ANNUAL TECHNICAL PROGRESS REPORT - II

"A STUDY OF GRAIN BOUNDARY SEGREGATION
USING THE AUGER ELECTRON EMISSION TECHNIQUE"

by

MASTER

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December 29, 1969

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DATE 2/2/70

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A STUDY OF GRAIN BOUNDARY SEGREGATION USING THE AUGER ELECTRON EMISSION TECHNIQUE

I. ABSTRACT

Auger Emission Analysis has shown that a segregation of certain elements to grain boundaries results in embrittlement. In steels which undergo temper embrittlement it has been shown that P, As, Ni, and Cr are segregated to grain boundaries in the embrittled condition, but not in the non-embrittled condition. In W, the amount of phosphorous at the grain boundary is related to the ductile brittle transition. Preliminary work in Mo indicates that P is primarily responsible for the embrittlement of this material.

A brief description of new work using Ga to embrittle grain boundaries in Al is given.

Preliminary results on O and P embrittlement of pure iron are also given.

II. PRESENT PROGRAMS

Low Alloy Steels

The studies on the temper embrittlement of low alloy steels has been completed and one report published. (1)

As a continuation of the earlier work to understand the temper embrittlement phenomenon in low alloy ^{steels}, and to analyze the role of Cr, Ni, Sb and other impurities, the steels with following compositions were selected for the Auger analysis.

Heat	C	Ni	Cr	Impurity (in ppm)	$\Delta T T (^{\circ}C)$
3710	0.40	3.5		650 Sb	50
2407	0.24	4.4	1.7	400 Sb, 0.26% he	295
2433	0.40			800 Sb	-7
3022	0.30	3.7	1.7	530 As	41
3023	0.31	3.7		520 As	22
3024	0.31	3.7		480 Sn	84

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The steels were given conventional step cooling (S.C.) and de-embrittling (D.E.) treatments and the standard samples in both conditions were fractured in vacuum and Auger analyses made. The fracture surface of the de-embrittled 3710 steel showed no sign of Sb, while ample evidence of its presence in fracture surface of a step cooled 3710 steel was found. The depth of Sb segregation was found by ion sputtering (Xe gas maintained at a pressure of 2×10^{-3} torr), in steps, followed by Auger analysis. Such a study indicated that the Sb concentration decreased rapidly and no detectable signals were received after sputtering 7 to 8 monolayers. The amount sputtered was calculated from the published data of Wehner.⁽¹⁾ A similar observation on Ni peak height indicated that Ni concentration decreased over a much larger region (~ 100 layers) and deeper sputtering resulted in little additional changes.

The Ni peak height in the spectra of 3710 D.E. is much smaller than that of step cooled steel and increased upon slight sputtering. Upon sputtering beyond 15 to 20 layers it showed a gradual decrease. Beyond ~ 100 layers, it was identical with that of 3710 S.C.

The fracture surface of 2407 S.C. indicated a strong segregation of Sb, Ni and Cr. Sputtering studies showed a similar behavior - the Sb signal was extinct after sputtering 5 to 8 monolayers and a decrease in the Ni peak height occurred primarily in the first 100 layers. Analysis of Cr peak in a similar fashion was rather difficult because of interference, with the adjacent (Fe and oxygen) peaks. However, it is clear that Cr showed a similar behavior (concentration profile) as Ni. Steel 2407 D.E. could not be fractured and hence no spectra were available for comparison.

The 0.4% C, 800 ppm Sb steel (2433) showed no segregation of Sb to the boundaries in the step cooled condition.

In the arsenic containing steels 3022 and 3023 Auger analysis of the fracture surfaces gave no indication of As, even in their step cooled states. However, the Auger spectra indicated an enrichment of Ni in 3023 and of Ni and Cr in 3022 at the grain boundaries upon step cooling.

Steel 3024 (C-Ni-480 ppm Sn), exhibits a larger ΔTT than corresponding As containing steels and it showed marked segregation of Sn in the boundaries upon step cooling. The de-embrittled steel showed a lower Ni and C segregations to the boundary than the step cooled specimen. Sputtering studies on the step-cooled specimen indicated that Sn is concentrated mainly within a region of 2 to 3 layers (approx.) from the fracture surface, in contrast to that of Ni which extended over a much larger region.

A paper describing the results of these experiments on steels is being prepared.

Refractory Metals

Tungsten and in some cases molybdenum are observed to fracture along grain boundaries. Therefore Auger analysis were made of the fracture surface to determine if segregation of certain elements had occurred at the grain boundaries. The material used in the investigation of tungsten were powder metallurgy tungsten targets that had been formed for use as X-ray tubes and single-crystals of zone refined tungsten.

Three different grades of targets were obtained from G.E. Co. All three targets were made from G.E. pressed and sintered W billets and then high energy rate forged. After coining to produce the shape required for an X-ray target they were recrystallized in Hydrogen at 1600°C. There was a large range of transition temperatures as indicated below.

Material	(DBTT) Ductile Brittle Transition Temp.
Code 10	250° C
Code 41	800° C
Code 50	600 - 800°C
Zone refined W	

All these materials were machined to the shape of standard specimens and fractured in vacuum. The most prominent peak in the Auger spectra of the target materials was that at 120 ev., which corresponds to P. It is more prominent in the spectra of code 41 and code 50 (which have a high DBTT 600 - 800°C) than in that of code 10 (DBTT = 250°C). The peak disappeared upon sputtering, indicating that it is only concentrated at or in the close vicinity of the fracture surface. Such a peak was entirely absent in the spectra of zone refined W and it can be seen from the accompanying plot that the peak height varied in an approximate linear fashion with DBTT. These observations indicate that P is primarily responsible for much of the brittleness exhibited by polycrystalline tungsten. A paper is in preparation on this study.

Al - 0.3% Ge

Segregation of Ge to grain boundaries in Al-0.3% Ge has been examined by using Auger analysis. Tri-crystals prepared at G.E. labs were used for this purpose. Following the suggestion of Dr. T. R. Anthony, Ga is used to penetrate the crystal boundaries so that an intercrystalline fracture may be easily obtained. The specimen is then held in a vice attached to the regular specimen holder and is forced to break along the boundary under vacuum.

The Auger spectra of the fracture surface indicated the presence of Ga and oxygen was probably introduced (unintentionally) along with Ga. The surface is then sputtered so that oxygen and Ga would be removed thereby exposing any Ge that is present in the boundary. However, Ga could not be removed completely and a quick cover up of the exposed surface by molten Ga occurred.

Deep sputtering in one stretch would probably remove all Ga but would also remove Ge from the surface. Careful experiments with limited application of Ga are being planned. At this time these experiments have not been as successful as those reported earlier, but because of the importance of establishing a technique for preparing fracture surface having segregates not in themselves embrittling we are continuing work in this direction. If we could be successful in developing this technique we could study the segregation of many elements in the same base metal system. With these experimental results it would then be possible to develop general theories covering the mechanism of grain boundary segregation.

Pure Fe

Experiments on Fe have mainly been carried out as a trial basis.

To the date most of the effort has been directed towards developing high purity iron with definite amounts of impurities added. We intend to prepare a series of 3 types of alloys

1. Fe-O alloys
2. Fe-O-C alloys
3. Fe - P alloys

Johnson Mat.hey iron rods are used as starting material for these alloys. These rods contain nearly 300 ppm O_2 and 300 ppm C, but are spectrographically pure.

Wet - Hydrogen treatments were used to remove carbon from these rods. One treatment consists in bubbling H_2 through water at room temperature and passing the moist hydrogen stream through a tubular furnace maintained at $890^\circ C$. The iron rods are introduced into these furnace through the other end and left in these streams for 150 hrs. This treatment would be expected to reduce the carbon to less than 5 ppm. The oxygen level in these wet hydrogen treated rods is expected to remain at 300 ppm. In order to prepare iron rods containing higher oxygen contents it is proposed that wet-hydrogen treated rods be melted in the atmosphere of O_2 and Argon. It is expected that oxygen levels as high as 0.1 could be obtained by this technique.

To obtain Fe-O-C alloys the Fe-O alloys are carburized to various levels in an atmosphere of a mixture of Acetylene and H_2 at $875^\circ C$. A final homogenizing treatment in Argon atmosphere will be given to obtain a homogeneous carbon composition.

Initial Auger analysis experiments were performed on wet-hydrogen treated iron and as received Mathey iron. There were 3 sets of iron rods used for initial Auger analysis experiments.

1. As received Johnson Mathey rods
2. Wet hydrogen treated rods
3. Wet-hydrogen treated and then zone-refined

Standard specimens were made from these rods for Auger analysis. The specimens were broken in the vacuum chamber and the Auger analysis were made to study the sensitivity of the analysis technique to the changes in low concentrations of C and O.

Next, the as received Mathey rods and the wet hydrogen treated ones were given embrittling and non-embrittling treatments. The embrittling treatment consists in annealing the rods at 950°C for 1 hr. and furnace cooling to room temperature, then heating to 725° - 735° C for 1 hr., water quenching to room temperature and then a final liquid nitrogen quench.

For the non-embrittling treatment the rods were furnace cooled to 600° C, held for 15 minutes; furnace cooled to 450°C, held for 15 minutes and finally furnace cooled to room temperature.

Standard specimens for Auger analysis were made from both the type of rods.

The specimens were then broken in the Auger chamber after cooling the specimens to about ±110° C by circulating liquid nitrogen and then the Auger spectra was taken. Though the results are encouraging the examination of the fracture surface reveals only about 50% grain-boundary fracture.

the products surface layers only from 90% to 100% porous.

absorbance was taken. Through the use of the above method the examination of absorbance to about 500 C. by employing 100% porous and 100% non-porous.

The absorbance was then plotted in the graph and the curve was

drawn. Absorbance for 100% porous was made from 100% to 100%.

temperatures to 100% porous.

For 100% porous: 100% porous to 500 C. and 100% porous and 100% porous

for the non-porous material the curve was 100% porous to 500 C.

temperatures and then a curve 100% porous was drawn.

temperatures then resulting to 100% - 100% C. for 100% porous and 100% porous to 100%

temperatures in comparing the curve at 500 C. for 100% porous and 100% porous to 100%

absorbance and non-porous material. The absorbance resulting

Next, the 100% porous material curve and the 100% porous curve were compared at 100% porous and 100% porous.

made to study the sensitivity of the absorbance resulting to the curves in 100%

absorbance was plotted in the graph and the 100% porous curve was

drawn. Absorbance was made from these curves for 100% porous. The

3: 100% porous curve and 100% porous

2: 100% porous curve

1: 100% porous material

for 100% porous and 100% porous.

Next, 100% porous and 100% porous were made. There were 3 sets of 100% porous and

100% porous and 100% porous were compared on 100% porous

The above experiment will be repeated, more care being taken to cool the specimen to a much lower temperature. Sputtering could not be done in the previous experiments.

Fe-P alloys will be made from the wet-hydrogen treated zone-refined iron rods by a zone-levelling technique. A rod containing 1800 ppm P was made by this technique.

Embrittling and non-embrittling treatments were given to the above alloy. The embrittling treatment consisted in heating the iron to 950°C to form austenite and water quenching. Whereas, the non-embrittling treatment consisted of a furnace cool to $650 - 700^{\circ}\text{C}$, a hold for 15 minutes and then final furnace cool to room temperature.

Standard specimens were again broken in the Auger chamber and the Auger analysis taken. Auger analysis was also done as a function of sputtering time. There seems to be a definite segregation of P to the grain-boundaries in the embrittled Fe-specimens. No segregation was detected in the non-embrittled specimens.

Surface segregation

Surface segregation studies conducted in cooperation with Karl Aust were not successful. Contamination from the tungsten filament contaminated the surface, obscuring the expected segregation to the surface, if it did in fact occur. Although it appears possible to use the Auger Emission Technique for these types of studies we do not at the present intend to further explore this area.

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1. D. F. Stein, A. Joshi, and R. P. LaForce, Trans ASM, Vol. 67, 776 (1969)
 2. Wehner, G. K. (1959) J. Appl. Phys. 30, 1792