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THE EFFECT OF IMPURITIES ON
IRON-CHROMIUM-YTTRIUM ALLOYS

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TABLE OF CONTENTS

	<u>Page</u>
ABSTRACT	1
INTRODUCTION	1
EXPERIMENTAL WORK	2
CONCLUSIONS	12

THE EFFECT OF IMPURITIES ON IRON-CHROMIUM-YTTRIUM ALLOYS

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A study has been made of the effect of carbon, manganese, oxygen, palladium, and sulfur on the structure and fabricability of iron-35 w/o chromium-1 w/o yttrium alloy. Using a vacuum-induction melting technique each of the additives except oxygen was introduced to 1-lb remelts of a single 15-lb master alloy. The master alloy and remelts were made under similar melting, pouring, and casting conditions. Oxygen was introduced as Fe_2O_3 by inert-electrode arc melting to avoid extraneous, uncontrolled contamination stemming from crucible contact. Photomicrographs were prepared of as-cast metal illustrating structural variations. Ingots obtained were fabricated to 0.050-in. sheet at 2000 F to compare fabrication characteristics with those of the control ingot containing no additives. As a qualitative measure of metal soundness and ductility, a portion of each of the 0.050-in. sheets was further reduced at room temperature to 3-mil foil.

During melting at 2900 to 3000 F under controlled conditions, the amount of yttrium present in the charge was reduced roughly 50 per cent by reaction with the alumina crucible. Sulfide, added as FeS , and oxide additions also lowered the amount of yttrium retained in ingots. The maximum amount of sulfur retained in an alloy of nominal composition iron-35 w/o chromium-1 w/o yttrium-500 ppm sulfur was found to be about 80 ppm, and an alloy containing this amount of sulfur seemed to show slightly improved fabrication characteristics. None of the impurities investigated affected the fabrication characteristics or the quality of the finished product sufficiently to be considered detrimental from this point of view.

INTRODUCTION

Iron-chromium alloys containing about 1 w/o yttrium have demonstrated remarkable resistance to oxidation at 2300 F. These alloys are relatively undeveloped, however, and research is required to provide additional knowledge that will assure reproducible casting, fabrication, and corrosion characteristics of the alloy. This report describes a portion of this developmental effort and deals with a study of the effect of carbon, manganese, oxygen, palladium, and sulfur on the structure and fabrication characteristics of the basic alloy, iron-35 w/o chromium-1 w/o yttrium.

The impurities, carbon, oxygen, and sulfur are often found in ingots and are believed to derive from the charge materials or in some cases from crucibles, molds, and furnace atmospheres. Sulfur usually affects the fabricability of alloys adversely, and manganese is added in an attempt to counteract any such effect. Palladium has been reported to allow the use of higher amounts of chromium in the basic alloy. Increasing chromium content at the expense of iron has been reported to improve high-temperature strength characteristics.

EXPERIMENTAL WORK

To circumvent the problem of reproducibility of the basic alloy a 15-lb master alloy, prepared from high-purity materials by vacuum-induction melting in an alumina crucible, was used as the base to which the various impurities were added separately. The master alloy had the composition iron-34.4 w/o chromium-2.0 w/o yttrium. A spectrographic analysis of this alloy showed no palladium to be present and less than 50 ppm of either manganese or aluminum. Sulfur and carbon contents were less than 30 ppm. A vacuum-fusion analysis showed the oxygen content to be 23 ppm and the hydrogen content to be 0.2 ppm. The as-cast structure of the master alloy (Figure 1) showed a well-distributed network of second-phase material, presumed to be a eutectic mixture of YFe_5 and alpha iron-chromium surrounding clean dendritic alpha iron-chromium solid solution. The master alloy was reduced to 1/16-in. sheet of excellent quality by forging and rolling at 2000 F. This sheet was cleaned by vapor blasting and cut up for use as remelt stock.

One-pound portions of the master alloy were induction melted in alumina crucibles in a vacuum furnace. Manganese and palladium were added as pure metals, sulfur as iron sulfide, and carbon as iron carbide. Each additive was thoroughly mixed with the melt by induction stirring. Each melt was made in a new alumina crucible and was held molten at a temperature of 2850 F and under a pressure of less than 2×10^{-3} mm of mercury. After holding each metal charge at 2850 F for 10 min the desired impurity was added, and the melt was stirred and poured within a 2-min period into a 1-lb-capacity Zirconite mold (or, as noted, into a copper mold).

Oxygen was added to the base alloy as a known amount of Fe_2O_3 to a charge of the master alloy, and the entire charge was arc melted. In this way, contact of this alloy with an alumina crucible was prevented and extraneous oxide reactions were avoided. A 1-lb control ingot (no impurities added) was made by remelting a portion of the master alloy in a new alumina crucible. Adjustments were made to bring the chromium composition of the control as well as that of all other remelts to 35 w/o. Analysis revealed that the yttrium content of the control alloy after remelting had decreased from 2.0 w/o to 1.17 w/o. Oxygen and hydrogen contents were found to be 11 ppm and 0.5 ppm, respectively. The as-cast structure of the control (Figure 2) was very similar to that of the original master-alloy casting except for some refinement in structure possibly caused by the increased cooling rate of the smaller ingot. Metallographic examinations were made of specimens cut from each ingot. A 10 per cent aqueous solution of oxalic acid was used for electrolytic etching. Pertinent analytical results obtained on all the ingots are shown in Table 1.

As mentioned earlier, the effect of manganese was of interest because of its possible use as a counteractant for sulfur contamination in the alloy. Consequently, two impurity conditions were considered: one in which the effect of manganese would be treated separately, and the other in which manganese would be introduced to neutralize the effects of sulfur already present in the alloy. Although admittedly somewhat arbitrary, the amount of manganese used was based on a "rule of thumb" steel practice of adding five parts of manganese for each part of sulfur present. On the assumption that 500 ppm of sulfur could be present as an impurity, 2500 ppm of manganese was considered a sufficient amount for the purpose of this experiment. This amount of manganese, added separately (Figure 3), or in conjunction with sulfur (Figure 4), appeared to have little effect on the as-cast structure or on the fabrication characteristics of the alloy.

FIGURE 1. AS-CAST SECTION OF MASTER ALLOY, NOMINALLY IRON-35 w/o CHROMIUM-2 w/o YTTRIUM

Second-phase material is presumed to be a eutectic mixture of YFe_5 and alpha iron-chromium.

FIGURE 2. AS-CAST SECTION OF CONTROL ALLOY

Alloy composition: iron-35 w/o chromium-1.2 w/o yttrium.

TABLE 1. ANALYSES OF INGOTS^(a)

Impurity Addition	Amount of Additive Charged, w/o	Ingot Weight, lb	Type of Melt	Yttrium Analysis, w/o	Additive Analysis, w/o	Total Number of Remelts
None, master alloy	--	15	Vacuum induction	2.0	--	--
None, control alloy	--	1	Ditto	1.17	--	1
Manganese	0.25 Mn	1	Ditto	1.12	0.23 Mn	1
Iron sulfide No. 1	0.05 S	2	Ditto	0.94	0.008 S	1
Iron sulfide and manganese	0.008 S 0.25 Mn	1	Ditto	0.59	0.008 S 0.19 Mn	2
Iron sulfide No. 2	0.25 S	1	Ditto	0.2	0.012 S	1
Palladium	1.0 Pd	1	Ditto	1.02	0.83 Pd	1
Iron carbide	0.08 C	1	Ditto	1.07	0.08 C	1
Iron oxide	(b)	0.3	Inert-electrode arc	<0.1	0.12 O	1
None, control alloy	--	1	Vacuum induction, chill cast	1.08	--	1
Iron carbide	0.08 C	1	Vacuum induction, chill cast	1.38	0.08 C	1

(a) Chromium content of alloys varied from 34.4 to 35.1 w/o.

(b) 110 per cent of the stoichiometric amount necessary to react with the yttrium.

100X 10 Volume Per Cent Oxalic Acid, Electrolytic Etch RM11482

FIGURE 3. AS-CAST SECTION OF IRON-35 w/o CHROMIUM-1.12 w/o YTTRIUM-0.23 w/o MANGANESE ALLOY

The manganese addition had no observable effect on structure. A comparison can be made with the structure of the control shown in Figure 2.

100X 10 Volume Per Cent Oxalic Acid, Electrolytic Etch RM11484

FIGURE 4. AS-CAST SECTION OF INGOT WITH SULFUR AND MANGANESE ADDITIONS

Alloy composition: iron-34.8 w/o chromium-0.59 w/o yttrium-0.19 w/o manganese-0.008 w/o sulfur.

A significant reduction of second-phase material occurred through reaction with the alumina crucible which contained the melt.

100X 10 Volume Per Cent Oxalic Acid, Electrolytic Etch RM11483

FIGURE 5. AS-CAST SECTION OF INGOT WITH SULFUR ADDITION

Alloy composition: iron-35 w/o chromium-0.94 w/o yttrium-0.008 w/o sulfur.

Only 16 per cent of the amount of sulfur charged to the melt as FeS was retained by the alloy.

The sulfur addition was made as FeS, and the charge contained 500 ppm of sulfur. A 2-lb melt was cast and the resulting ingot was cut into two pieces: one portion to be used for a fabrication test and the second to be used as remelt stock to which manganese was to be added. The ingot was found to contain only 80 ppm sulfur or only 16 per cent of the amount charged to the melt. Yttrium content was reduced to 0.94 w/o. The as-cast structure, as shown in Figure 5, was essentially the same as that of the control alloy. The remelt of this material with an addition of 0.25 w/o manganese resulted in an alloy with a composition of iron-34.8 w/o chromium-0.59 w/o yttrium-0.008 w/o sulfur-0.19 w/o manganese. It is noteworthy that in remelting the alloy a second time the yttrium content was reduced by about the same order of magnitude as occurred in the case of almost every remelt of master-alloy material. These reductions of yttrium content constitute strong evidence of a crucible surface reaction of roughly the same order of magnitude. The as-cast structure, shown in Figure 5, of the sulfur-manganese alloy was similar to that of the control alloy except for an obvious reduction in second-phase material.

A second attempt to introduce sulfur into the base alloy was made by charging five times as much FeS to the melt, 0.25 w/o sulfur. An analysis of the resulting ingot revealed a sulfur content of only 120 ppm and an yttrium content of only 0.2 w/o. This disproportionate loss of yttrium suggests an yttrium-sulfur reaction which removes yttrium from the melt. The loss can be accounted for if the yttrium is assumed to combine with sulfur as YS and is lost from the melt as vapor, dross, or slag. The as-cast structure (Figure 6) revealed much larger grains, a reduced amount of grain-boundary material (YFe_5), and a dispersion of unidentified foreign matter in the matrix.

A 1.0 w/o addition of palladium to a remelt of the master alloy produced an as-cast structure similar to that of the control alloy except for the presence of a fine and fairly uniform dispersion of second-phase material in the iron-chromium phase. This particular second-phase material as well as the grain-boundary network etched black in a 10 per cent solution of oxalic acid (Figure 7), whereas in the metallographic etching of all the other alloys the second-phase material, when present, appeared light. This etching behavior suggests the presence of a palladium-yttrium compound perhaps similar to PdAl .

The as-cast structure of an ingot containing 800 ppm carbon (Figure 8) was very similar to that of the control alloy but showed uniformly distributed agglomerations of square platelets in the second phase suggesting graphitic carbon. The iron-chromium phase was exceptionally clean. A duplicate melt containing 800 ppm carbon was cast in a 1-in. -diameter copper mold rather than in Zirconite to check the effect of an increased cooling rate on structure and fabricability. This resulted in the as-cast structure shown in Figure 9b, which shows practically no precipitated carbon. A macroetched cross section of the ingot (Figure 9a) revealed needlelike columnar grains roughly 1/6 in. long extending inward from the edge. Small equiaxed grains comprised the center of the ingot. The grain size appeared to be smaller than that of a control alloy which was also cast in copper (Figure 10).

The alloy prepared by arc melting was intended to demonstrate the effect of oxygen on the yttrium content of the alloy. Iron oxide, Fe_2O_3 , was added to the master alloy to the extent of 110 per cent of the stoichiometric amount required to react with all the yttrium present to form Y_2O_3 . The resulting bar ingot contained less than 0.1 w/o

FIGURE 6. AS-CAST SECTION OF INGOT WITH LARGE SULFUR ADDITION

Alloy composition: iron-35 w/o chromium-0.2 w/o yttrium-0.012 w/o sulfur.

Large amounts of sulfur added as FeS to the melt removed essentially all yttrium as dross.

FIGURE 7. AS-CAST SECTION OF INGOT WITH PALLADIUM ADDED

Alloy composition: iron-35 w/o chromium-1.02 w/o yttrium-0.83 w/o palladium.

Note that this was the only case that the second-phase material etched black, suggesting the presence of a palladium-yttrium compound.

FIGURE 8. AS-CAST SECTION OF INGOT WITH CARBON ADDED

Alloy composition: iron-35 w/o chromium-1.07 w/o yttrium-0.08 w/o carbon.

Carbon appears to be present as agglomerations of platelets.

3X

a. Macroetched Section

RM11648

100X

10 Volume Per Cent Oxalic
Acid, Electrolytic Etch

RM11644

b. Micro structure of Center of Ingot

FIGURE 1. AS-CAST SECTIONS OF INGOT WITH CARBON ADDITION CAST
IN COPPER MOLD INSTEAD OF ZIRCONITE

Alloy composition. iron-35 w/o chromium-1.38 w/o yttrium-0.08 w/o carbon.

Rapid chilling of the heat prevented the precipitation of carbon.

3X

RM11649

FIGURE 10. MACROETCHED SECTION OF CONTROL ALLOY
CAST IN COPPER MOLD

Alloy composition: iron-35 w/o chromium-1.08 w/o yttrium.

100X

10 Volume Per Cent Oxalic
Acid, Electrolytic Etch

RM11606

FIGURE 11. AS-CAST SECTION OF INGOT ARC MELTED WITH Fe_2O_3

Alloy composition: iron-35 w/o chromium-0.12 w/o oxygen.

Iron oxide reacted directly with the yttrium contained in the initial alloy.

TABLE 2. FABRICATION OBSERVATIONS

Alloy Addition	Amount Retained, w/o	Observations During Hot Rolling of 0.050-In. Sheet	Rating ^(a)	Observations During Cold Rolling of 0.003-In. Foil	Rating ^(a)
None, master alloy	--	Very slight edge cracking	2	--	--
None, control alloy	--	Sawtooth (1/16-in.) edges	4	Blistered at edges	3
Manganese	0.23 Mn	Slight edge cracking	3	Extensive surface blistering	4
Iron sulfide No. 1	0.008 S	Very slight edge cracking	2	Very slight blistering	1
Sulfur-manganese	0.008 S 0.19 Mn	No edge cracks	1	Very slight blistering	1
Iron sulfide No. 2	0.012 S	No edge cracks	1	Slight blistering	2
Palladium	0.83 Pd	No edge cracks	1	Slight blistering	2
Iron carbide	0.08 C	Very slight edge cracking	2	Slight blistering	2
Iron oxide	0.12 O	No edge cracks	1	Blistering at center ^(b)	3
None, control alloy ^(c)	--	Slight edge cracking	3	Slight blistering	2
Iron carbide ^(c)	0.08 C	Slight edge cracking	3	Severe blistering	4

(a) Ratings give the order of quality of surfaces and edges, e. g., No. 1 was highest quality.

(b) Rolling of this alloy was stopped at 0.010 in.

(c) Cast in copper molds.

yttrium and the oxygen content was 1200 ppm. The as-cast structure (Figure 11) showed long columnar grains, typical of an arc-melted bar casting. A fine dispersion of foreign matter, possibly Y_2O_3 , was observed in the matrix.

All ingots were forged and rolled at 2000 F to 0.050-in. sheet. A small section of the resultant sheet from each ingot was subsequently cold rolled at room temperature to 3-mil foil as a qualitative measure of ductility and metal soundness. When present, voids and solid inclusions in the metal produced exaggerated surface defects in the foil. A summary of the fabrication data is shown in Table 2. All ingots produced during this program fabricated to sheet of good quality. However, the surface appearance of the cold rolled, 3-mil foil produced from the manganese alloy gave evidence of several internal voids. The ingots containing 80 ppm sulfur and 800 ppm carbon gave indications of slightly lower ductility than the control alloy during cold fabrication. The ingot containing added oxygen appeared harder than any of the others during cold fabrication and rolling was discontinued at a thickness of 0.010 in.

CONCLUSIONS

This study of the effect of impurities on the iron-35 w/o chromium-1 w/o yttrium alloy has shown that under the melting, casting, and fabrication conditions imposed none of the impurities investigated affect fabrication characteristics to any major extent. Large amounts of oxide and carbide slightly decreased the ductility of the sheet. Fabrication of master alloys produced indications that variations in yttrium content up to 2 w/o do not affect fabrication characteristics adversely. The excellent fabrication characteristics displayed by the master alloy and by the products of successive remelts suggest that other melting and fabrication parameters such as pouring temperature and ingot size, perhaps in conjunction with certain combinations of impurities, should be investigated to produce a better understanding of fabrication inconsistencies of production-size ingots.

It was found that oxygen and sulfur contamination introduced before or during melting affects the amount of yttrium that will be retained in the alloy. Attempts to build up the sulfur content of the iron-35 w/o chromium-1 w/o yttrium alloy indicated a maximum tolerance of between 80 and 120 ppm.

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