
d the thickness of the grain boundary.

It may be reasonably assumed that to a first approximation, the grain boundary hardening increment is proportional to the segregation concentration of the gaseous impurity at the boundary. With this assumption, McLean's expression [Eq. (1)] may be tested with the data of Fig. 8 by fitting the curve at a single point. The point where $f(C) = 0.5$ was chosen and a conversion factor was calculated for converting values of the argument x to times. McLean's function can thus be compared with experiment. The agreement of experimentally obtained points with such a calculated curve, Fig. 15, lends support to the concept that the solute segregation is, in fact, temperature dependent.

The bulk hardening which was observed during the aging experiment on quenched AgMg, as shown in Fig. 8, must be by an entirely different mechanism than the grain boundary hardening. It cannot be normal precipitation or internal oxidation because of the reversibility of the effect. It would seem that the observation must be accounted for by localized atom movements, perhaps by changes in short range order, e. g., a clustering of lattice defects, or perhaps by segregation of gaseous impurities to dislocations within the bulk.

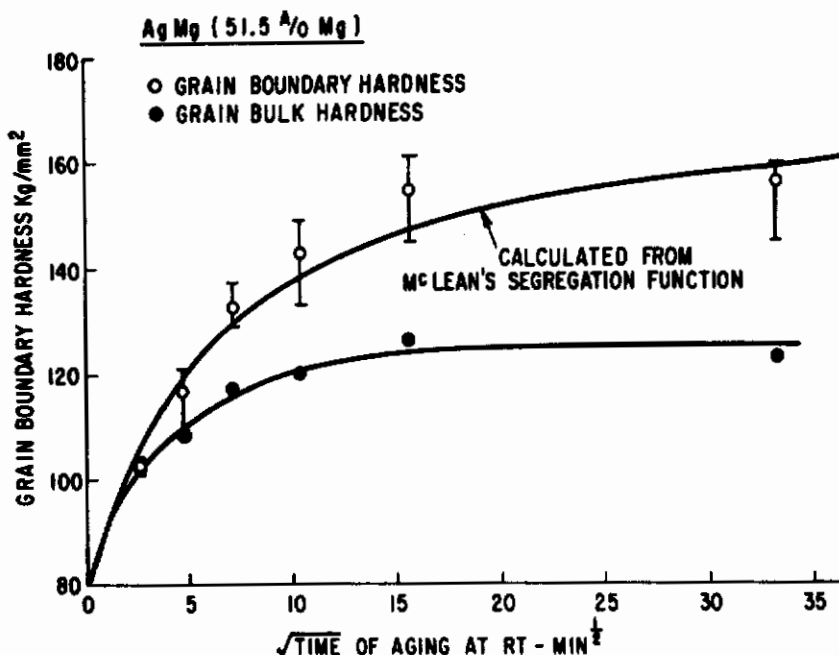


Fig. 15 Comparison of experimental points with the calculated curve [after McLean⁽¹⁰⁾] for the increase in grain boundary hardening with the square root of time of aging at room temperature after quenching in liquid N₂ from a temperature of 225°C.

2. Composition Effects

Although equilibrium segregation seems plausible as the basic cause for the effects observed, and the mechanism outlined above satisfactorily accounts for the observed influence of time and temperature, the several effects of composition on segregation remain to be considered. In the first place, the necessity for a reactive element is by no means clear. A conventional chemical reaction might be supposed but the experiments show that the reaction product between the active element, e. g., Mg, and the gaseous element, e. g., O₂, can scarcely be the highly stable oxides and nitrides of these active materials since such stable precipitates could not be dissociated at a temperature of 200°C, as was shown to be the case in Fig. 7.

A further problem exists in explaining why oxygen and/or nitrogen should result in grain boundary hardening only when the active element is in excess of the stoichiometric composition. It could be argued on the basis of the previously proposed models that such behavior is due to effects of stoichiometry on the solubility for the gaseous impurities, but it is difficult to visualize such sharp changes in solubility with composition of the solvent compound. Some insight into the problem may be gained, however, by consideration of the thermodynamic behavior of magnesium in AgMg. Figure 16, which reproduces some results of Kachi, ⁽¹⁵⁾ shows that at magnesium concentrations only slightly in excess of stoichiometry the activity of Mg is greatly increased over that for the stoichiometric and all silver-rich compositions. Mg atoms in excess of the stoichiometric ratio, therefore, are loosely bound and, such compositions may thus show sharply increased reactivity with or solubility for extraneous elements. The exact manner in which the increased activity of magnesium is associated with an increased tendency for gaseous impurity segregation is not yet clear.

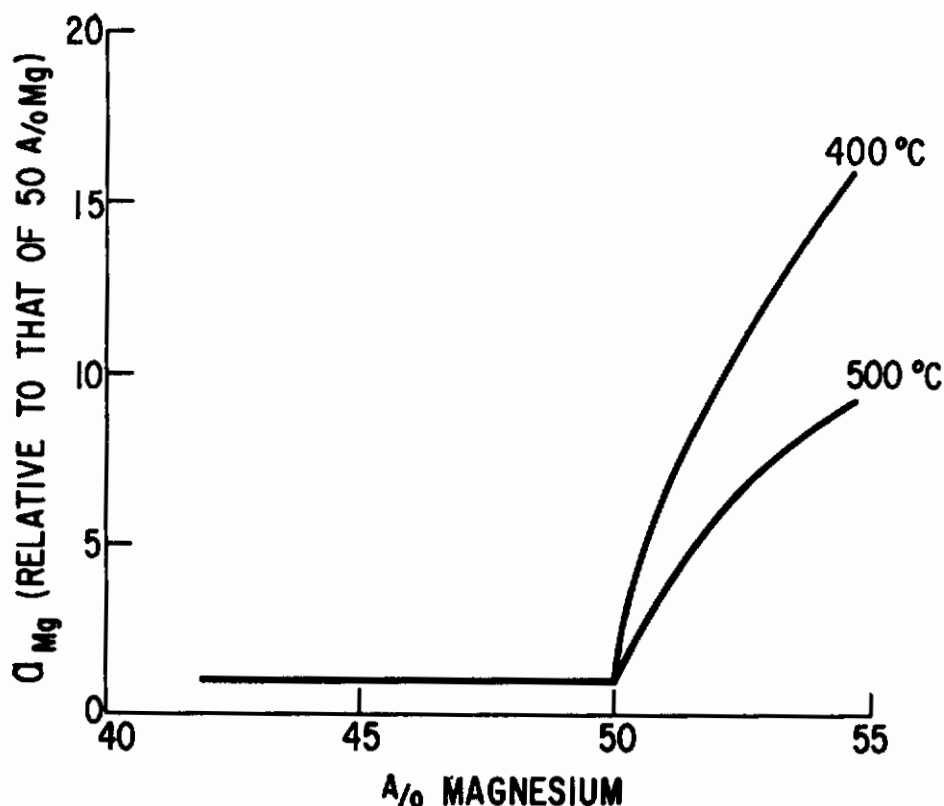


Fig. 16 Variation with composition of the activity of Mg in AgMg [after Kachi⁽¹⁵⁾].

Other instances of compositional factors are the effects noted in Table II of ternary solute additions. On the one hand they afford some hope for practical cure for intergranular brittleness, at least in specific cases. On the other hand, they may ultimately serve to define the particular mechanisms which are operative in this phenomenon. Several kinds of role for solute elements might be envisioned. They may:

- (a) segregate to grain boundaries,
- (b) affect the activity of Mg in the compound,
- (c) affect the solid solubility of O₂ and N₂ in the compound,
- (d) complex with O₂ and N₂,
- (e) affect the grain boundary diffusion rates for O₂ and N₂.

Unfortunately, without a knowledge of these solid solubilities, activities, diffusion rates, and segregation and "complexing" tendencies, it is impossible to make a detailed interpretation of the results obtained. It is worth noting, however, that analogous effects of third elements on segregation have been noted for metals. Some of these are listed in Table IV.

TABLE IV

Some Effects of Third Element Modifiers on Segregation

<u>Base Metal</u>	<u>Segregant</u>	<u>Modifier</u>	<u>Effect on Segregation</u>	<u>Reference</u>
Fe	O	C	Alleviates	Low and Feustel ⁽¹⁶⁾
Fe	P	Mo	Alleviates	Steven and Balajiva ⁽¹⁷⁾ Archanov <u>et al.</u> ⁽¹⁸⁾
Fe	P and Sb	Cr	Aggravates	Russian work ⁽¹³⁾
Fe	S	C	Alleviates	Ainslie <u>et al.</u> ^(11, 12)
Cu	Sn	P	Aggravates	Perryman ⁽¹⁹⁾

C. Hardening and Embrittlement by Segregation

The experimental evidence in this report presents a strong empirical correlation between segregation of the gaseous elements oxygen and nitrogen and grain boundary hardening. The above discussion further implies a causal relationship between the two factors. There is also a considerable body of evidence summarized in Table V to indicate that grain boundary segregation in a variety of metals can significantly affect mechanical properties. There are tabulated here only those observations on tests at low or moderate homologous temperatures. The principal mechanical effects observed as a result of segregation are sharp yield points, intercrystalline fracture, and reduced toughness (either in the sense of a reduction in some toughness parameter at a reference temperature or in an increase in a ductile-brittle transition temperature).

Despite the number of previous investigations in which grain boundary hardening and embrittlement by segregation have been implied or specifically suggested, there has been little discussion of mechanism by which such small concentrations of impurity elements in such small regions might exert such marked effects on mechanical properties. Explanations for intergranular fracture have been proposed based on changes in surface energy or internal stress imparted by the segregants, but such effects can hardly lead to the boundary hardening observed in the present case. Perhaps the boundary regions are hardened by a solid solution mechanism but a more likely mechanism is that demonstrated by Ainslie et al. ⁽¹²⁾ for the case of sulfur segregation in α -iron. They showed by high resolution transmission electron microscopy that dense dislocation networks were associated with the grain boundaries of sulfur-segregated iron. These networks were quite extensive, up to 15μ on either side of the boundary, and had an over-all density of dislocations comparable to that of fully cold-worked metal. The width of this unusual structure is of nearly the same order as was noted for the hardness profiles in the present studies on AgMg. Although the particular mechanism that

TABLE V

Some Effects of Equilibrium Segregation on Mechanical Properties

<u>Base Metal</u>	<u>Segregant</u>	<u>Evidence for Segregation</u>	<u>Mechanical Property</u>	<u>References</u>
Cu	Bi	Inferential	Notched bar impact reverse bending	Voce and Hallows ⁽²⁰⁾
Cu	Bi	Metallographic	See Ref. 20	Samuels ⁽²¹⁾
Cu	Sb	Metallographic	Notched bar impact	McLean ⁽²²⁾
Cu	Sb	Inferential	Impact, tensile yield	Hopkin ⁽²³⁾
Cu	Sn	See Ref. 19	Tensile impact	Eborall ⁽²⁴⁾
Cu	Sn	Metallography	See Ref. 24	Perryman ⁽¹⁹⁾
β brass	Al	Electrochemical behavior	Tensile impact, tensile	Perryman ⁽¹⁹⁾
β brass	Al	See Ref. 25	Tensile impact	Harper ⁽²⁶⁾
β brass	Al	See Ref. 25	Notched bar impact	Bailey <u>et al.</u> ⁽²⁷⁾
Fe	C, O, N ?	Inferential	Scratch hardness	Ljunggren ⁽²⁸⁾
Fe	C, O, N ?	Inferential	Micro vs macro hardness, Y. P.	Eborall <u>et al.</u> ⁽²⁹⁾
Fe	C	Metallographic, electrochemical behavior	Notch bar impact	McLean and Northcott ⁽³⁰⁾
Fe	N	Inferential	Tensile, notch impact	Hopkins <u>et al.</u> ⁽³¹⁾
Fe	O	Inferential	Tensile and impact	Rees and Hopkins ⁽³²⁾
Fe	O	Inferential	Tensile	Low and Feustel ⁽¹⁶⁾
Fe	P	Chemical Analysis	Impact	Archanov <u>et al.</u> ⁽¹⁸⁾
Fe	P	Radio tracer	Bending	Inman and Tipler ⁽³³⁾
Fe	?	Metallographic	Impact	Cohen <u>et al.</u> ⁽³⁴⁾
Al	Mg	Inferential	Tensile, yield point	Phillips <u>et al.</u> ⁽³⁵⁾

Ainslie et al. suggest for formation of the dislocation network may not have general applicability, other features of their model seem quite attractive. The high dislocation density near grain boundaries affords a direct basis for hardening with consequent brittle intergranular fracture. There is also an autocatalytic aspect of the model since the networks will provide a greatly increased capacity of the grain boundary region for the preferential transport as well as for the ultimate adsorption and retention of solute.

As indicated above, segregation may also have some other consequences. The previous study of the mechanical behavior of AgMg disclosed an intermediate temperature range where the deformation process appeared to be dominated by dislocation interactions with solute atoms. Among the effects observed leading to this conclusion were: deviation from monotonic stress-temperature curves, maxima in the change of strain rate sensitivity with temperature, minima in the temperature dependence of the strain hardening coefficient, pronounced yield points, inverse yielding in rate change tests, serrated stress-strain curves, strain aging, and strong relaxation effects. In addition, the following relationships were found between the flow stress σ , the strain rate $\dot{\epsilon}$ and the temperature T

$$\sigma \sim 1/T \quad (2)$$

$$\log \sigma \sim \log \dot{\epsilon} \quad (3)$$

In analyzing these mechanical effects, the identification of possible interacting solute species was discussed. Both (1) the discontinuous change at the stoichiometric composition for the apparent activation energy for strain aging and (2) the inability of simple (substitutional) point defects to pin screw dislocations as well as edge dislocations weighed against the possible operation of excess component elements (i. e. , Ag or Mg) in this fashion.

The studies of McLean⁽²²⁾ on intergranular brittleness in copper-antimony alloys present some interesting parallels. Not only did he show that embrittlement was associated with equilibrium segregation of antimony in compositions well within the solid solution field, but also he demonstrated the existence of sharp yield points, flow curve serrations, strain aging, and a $1/T$ dependence of yield stress. It would therefore appear likely that the similar effects observed on the flow stresses of AgMg are due to the presence of oxygen and/or nitrogen.

McLean found equilibrium segregation to be associated with two different types of embrittlement, one at high and one at low temperatures as evidenced by peaks in impact energy-temperature curves. He suggested that the former is influenced by the presence of excess vacancies while the latter results from dislocation pileup on slip planes terminating against the hardened grain boundaries. The present results do not suggest two different mechanisms of embrittlement, but inasmuch as quantitative measurements of fracture energy as a function of temperature were not made, such a possibility still exists.

D. Other Considerations of Brittle Behavior

There seems little doubt that the anomalously high ductile-brittle transition in intermetallics having a stoichiometric excess of active element is a result of grain boundary hardening. Such a conclusion is substantiated by the temperature coincidence of the disappearance of grain boundary hardening with the onset of ductility in AgMg, and with the impact transition temperature in NiAl.

Experiments on AgMg were successful in affecting the temporary retention of the high-temperature condition of grain boundaries without anomalous hardening, as was shown in Fig. 8. It proved impossible, however, to demonstrate a concomitant temporary improvement in ductility. Perhaps this failure is rational, however, in that the transition temperature would need to be lowered to some temperature below room temperature if ductile behavior were to be observed. Testing at temperatures above room temperature, but below the temperature of loss of grain boundary hardening (200°C) in order to ascertain a shift in transition temperature, is experimentally unfeasible. At such a high homologous temperature, the return of grain boundary hardening by an aging process would proceed even faster than at room temperature and thus would hamper any ductility measurements at even only slightly elevated temperatures.

Similar studies of the effects of quenching on the toughness of NiAl could be safely carried out at room temperature because this is a low homologous temperature for this material. Quenching from above a critical temperature ($\sim 985^\circ\text{C}$) was found to improve the impact strength, while quenching from below that temperature resulted in a lower toughness relative to that of material slowly cooled from above the critical temperature. The slowly cooled material is believed to have an impact strength at room temperature intermediate relative to the other two treatments because it was in the critical temperature range for only a short time. These results have strong practical implications in that they point out a method for metastable improvement of room temperature ductility of relatively high melting intermetallics. The data indicate that a change in impact strength of a factor of 4 or 5 can result from variation in annealing practice.

E. "Pest" Phenomena

It is interesting to consider the possible relation of the present observations to the "pest" phenomenon frequently observed in such compounds as the beryllides, silicides, and aluminides. The common phenomenology of the "pest" is that the compound is very resistant to oxidation at low temperatures and only slightly less so at high temperatures. An intermediate temperature range exists, however, where degradation is very rapid with failure occurring by virtually complete intergranular disintegration. The intergranular nature of the failure may be verified by microscopic investigation and is further supported by the fact that individual grains remain malleable. Experiments conducted in vacuo have proven that gaseous contaminants are a necessary component of the pest effect. The present results lead to the following interpretation of such phenomena.

At low temperatures, rates of diffusion through both bulk and grain boundaries are very low and oxidation, if observable at all, is confined to a very thin surface layer. At some intermediate temperature range, grain boundary diffusion rates become sufficiently enhanced for complete intergranular penetration by oxygen and/or nitrogen to occur. This temperature is also such that the gaseous elements remain segregated and embrittle by one or another of the mechanisms suggested above. Disintegration is then assumed to occur under the action of internal stresses, either transient stresses due to the heating and cooling cycle or those resulting from crystalline anisotropy. At high temperatures intergranular embrittlement does not take place, most probably because bulk diffusion rates are sufficiently great at these temperatures to drain off laterally any gaseous element concentration tending to build up along the boundaries; only normal surface controlled oxidation appears. It is not implied that the model just described accounts for all cases of "pest" degradation. In special instances liquid phase formation at grain boundaries or changes in the type of oxide forming at different temperatures may be more important.

V. CONCLUSIONS

Grain boundary hardening is found in this investigation to exist in many intermetallic compounds having a stoichiometric excess of active metal component and is shown to be associated both with the anomalously high ductile-brittle transition temperatures common in these materials and with the "pest" phenomenon occurring in certain intermetallics. Although experiments show clearly that such grain boundary hardening is due to the adsorption of gaseous impurities such as oxygen and/or nitrogen and their segregation to grain boundary regions, the manner in which the resistance to plastic deformation is increased in these areas is not clear. The most likely mechanism is the formation of a dislocation network as found by Ainslie et al. in Fe-S alloys. Ternary additions as well as appropriate annealing treatments are shown to be a promising approach to alleviating intergranular brittleness in these materials.

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