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IDENTIFICATION OF GRAIN BOUNDARY PHASE IN 26 PER CENT CHROMIUM-IRON ALLOYS WITH AND WITHOUT SILICON

by

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SUMMARY

Three methods were used to identify a grain boundary phase in 26 percent chromium-iron alloys, with and without silicon. These methods were: etch tests, intermetallic phase extraction and heat treatment. The etch tests indicated the phase to be sigma, but the other two methods showed the phase to be predominately $Cr_{23}C_6$. These latter two methods were considered to be the more reliable tests, and it was concluded that the phase was likely $Cr_{23}C_6$.

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CONTENTS

(14 pages, 7 illus.)

INTRODUCTION

A request was received from Dr. D. Caplan, Division of Applied Chemistry, National Research Council, Ottawa, to identify, if possible, a grain boundary phase which he found in 26% Cr-Fe alloys. This phase was quite pronounced in the alloy containing 0.5% silicon (identified as #40), but was not so obvious in the alloy in which no silicon was present (identified as #41). These alloys are being used in an investigation into the effect of silicon on the high temperature oxidation resistance of the 26% Cr alloy, and identification of the phase is important from this standpoint. The silicon content of the phase was to be determined as well. The alloys had been produced in a consumable electrode vacuum furnace.

CHEMICAL ANALYSIS

The chemical analysis of Alloy #40 was obtained from the sample supplied. There was an insufficient amount to analyse Alloy #41, and the analysis given is that supplied in the covering letter.

	Alloy #40	Alloy #41
Carbon	0.03%	0.015%
Chromium	26.30%	26.40 %
Silicon	0.57%	?
Nickel	0.02%	?

METALLOGRAPHY AND ETCH TESTS

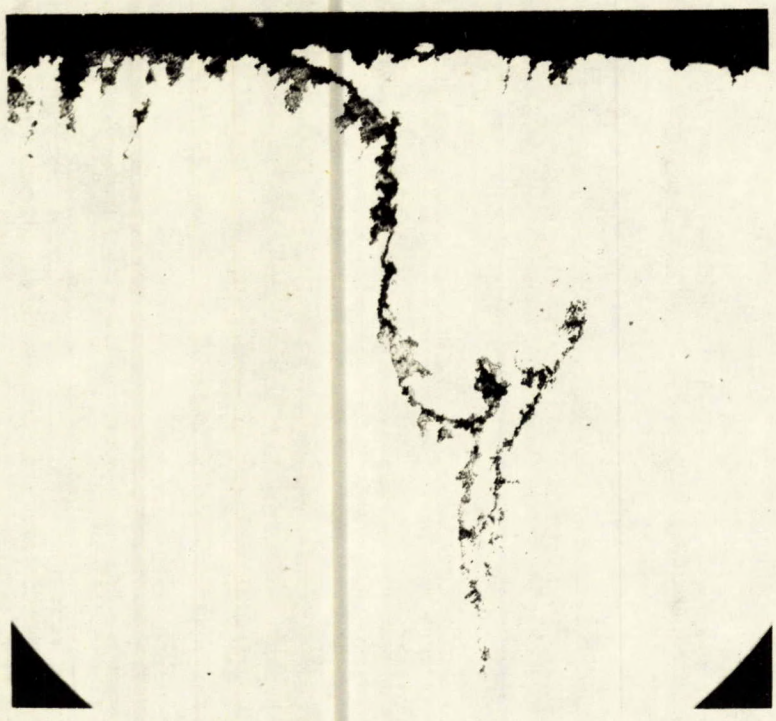
The unetched specimens revealed a larger number of inclusions than was expected for an alloy prepared under vacuum by the consumable electrode method. This was especially true for the alloy containing silicon (#40). The general concentration of the inclusions in alloys #40 and 41 are shown in Figures 1 (a) and (b) respectively. In addition, a large stringer inclusion found in Alloy #40 is shown in Figure 2.

(a) (b)

Figure 1

(Mag. X500 - Unetched)
Inclusions in Alloy #40.

(Mag. X500 - Unetched)
Inclusions in Alloy #41.



(Mag. X100 - Unetched)

Figure 2 - Oxide stringer originating at the surface in Alloy #40.

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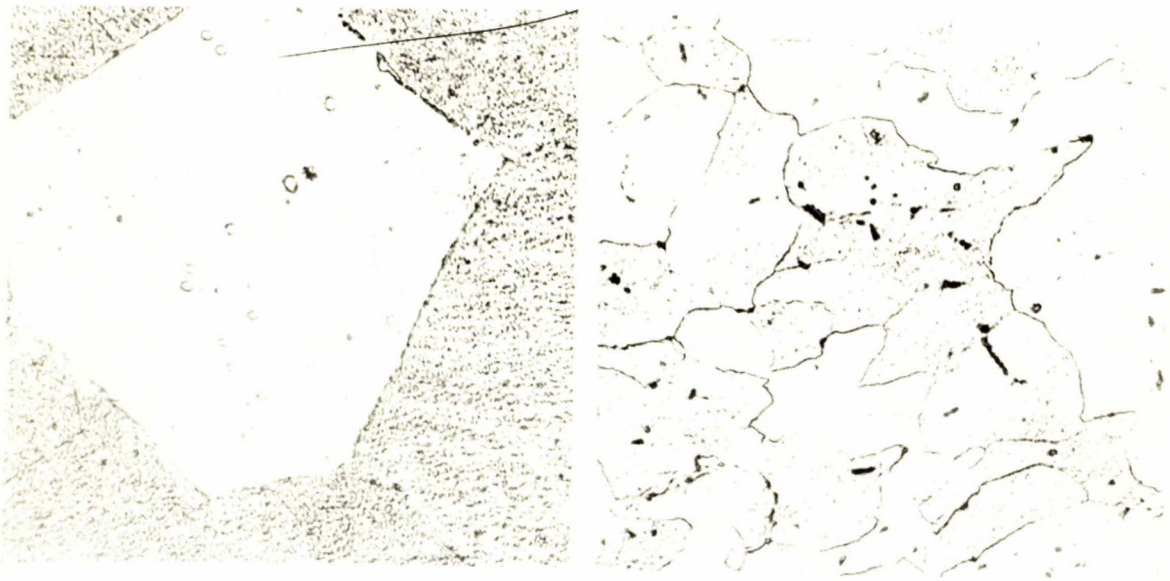
The general microstructure of the two alloys, after etching in Vilellas' reagent is shown in Figures 3(a) and (b). The grain boundary phase is quite evident in alloy #40, Figure 3(a).



(a) (b)

Figure 3

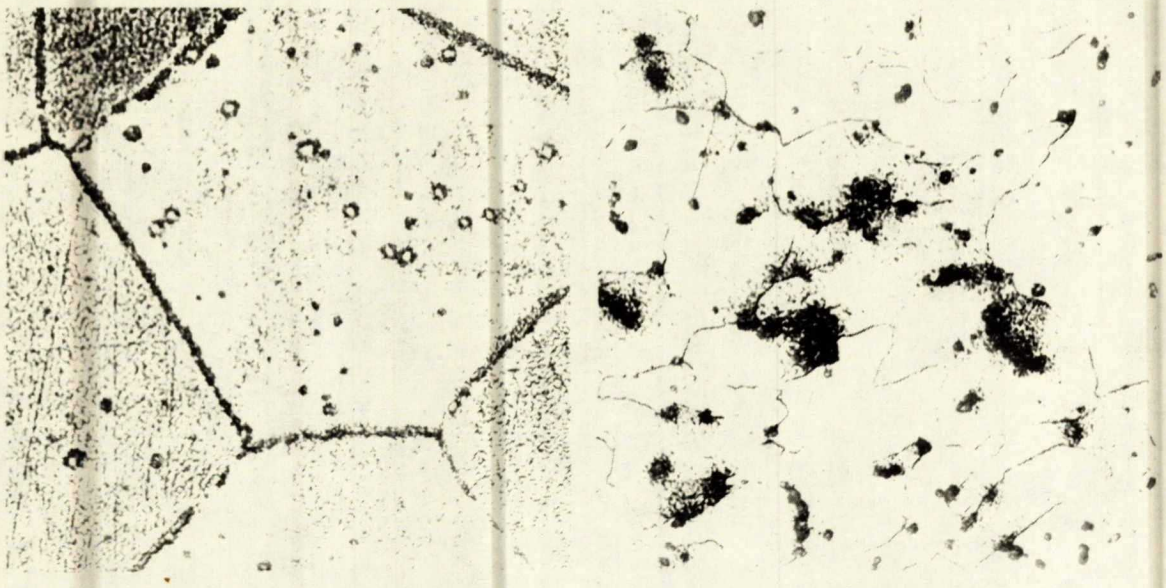
(Mag. X500 - Etched in Vilellas') Alloy #40 microstructure. Note grain boundary phase as well as phase within the grains. Grain size is quite large.

(Mag. X500 - Etched in Vilellas') Alloy #41 microstructure. Heavy etching of grain boundaries indicates the presence of a separate phase.

Figure 4 (a) and (b) are the structures obtained for alloys #40 and 41 respectively, after etching for 30 seconds in glyceregia. This etch reportedly[1] attacks sigma phase previously outlined by Vilellas' reagent, but will not affect the carbides. Identical fields

(1) Embrittlement of Metals, ASM Publication 1956, pp. 64-65.

to those used in Figures 3 (a) and (b) were rephotographed.



(a) (b)

Figure 4

(Mag. X500 - Etched in Glyceregia) Same field as in Figure 3 (a). The grain boundary material appears to have been attacked, but the phase within the grains has not been significantly changed.

(Mag. X500 - Etched in Glyceregia) Same field as in Figure 3 (b). Some areas appear to have been attacked by the glyceregia, as well as some particles within the grains.

HEAT TREATMENT TRIALS

Specimens removed from the material available of alloy #40 were first annealed for 250 hours and 500 hours at

1390°F. This treatment should dissolve any sigma phase present in the specimens. Figure 5 (a) and (b) show photomicrographs taken of these specimens after these annealing treatments.

(a) (b)

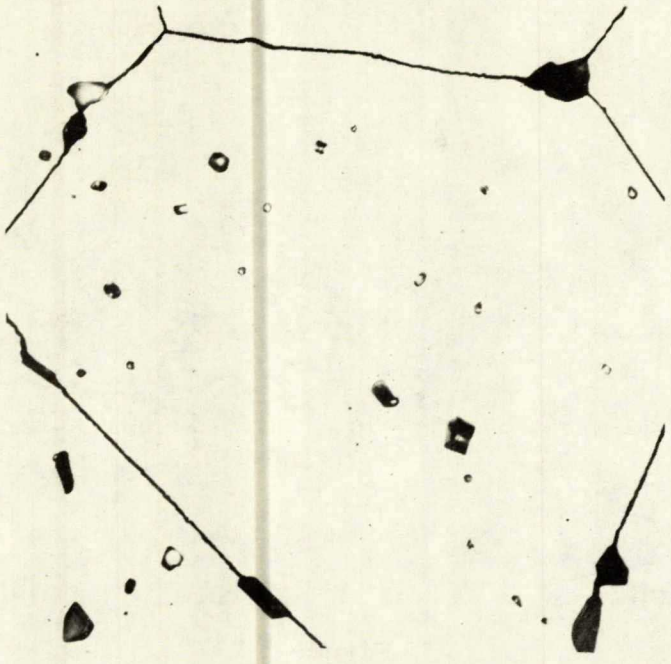
Figure 5

(Mag. X500 - Etched with 10% Oxalic acid, 5 amps, 5 sec)
Alloy #40, annealed at 1390°F, 250 hours.

(Mag. X500 - Etched with 10% Oxalic acid, 5 amps, 5 sec)
Alloy #40, annealed at 1390°F, 500 hours.

The annealing treatments did not produce any significant changes in the microstructure. It was decided therefore to attempt to produce sigma phase by normalizing the alloy #40 from 1950°F. Figure 6 shows the resulting microstructure after holding for 19 hours at 1950°F, and Figure 7 shows the microstructure of a sample held 10 hours at 1950°F, air cooled and then annealed

at 1390°F for 500 hours. This latter treatment was included as it should dissolve any sigma formed by the normalizing treatment.



(Mag. X500 - Etched in 10% Oxalic acid, 3 amps, 10 sec)
Figure 6 - Alloy #40, held 19 hours, 1950°F, air cooled.

- (Mag. X500 - Etched in 10% Oxalic acid, 5 amps, 5 sec)
Figure 7 - Alloy #40, held 10 hours, 1950°F, air cooled, annealed at 1390°F, 500 hours.

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EXTRACTION OF INTERMETALLIC PHASES

Electrolytic extraction techniques were employed to separate and identify the phases in the two alloys. The following lists the data collected for the two alloys:

(a) Alloy #40

Analysis of base alloy

C	-	0.03%
Cr	-	26.30%
Si	-	0.57%
Ni	-	0.02%
Fe	-	73.08%* (By difference)
		100.00%

* Actual analysis was reported to be 72.50% Fe.

1) Weight per cent of extracted intermetallic phases 1/ - 0.0725%
Loss in weight of test specimen after 49 hours run - 4.6897 gm
Weight of intermetallic phases collected - 0.0034 gm

2) Analysis of used electrolyte:

Cr	-	0.76 g/l
Fe	-	2.11 g/l
Si	-	0.019 g/l

3) X-ray analysis of intermetallic phases:

Austenite, $Cr_{23}C_6$, Fe and ε Fe_2C

Note: No sigma phase was reported

b) Alloy #41

Analysis 2/ of base alloy

C	-	0.015%
Cr	-	26.4 %
Si	-	?
Fe	-	75.385% (By difference)
		100.00 %

1) Weight per cent of extracted intermetallic phases 3/ - 0.05907%
Loss in weight of test specimens after 26-3/4 hours run - 5.4169 gm
Weight of intermetallic phases collected - 0.0032 gm

1/Electrolyte used: 10% HCl in alcohol; amount used was 1700 ml; current density: 4-6 in A/cm^2.

2/Complete analysis of this alloy is not known.

3/Electrolyte used 5% HCl + 5% citric acid; amount used: 1610 ml; current density: 12-14 in A/cm^2.

2) Analysis of used electrolyte:

Cr	-	0.81 g/l
Fe	-	2.39 g/l
Si	-	0.01 g/l

3) X-ray analysis of intermetallic phases:

Major	-	$Cr_{23}C_6$ (also called Cr_4C)
Minor	-	Cr
Possible minor	-	Fe_2C (also called $Fe_{20}C_9$)
Trace	-	Quartz (SiO_2)

Note: No sigma phase was reported.

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DISCUSSION

Although the etch tests indicated the presence of sigma phase at the grain boundaries as well as in the grains, the heat treatment trials and the intermetallic phase extraction experiments are considered to give the more reliable results. Neither of these latter two techniques indicated the presence of sigma phase. They do show, however, that the grain boundary phase is a carbide of the $Cr_{23}C_6$ type, with some possibility of epsilon carbide ($Fe_{2.4}C$) also being present. Even though the amount of carbon present is not large, there is enough to account for the amount of $Cr_{23}C_6$ type carbide present in the alloys.

The extraction technique did not show silicon to be concentrated in the extracted residue.

CONCLUSIONS

(1) The results of the tests carried out on the two alloys indicate the grain boundary phase to be predominatly $Cr_{23}C_6$. The etch tests indicated sigma to be present, but these tests are not considered too reliable.

(2) The silicon content of the extracted residue in the electrolytic separation experiments was not high.

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