

WADC TECHNICAL REPORT 57 - 298

Part 11

ASTIA DOCUMENT NUMBER 207 907

IRON-ALUMINUM ALLOY SYSTEMS

**PART 11 COMPARTIVE STUDY OF OXIDATION RESISTANCE IN
THE FE-AL SYSTEM**

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NOVEMBER, 1958

MATERIALS LABORATORY

CONTRACT NO. AF 33(600)-32448

PROJECT NO. 7351

**Industrial Resources Division
Air Materiel Command
and
Wright Air Development Center
Air Research & Development Command**

**United States Air Force
Wright Patterson Air Force Base, Ohio**

FOREWORD

This report was prepared by the Metallurgical Department, Scientific Laboratory, of the Ford Motor Company, Dearborn, Michigan, under USAF Contract No. AF 33(600)-32448, which was initiated under AMC Project No. 7-564, "Ford R&D Program", and WADC Project No. 7351 "Metallic Materials", Task No. 73512 "High Temperature Alloys". This contract was administered jointly by the Manufacturing Methods Branch (MCPBM), Industrial Resources Division, Air Materiel Command, with Mr. A. H. Langenheim acting as Project Monitor, and by the Materials Laboratory, Directorate of Laboratories, Wright Air Development Center, with Mr. Charles B. Hartley acting as project engineer.

This report covers work conducted from April through September, 1958 and is a portion of the work scheduled by the contract under Item 4.

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ABSTRACT

A study of the oxidation resistance of Fe-Al alloys with varying aluminum content has been made. Visual observations confirm the effect of aluminum (0 - 16 percent) on the oxidation resistance of Fe-Al alloys at temperatures to 2200°F and for periods of up to 500 hours.

Attempts to quantitatively determine weight gain of Fe-Al alloys were not successful. The lack of reproducible weight gain data is suggested to be a result of oxide seams and inclusions.

The addition of chromium was found to be beneficial only at the 7.50 percent chromium level. The apparent deleterious effects of chromium at levels both higher and lower than 7.50 percent is to be further investigated. An alloy containing 7.50 percent aluminum and 7.50 percent chromium is recommended for further study in view of its good oxidation resistance, corrosion resistance, and ductility.

PUBLICATION REVIEW

This report has been reviewed and is approved.

FOR THE COMMANDER:



RICHARD R. KENNEDY
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I - INTRODUCTION

Much effort has been expended in the development of alloys of the Fe-Al system in this and other laboratories of the world ^{1,2,3,4}. Considering the fact that major interest lies in the ability of Fe-Al to withstand destructive oxidation at elevated temperatures, little has been done with regard to a comparative or quantitative evaluation of its resistance to oxidation.

For this reason a program was initiated to determine the dependence of oxidation resistance upon aluminum content. This program began with a visual study of the differences in oxidation resistance of specimens ranging in composition from pure iron to 16 weight percent aluminum. The preliminary comparisons were then to be followed by a more detailed study involving a method of determining weight gain with respect to time at various elevated temperature levels, and finally to identify the structure of the individual oxide layers that are formed.

Manuscript released by author October 1958 for publication as a WADC Technical Report

II - DISCUSSION

Fe-Al Binaries

For the visual comparisons specimens were prepared from stock already on hand. Nine pieces of 7/8 inch bar stock from air melted heats of pure iron, 2 percent Al, 4 percent Al, 6 percent Al, 8 percent Al, 10 percent Al, 12 percent Al, 14 percent Al, and 16 percent Al were rolled into flats of .085 inch thickness and then machined into specimens of the following dimensions: .050 inch x .750 inch x 2.750 inches. All surfaces were microfinished to 16 micro-inches. The specimens were left in the as rolled/as machined condition.

These specimens, placed on an alundum slab, were oxidized in a dry air atmosphere at 1600, 1800 and 2000°F. The specimens were not placed in the furnace until the desired operating conditions had been attained. At the end of 10, 50 and 100 hours, the specimens were removed from the furnace, slow cooled in an insulated chamber, carefully examined and then photographed in color. Color Plate I.

The results of this comparative study showed very conclusively how the degree of oxidation resistance is enhanced by increasing the aluminum content.

The specimens ranging from pure iron to 4 percent Al were either completely converted to oxide or showed indications of complete permutation if exposed for a period longer than 100 hours.

The specimens from 6 to 8 percent aluminum, after forming a tenacious gray oxide layer, appeared to resist further oxidation very well. The oxide layer increased in thickness very slowly with increase of time and temperature.

At an aluminum content of 10 percent a complete change in appearance was observed. The oxide layer was much thinner, less tenacious, and a red, not gray, oxide was formed. A slight warpage in the specimen, indicating internal stresses were present, seemed to point up the fact that a transformation was taking place at this aluminum level. It is unlikely that ordering has any real effect upon the diffusion process accompanying oxidation since ordering is believed to occur far below the temperature at which the specimens were maintained for 100 hours. It is probable, however, that the particular ratio of Al to Fe in the 10 percent alloy encourages the formation of a spinel which differs from the oxides or double oxides formed by the 8 percent and 12 percent alloys. Only a slight tinge or red appeared in specimens containing 12 to 16 percent aluminum after 50 hours at oxidizing temperature. By the time these last three specimens had been at 2000°F for 100 hours a gray-white filmy oxide covered them completely. This oxide could be wiped off easily to expose a shiny metal sub-surface.

Fe-Al-Cr Ternaries

In order to increase the corrosion resistance of the Fe-Al binary, an additional alloying element was sought; one that would not destroy or appreciably alter existing oxidation resisting properties. Chromium, because of its proven ability to enhance corrosion resistance of other alloys, seemed a logical choice. A series of Fe-Al-Cr heats were vacuum melted. The heats selected for additional oxidation studies contained 8 percent aluminum with an addition of 2.50, 4.75, 7.25 and 9.50 weight percent chromium.

The specimens were prepared in the same manner as previously described. The time and temperature of exposure was increased, however. It was felt that more conclusive information could be obtained if temperatures of 1800, 2000 and 2200°F were used for 100 and 500 hour periods. Color Plate II shows the comparison of oxidation resistance among Fe-Al-Cr and Fe-Al alloys.

No destructive oxidation was evident in any of the specimens after 500 hours at 1800°F. Those specimens subjected to 2000°F for 100 hours were also relatively unharmed. After 100 hours at 2200°F the 2.50 percent chromium alloy was rather badly scaled, and the 4.75 percent chromium was also scaled, though not as extensively. The only specimen which held up well for 500 hours at 2000 and 2200°F was the 7.25 percent chromium alloy. All other specimens in the series suffered severe blistering, desquamation, and edge disintegration.

Since the 7.25 percent chromium alloy was unharmed while the 9.50 percent chromium alloy was almost completely destroyed, it was thought that perhaps the latter lacked homogeneity. However, repeated tests showed quite conclusively that chromium at higher levels and at this aluminum level does have a deleterious effect upon the oxidation resistance of Fe-Al above 2000°F. Why this is not evident at the 7.25 percent chromium level is not known at this time. The anomalous effect of chromium contents higher than 7.50 percent will be further investigated. Present planning calls for an investigation of the effects on oxidation resistance of the higher carbon present in the 9.50 percent chromium alloy.

Another heat having the composition 7.50 percent aluminum and 7.50 percent chromium was prepared. Upon oxidation at 2200°F for 500 hours the specimens from this heat also exhibited excellent oxidation resistance. A thin white oxide layer was formed which, upon cooling, was easily removed to expose a shiny sub-surface similar to that observed on a 12 to 16 percent Fe-Al binary.

The addition of .32 weight percent silicon appeared to decrease the oxide film thickness slightly.

In the course of studying the corrosion and oxidation resistance of the Fe-Al-Cr alloys, room temperature tensile tests were made to establish the ductility of these alloys. The data from these tests are presented in Tables V and VI and graphs I and II.

Although the few mechanical tests that were made do not permit any definitive conclusions to be drawn, several features of these data are of interest. At the 8 percent aluminum level, additions of chromium to 5 percent do not deleteriously affect the ductility. Above this chromium level, both elongation and reduction of area appear to be adversely affected. Lowering the aluminum level to about 7.50 percent, however, brings the ductility parameters back to their former high levels.

The presence of silicon, at levels normally found in commercial electric furnace practice, decreases ductility rather severely. Part of the ductility drop might be due to the carbon present, and this can probably be compensated for by the addition of .50 percent of a carbide former such as titanium. Alloys containing 7.50 percent Al, 7.50 percent Cr, 0.35 percent Si, 0.50 percent Ti, and .05 percent C are presently being prepared for mechanical testing.

Weight Gain Determinations

A study of weight gained by oxidation of Fe-Al under controlled conditions was planned. If the rate of oxidation could be determined by measuring the weight gain of a specimen with respect to time, then a graphic representation could be established for various concentrations of aluminum at any desired temperature level. Assuming the oxidation rate curve of Fe-Al resembles that of other refractory oxides, then weight gain squared vs. time will follow the parabolic relationship $x^2 = Kt$ presented by Pilling and Bedworth for a dense and adherent scale^{5,6}.

Equipment

A method considered suitable for determining weight gain was very similar to the one employed by C. A. Siebert for investigating intergranular oxidation in stainless steel⁷. The equipment (Figure 1) consisted of a precision balance mounted above an open end tube furnace through which an oxidizing atmosphere was circulated.

Direct weighings could then be made as the specimen, attached to the balance, was suspended inside the furnace tube. The balance selected was a Beckman specific gravity balance which was modified and recalibrated to give direct readings. The furnace tube was ducted directly into a circular opening in the floor of the balance housing. The specimen was then suspended inside the furnace by means of a heavy gauge platinum wire connected to the balance arm. Heat reflecting plates were mounted in the duct between the furnace and the balance. The oxidizing atmosphere was admitted at the bottom end of the furnace tube which was packed with refractory saddles to permit dispersion of the incoming gas stream. The furnace consisted of three separate elements wound on a 4-1/2 inch diameter aluminum core. By using three windings, compensation could be made for heat loss at the tube ends, thus forming a long hot zone with a minimum gradient. A quartz tube was used to minimize any diffusion of the oxidizing atmosphere. The oxidant selected was commercially available extra dry oxygen having a dew point of -70°F. The need for a dehumidifying train was, therefore, eliminated. The oxygen flow was regulated by a needle valve in conjunction with a flowmeter installed between the oxygen cylinders and the furnace inlet.

Specimen Preparation

All specimens used in weight gain determinations were machined from vacuum melted stock. The stock was hot rolled from 7/8 inch bar to .085 inch thick flat. The following machining specification was rigidly adhered to:

1. Each specimen will be machined to a size of 2.75 in. x .750 in. x .050 in. \pm .003 in.
2. Both flat surfaces of each specimen must have a micro-finish of 16 microinches. An equal amount of metal must be machined off from each surface.
3. All specimens must be free from defects, and any specimen which develops defects while machining should be scrapped and returned with all excess material.

4. All specimens should be coated with machine oil and wrapped individually with their identity marked on the wrapper; not on the specimen.

Aside from the above preparation, the specimens received varying additional treatment, which will be described later when the experimental data are presented.

After the machined specimens were received from the shop their identity was confirmed by a resistivity check. They were carefully cleaned with a suitable solvent and stored in a desiccator.

Operating Conditions

All specimens were taken from vacuum melted heat A66, which had the following chemical analysis: 7.97 percent Al- .03 percent C- balance Fe. The operating temperature during all oxidation runs was 1800°F. A flow rate of 5 ft.³/hr. was maintained. This was considerably higher than necessary, however, since the minimum requirements were not known, some definite excessive rate had to be established.

Operating Procedure

The specimen was not introduced until the furnace had been at the desired operating temperature for several hours and the tube had been flushed with oxygen at the predetermined flow rate. After suspending the specimen in the furnace, ten minutes were allowed to elapse so that the temperature could reach equilibrium before the initial reading was taken. The oxygen flow was momentarily discontinued whenever a reading was taken. Each run had an intended duration of 100 hours.

Data

The only heat treatment given the test material used in the first three runs was performed upon the "as rolled" stock prior to machining. This treatment consisted of heating the material for one hour at 2000°F and furnace cooling. Data obtained from the first three runs is presented in the Table below, and in Graph III.

TABLE I

Run No. 1		Run No. 2		Run No. 3	
Wt. Gained mg/in ²	Time In Hours	Wt. Gained mg/in ²	Time In Hours	Wt. Gained mg/in ²	Time In Hours
0.224	3	1.073	5	0.224	2
3.487	6	10.270	20.5	0.313	4
13.230	22	11.000	23	0.626	7
14.480	24	16.850	41.5	4.920	23
15.640	27	17.520	43.5	6.440	28
16.400	29.5	18.060	47	7.650	31.5
26.060	55	19.170	49.5	10.140	43
36.460	93	21.860	65.5	11.000	48.5
		22.800	68.5	11.300	51.5
		27.600	90.5	13.550	67
		27.850	93	14.520	75
		28.800	98	18.150	102
Total Specimen					
Area 4.475 in ²					

The lack of reproducibility among these runs could possibly be attributed to segregation, specimen preparation, faulty procedure, or faulty equipment. Considering the history of the heat, the occurrence of segregation seemed unlikely. In order to check against faulty procedure and equipment it was decided to make two more runs using some other alloy which would oxidize at such a rapid rate that any effect due to specimen preparation would be insignificant. An alloy having the composition 8.5 percent Cr- .03 percent C- balance Fe was selected. The specimens from this alloy were vacuum annealed for four hours at 1800°F.

The data from these runs is recorded in the following Table and in Graph IV.

TABLE II

Run No. 4		Run No. 5	
Wt. Gained mg/in ²	Time In Hours	Wt. Gained mg/in ²	Time In Hours
29.53	3.16	24.88	4.66
105.20	19.00	49.65	7.16
113.50	24.66	115.30	25.90
118.80	27.50	129.00	34.00
136.00	33.00	145.50	51.25
142.00	38.00	168.50	74.16
142.30	41.00		
151.00			

Since the extreme rate of oxidation would cause disintegration of the specimen, these runs were not allowed to continue for the full 100 hours. After examining the above data it appeared evident that the equipment and the procedure were both satisfactory. The source of error, then, was believed to be in the specimen preparation.

The varying degree of work in the surface of the specimens after machining was considered a likely cause of inconsistency in the oxidation rate. A different heat treating procedure was followed for two more specimens from heat A66. The "as rolled" stock was heated to 2000°F and furnace cooled as before; however, the machined specimens were then vacuum annealed for four hours at 1800°F. Upon completion of annealing the surfaces of the specimens appeared to be slightly heat etched. The etch lines were removed with four "0" paper. The data in the Table below and in Graph V were obtained from these newly prepared specimens.

TABLE III

Run No. 6		Run No. 7	
Wt. Gained mg/in ²	Time In Hours	Wt. Gained mg/in ²	Time In Hours
.403	10	.134	4
.626	15.5	.358	7
.804	34	3.310	23
1.0280	42	4.20	27
1.340	59	5.32	31.5
1.475	66	9.34	47.5
1.790	87.5	10.30	52
2.260	110.5	10.95	55.5
2.640	130	13.95	71
		14.75	75.5
		15.37	79.5
		18.00	95

The specimen from run number 6 was covered by a thin gray oxide while the specimen from run number 7 was covered by a heavy gray and red oxide which scaled considerably upon cooling. Although some peculiarity in the specimen is preventing reproducibility, it is difficult to believe that a difference of such magnitude could be the result of any surface effect.

In order to definitely establish whether or not the inconsistency of data was the result of a surface effect, a method for producing exactly the same surface conditions on all test specimens was required. While grain size and degree of surface finish can be duplicated to a reasonable extent, the effect of surface strain presents a greater problem. The strain effect can be minimized by vacuum annealing; however, when this procedure is followed some degree of heat etching nearly always results. On the other hand, when the specimens are annealed before surface preparation is complete, the unrelieved strain resulting from surface finishing will be present unless a chemical rather than mechanical method is used. For this reason electropolishing appeared to be the only remaining choice.

Five newly machined specimens from heat A66 were annealed at 1800°F for two hours and furnace cooled. The surfaces were then finished by light application of four "0" paper to remove all traces of heat etching. Several thousandths of an inch was then removed by electropolishing to a bright luster with an acetic anhydride-perchloric acid solution. Care was taken to prevent pitting from occurring. Careful examination of the polished specimens disclosed traces of what appeared to be seams of included oxide from the rolling process. It is probable that these seams were present and undetected on the specimens used in previous runs. This could completely account for the lack of reproducibility. If thicker flat stock was used the included oxide could be removed by machining. While awaiting preparation of new specimens the three best electropolished specimens were used as planned. The data are recorded in the Table below and in Graph VI.

TABLE IV

Run No. 8		Run No. 9		Run No. 10	
Wt. Gained mg/in ²	Time In Hours	Wt. Gained mg/in ²	Time In hours	Wt. Gained mg/in ²	Time In Hours
.358	2	.268	2	.894	16.5
1.43	18	.581	8	1.07	18.75
1.70	21.33	2.05	22	1.21	24
2.06	23.5	2.28	24	1.83	35.75
2.64	42	3.80	46.5	1.97	41
2.82	47	4.38	66.5	2.06	60
2.95	50	4.56	71.0	2.15	67.5
3.35	66	4.65	75.0	2.24	83.5
3.67	73.5	4.74	91.0	2.37	91.5
4.11	90	4.92	96.0		
4.38	95				

III - CONCLUSIONS

It is believed that the scatter appearing in plotted data from the last three runs is due to inconsistent oxidation at the seams. The effect of this "seam oxidation" is accentuated by electropolishing, since the electropolished surfaces would oxidize at a slower rate than the micromachined surfaces of specimens used in previous runs.

At this writing no new data have been obtained, however, future runs are planned using electropolished specimens machined from stock which can be made free of included oxide.

Attempts to identify the structure and exact composition of the individual oxide layers will be deferred until the oxidation rate studies have been concluded.

After thorough evaluation of data currently available it would seem that an alloy having the composition 7.50 Al, 7.50 Cr, 0.50 Ti, 0.50 Si, 0.05 C, is worthy of further study. Present information indicates that this alloy would exhibit sufficient oxidation resistance, corrosion resistance, and ductility to warrant further investigation by the Universal-Cyclops Steel Corporation.

Appendix

TABLE V

Heat No.	Chemical Analysis	Condition		T.S.	Y.S.	E.	R.A.
		1 Hr. at 1500°F					
A66	7.97 Al- .03 C- bal Fe	O.Q.		74,300	58,100	25	38
		F.C.		73,900	59,700	23	29
A68	8.19 Al- 2.13 Cr- .03 C- bal Fe	O.Q.		84,300	71,300	23	33
		F.C.		84,600	69,300	22	40
A69	8.30 Al- 4.60 Cr- .03 C- bal Fe	O.Q.		85,200	73,300	34	68
		F.C.		86,900	71,800	27	60
A70	8.28 Al- 6.93 Cr- .03 C- bal Fe	O.Q.		83,250	61,200	15	15
		F.C.		84,200	61,200	21	27
A71	8.22 Al- 9.57 Cr- .05 C- bal Fe	O.Q.		86,900	59,600	13	15
		F.C.		88,800	---	18	19
A159	7.64 Al- 7.46 Cr- .026 C- bal Fe	O.Q.		77,700	60,400	35	74
		F.C.		79,800	59,600	26	58
A160	7.47 Al- 7.53 Cr- .32 Si- .05 C- bal Fe	O.Q.		79,600	62,200	17	17
		F.C.		86,800	61,700	12	12

TABLE VI

ELEVATED TEMPERATURE PROPERTIES OF HEAT A160
Heat Treatment: 1500°F 1 Hr. F.C.

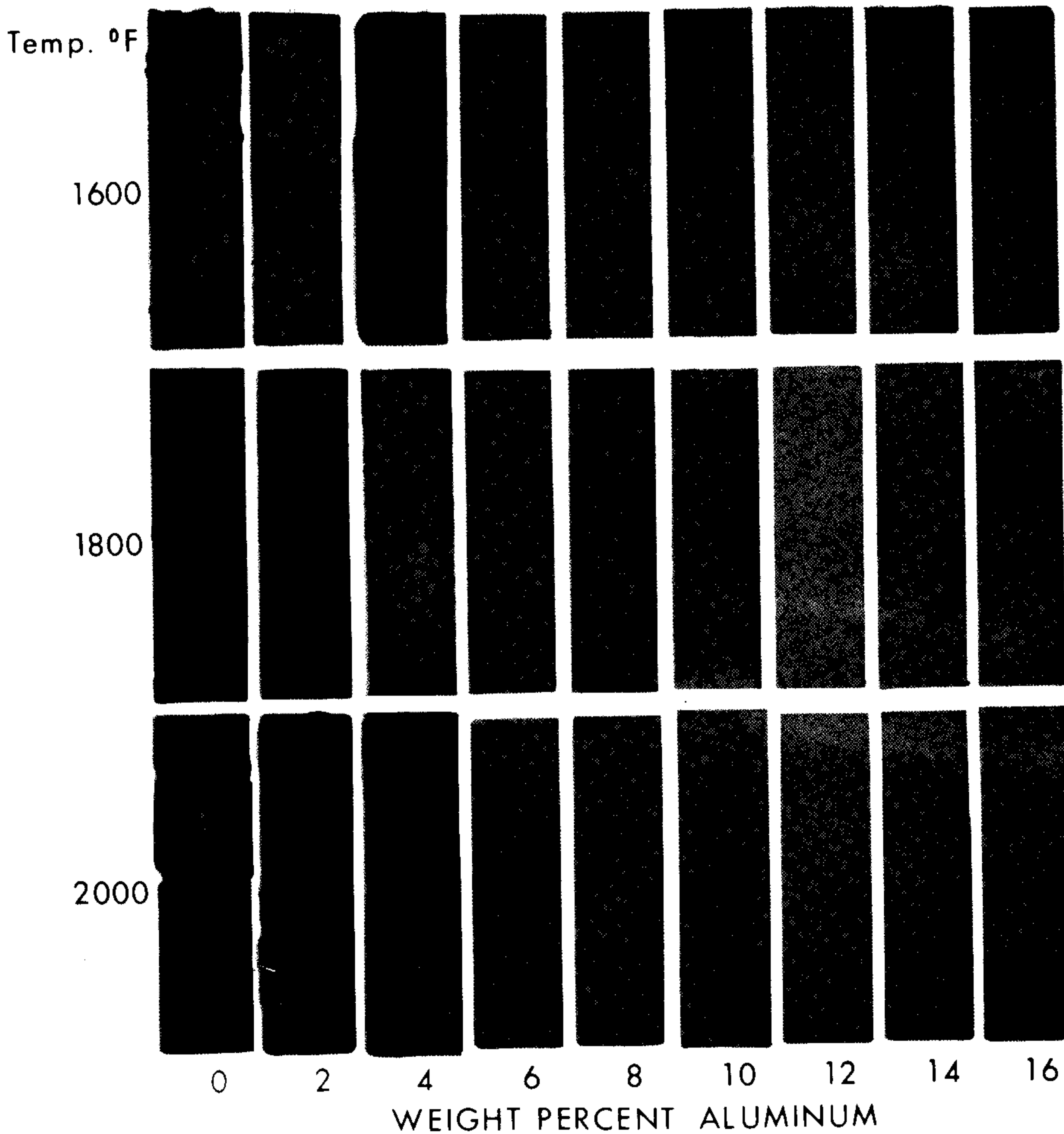
<u>Temperature</u>	<u>T.S.</u>	<u>Y.S.</u>	<u>E.</u>	<u>R.A.</u>
950°F	57,000	39,500	40	81
1070	33,200	33,200	86	92
1190	19,400	19,400	108	97
1310	11,900	11,900	109	98
1430	7,420	7,420	195	99.7
1550	5,220	5,220	111	99.8
1670	3,540	3,420	102	99.9

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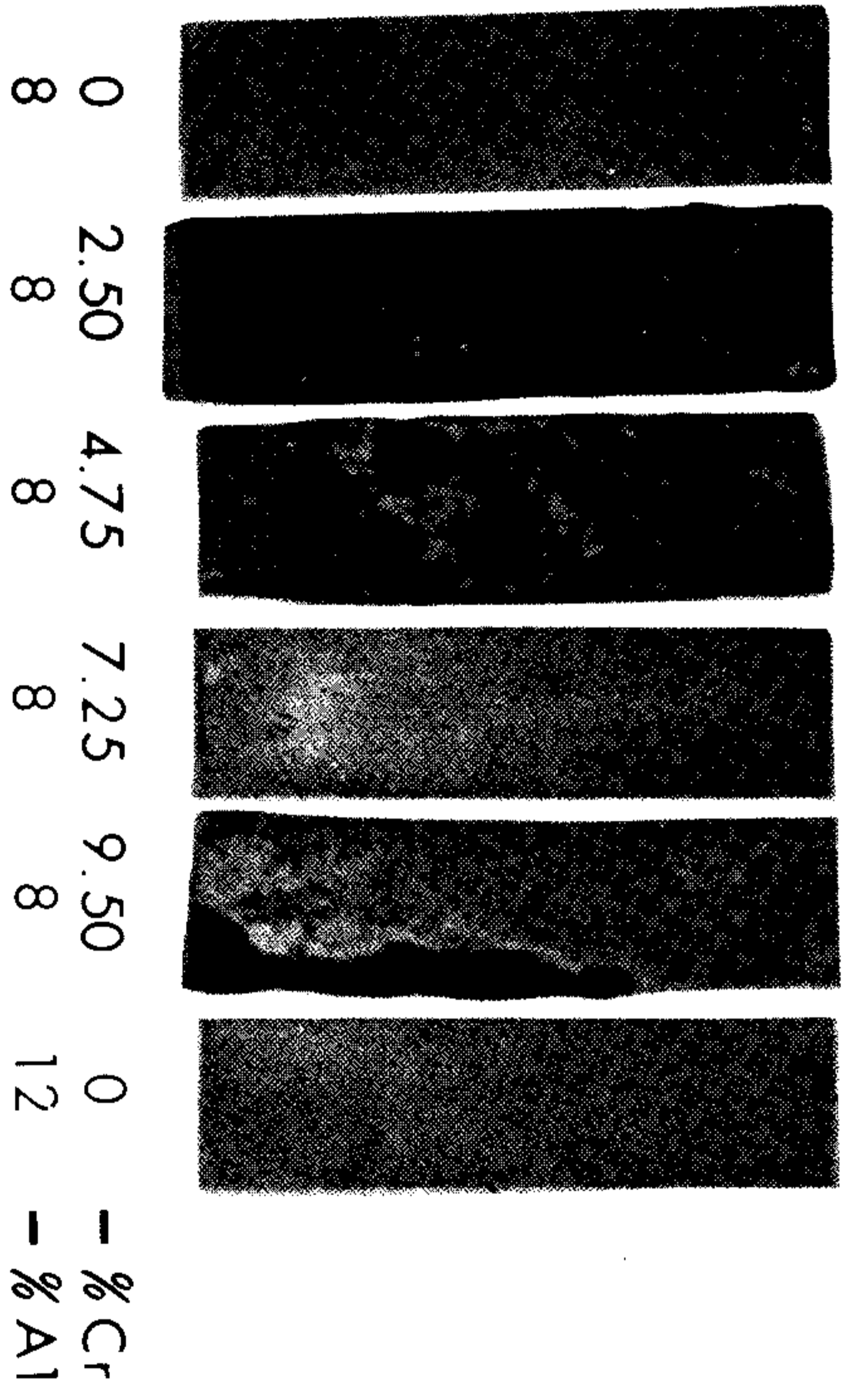
THE OXIDATION RESISTANCE OF IRON ALUMINUM ALLOYS

TEMPERATURE vs ALUMINUM CONTENT
(100 Hrs. Exposure in Air)

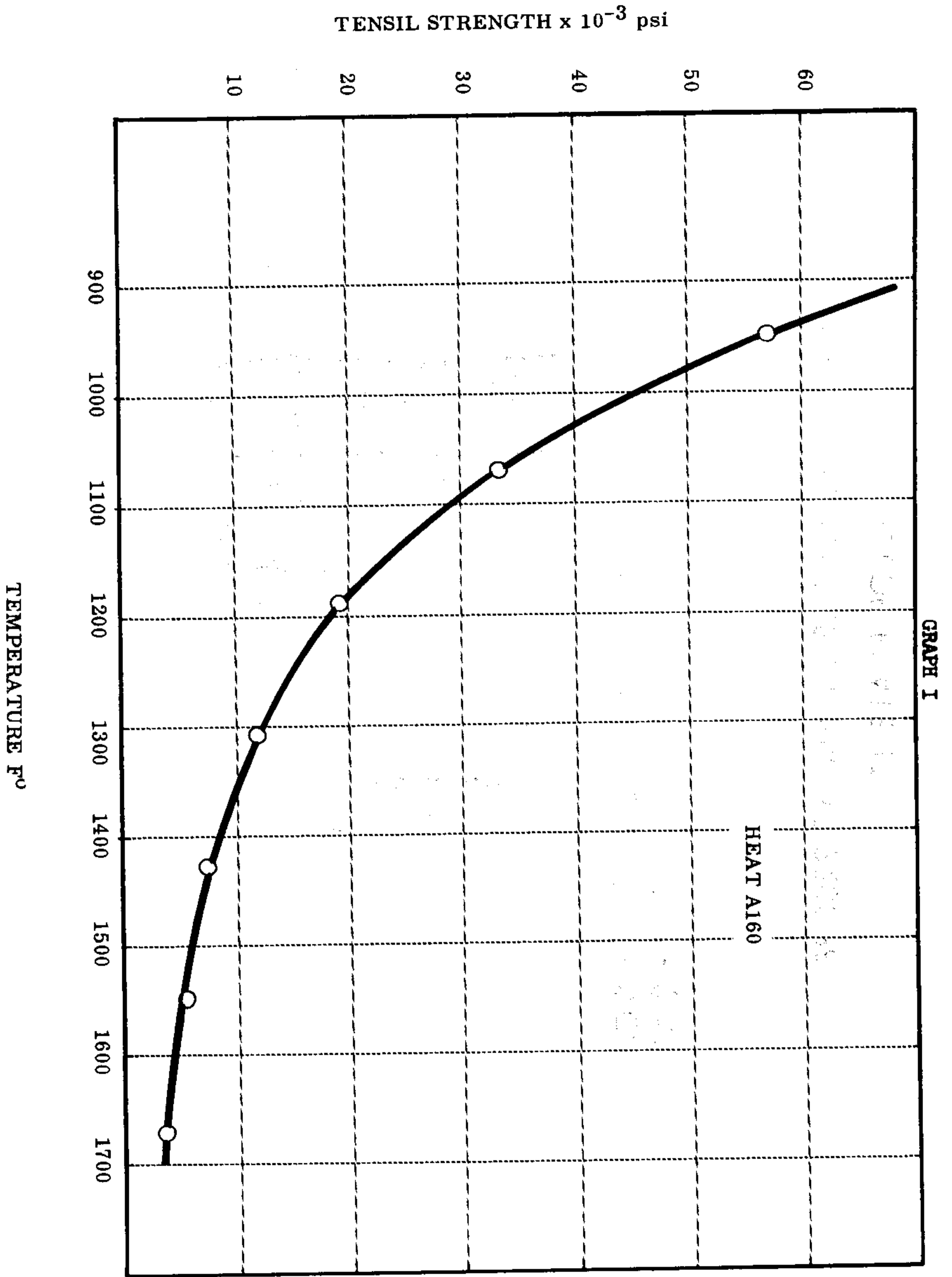


COLOR PLATE 1

THE EFFECT OF CHROMIUM UPON THE OXIDATION RESISTANCE OF Fe-Al ALLOYS



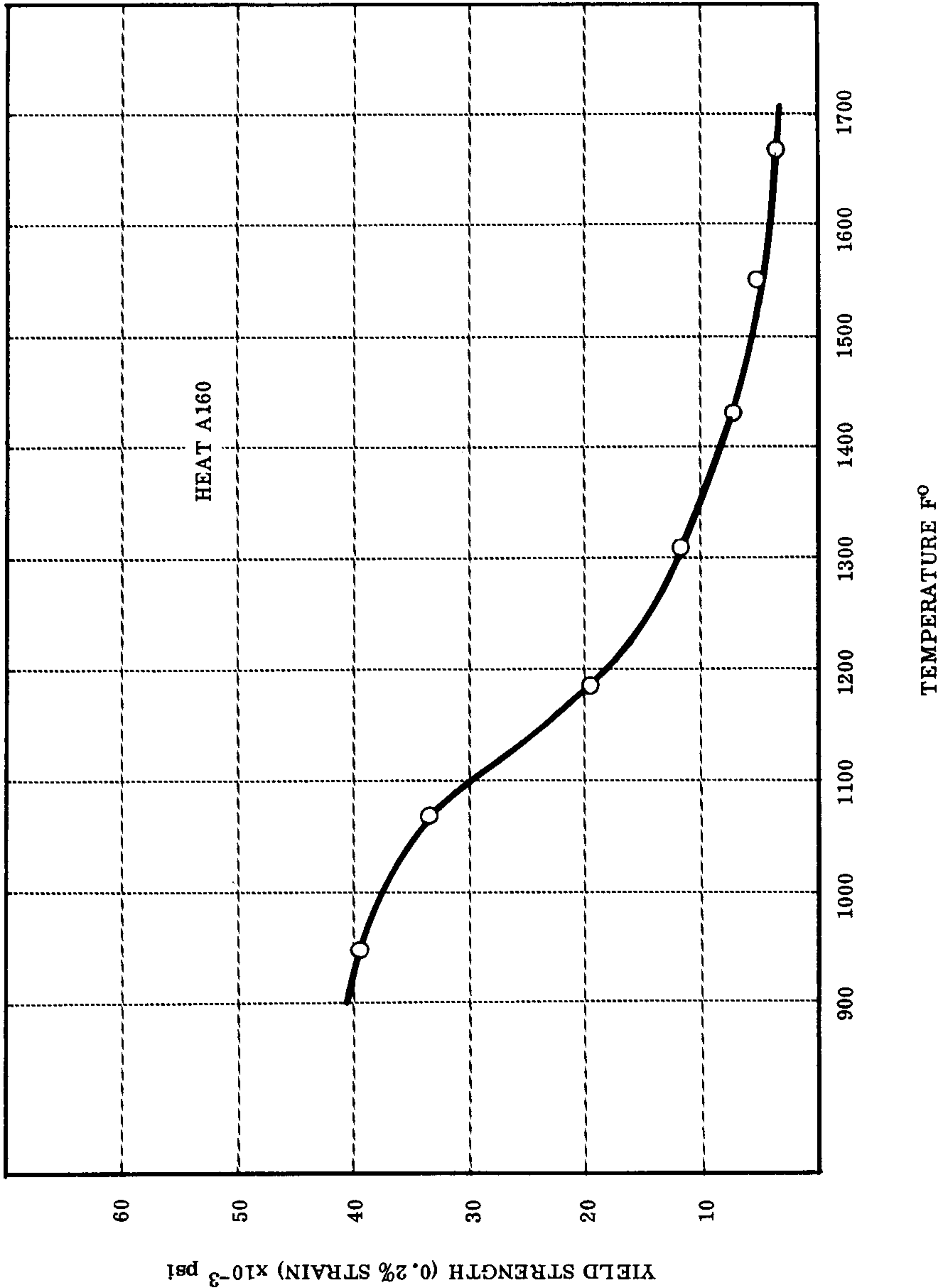
500 HR. EXPOSURE IN AIR AT 2200 °F
COLOR PLATE II



GRAPH I

HEAT A160

GRAPH II



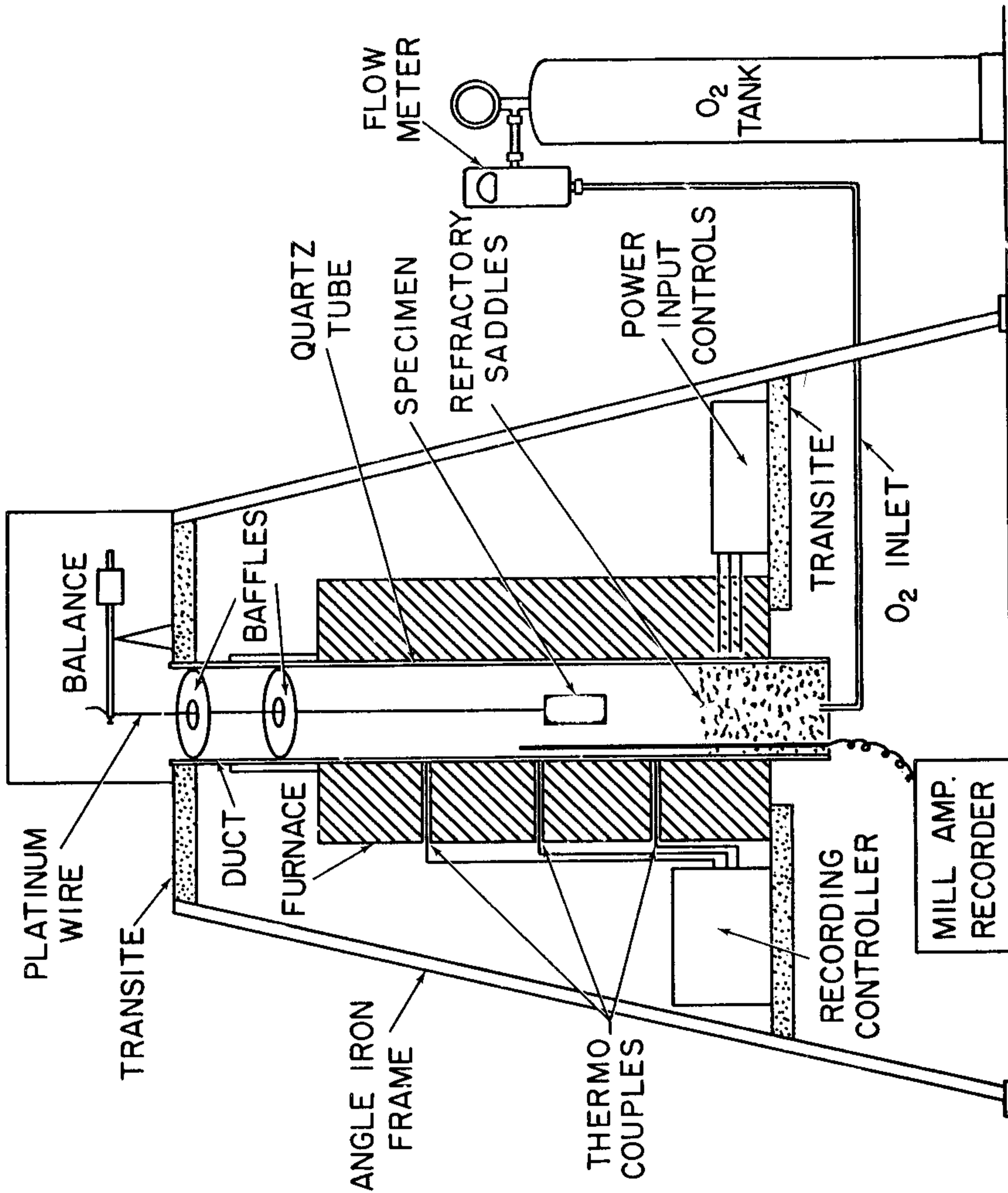
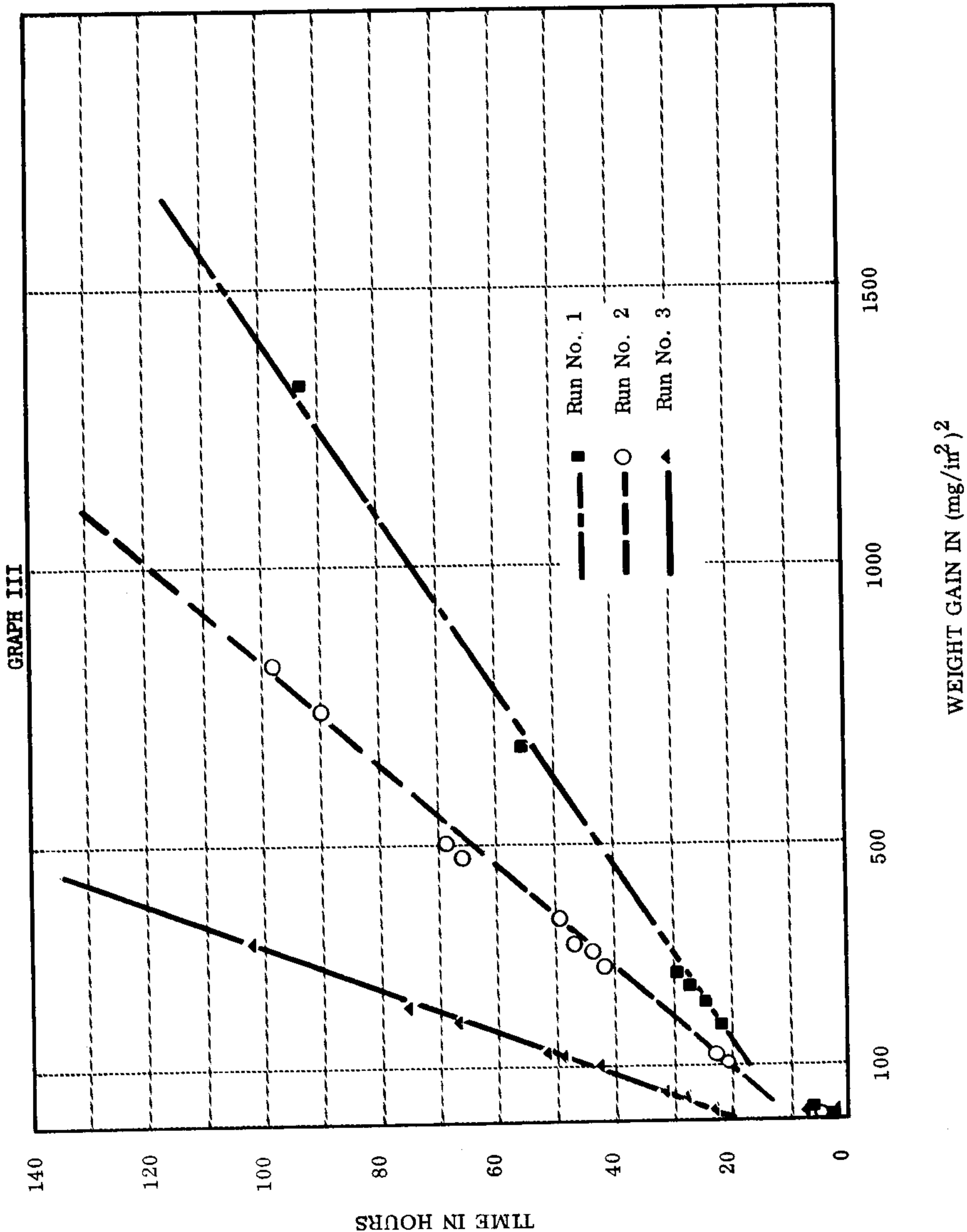


Fig. 1



GRAPH IV

