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**A Study of Grain Boundary Segregation
Using the Auger Electron Emission Techniques**

by

D. F. Stein

**University of Minnesota
Mechanical Engineering Department**

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I. INTRODUCTION

This report summarizes the work performed under contract AT(11-1)-1778 at the University of Minnesota from April 1, 1968 to date. The work proposed in the renewal proposal for April 1, 1971 to March 31, 1972 and is expected to be continued at Michigan Technological University starting September 1, 1971. The work will continue at the University of Minnesota until August 31, 1971.

This program has been directed toward the utilization of Auger Spectroscopy to study segregation of impurities to grain boundaries that result in a deterioration in the properties of materials. Included in the properties of interest are embrittlement due to grain boundary fracture, corrosion at grain boundaries and grain boundary mobility during annealing and sintering operations.

II. GRAIN BOUNDARY FRACTURE

a) Temper Embrittlement of Low Alloy Steels

A program to understand the mechanism responsible for the marked increase in the transition temperature of steels which have been tempered between 325-600°C or slowly cooled through this temperature range was undertaken. Part of the results have been published^(1,2), some submitted for publication⁽³⁾, and other results are in process of analysis⁽⁴⁾. The following is a brief summary of results.

- (1) Antimony, nickel and chromium segregate to grain boundaries upon step cooling a steel containing Cr, Ni, Sb and C.
- (2) Segregation of Sb, Ni and Cr and the associate shift in transition temperature upon step cooling increased with increasing antimony content of the alloy steel.

- (3) Significant amounts of Sn and Ni segregated in a Ni-C-Sn steel upon step cooling.
- (4) Ni and Cr segregated in most steels upon step cooling. No such segregation occurs in non-embrittled steels.
- (5) Segregation is not observed in steels containing As-Ni-Cr-C. These steels show only a very small shift in transition temperature upon step cooling.
- (6) Segregation of carbon is observed in many steels after step cooling; particularly in those not containing chromium.
- (7) Segregation of Sb and Sn appears to be concurrent with that of alloying elements Ni and Cr. This indicates that no segregation of Sb occurs in the absence of Ni or Cr and vice versa.
- (8) Segregation of antimony, even in the most embrittled case, is limited to about 15-20 atomic layers from the grain boundary. Segregation of tin is not observed beyond 5 atomic layers. In contrast, the segregation of Ni and less obviously of Cr is observed even beyond 100 atomic monolayers.
- (9) The segregation of Sb as well as Ni (and Cr) is observed to occur almost simultaneously during the entire step cooling process. The Ni concentration profile which exhibits a hump in the close vicinity of the grain boundary. It is apparent that the hump moves closer to the grain boundary with progression in the step cooling process.

b) Boron Containing Steels

This program is performed with the cooperation of A. P. Coldren of Climax Molybdenum Company of Michigan.

Direct experimental confirmation has been made of the often predicted adsorption of atomic boron at grain boundaries in boron containing steels. Attempts to correlate the degree of boron adsorption at grain boundaries with impact transmission temperatures were complicated by the presence of sulfur which was also present at the grain boundary. It appeared, however, that the impact transition temperature could be correlated with the percent of boron in the boron plus sulfur mixture present at the prior austenite grain boundaries. The transition temperature rose at an increasing rate as the amount of boron increased beyond 50% in the boron plus sulfur mixture. Further research is needed because these preliminary results represent too limited a sampling to be considered general.

This work⁽⁵⁾ will be presented at the fall meeting of the AIME.

c) Copper-Bismuth Alloys

A program has been completed to determine the role of bismuth in embrittling copper base materials⁽⁶⁾. A manuscript has been completed and has been accepted for publication in the Journal of the Institute Metals. Briefly, the results show that bismuth segregates to grain boundaries and this results in the embrittlement of copper. It was found that in an alloy containing 0.009%Bi that the region within $3\text{\AA}$ of the grain boundary was about 30%Bi. This bismuth segregation was not detectable beyond 10 atomic layers from the boundary. Using the surface energy measurements of Hondros and

the measured values of segregation it was possible to quantitatively determine the expected deterioration in fracture strength and good agreement was found. The driving force for segregation was explained on the basis of the Gibb's adsorption model.

d) Refractory Metal Embrittlement

a. Tungsten

The work on powder metallurgy tungsten has been published in⁽⁷⁾ Metallurgical Transactions. The Auger spectroscopic analysis of tungsten clearly indicated segregation of phosphorous to the grain boundaries and the grain boundary concentration of phosphorous could be directly related to the ductile-brittle transition temperature. Fractographic analysis using a scanning electron microscope indicated that the actual amount of segregation was dependent upon the grain size -- the larger the grain size, the greater the concentration of phosphorous at the grain boundary and the associated embrittlement. Oxygen or carbon was not responsible for the observed variations in ductile-brittle transition temperature of various materials under investigation.

b. Chromium

Fracture surfaces of chromium polycrystals prepared in different ways have been analyzed using Auger Spectroscopy. Powder metallurgy chromium specimens were found to have high sulfur, oxygen and carbon along the fracture surfaces and the material is extremely brittle. Polycrystals of differing grain size prepared by melting in vacuum did not show any unusual amount

of impurity on the fracture surfaces even though they broke in a brittle fashion at room temperature. Scanning microscopy is now being performed to determine the fracture morphology of each specimen.

e) Iron Base

a. Fe-P System

Several Fe-P alloys have been made in order to study the heat treatment condition under which these alloys showed grain-boundary weakness. It was found that holding at temperatures in the range of 670 to 900°C or very slow cooling (in furnace) from 1000°C caused severe grain boundary embrittlement in these alloys. The only way grain boundary weakness could be avoided in these alloys is by water quenching from temperatures above 1000°C.

b. Fe-O-C

We have been unable to solve the problem of slight oxygen contamination of pure iron fracture surfaces. Therefore, it is difficult to obtain reproducible results and the Fe-O-C program has been halted until this problem can be solved. We are not actively working on it.

c. Fe-Sb System

Fe-600 ppm Sb and Fe-200 ppm Sb alloys have been prepared and are under study using Auger Spectroscopy and Mossbauer Spectroscopy. The effect of heat treatment of these alloys are being studied in order to further elucidate the role of Ni and Cr in temper embrittlement.

This program on iron base alloys is part of a Ph.D.⁽⁴⁾ thesis research program of P. V. Ramasubramanian which is

expected to be complete by late summer.

f) Naval Reactor Steels

An investigation of steels used in reactor pressure vessels that have shown a shift in the ductile to brittle transition temperature when irradiated was made in cooperation with F. A. Smidt and L. E. Steele⁽⁸⁾ of the Naval Research Laboratory.

No copper or phosphorous segregation was detected in any of the samples which would indicate that these elements should not be of major concern. In a weld metal steel a substantial segregation of chromium was observed, 5% at fracture surface compared to 2% nominal composition. In most of the steels a peak occurred at about 220 e.v. which is usually associated with argon. The argon peak could be explained for the low copper steels and the weld metal since that had been treated in argon at some point in their fabrication history. However, one heat of steel had not been exposed to argon at any point in its history, but the argon peak was still present. It was possible that the argon found was a transmutation product and therefore non-irradiated specimens were prepared. The peak at 220 e.v. persists in these steels which indicates that the element causing this peak is present in the virgin material. Since this peak has never been observed in other steels studied in this program it appears that it is associated with the naval reactor steels and the evidence is strong that the element giving the peak is argon. This study is continuing.

III. CORROSION

a) Sensitization

By treating 304 type stainless steels at very high temperatures we have been able to produce very large grain sizes and induce

grain boundary fracture. Auger analysis of the fracture surface shows a high concentration of nitrogen at the grain boundary. Reflection Mossbauer spectroscopy indicates a magnetic phase is also present at the surface. Therefore it appears that nitrogen is segregated to grain boundaries during sensitization and that either a magnetic carbide is formed or a thin layer of material has become ferritic. These studies are continuing and the chemistry of the fracture surfaces will be the basis of a paper⁽⁹⁾ now in preparation to be presented at the fall meeting of AIME.

IV. ANNEALING AND SINTERING

a) Powder Metallurgy Tungsten

The mobility of grain boundaries is often markedly altered by the addition of trace amounts of certain elements. Tungstens used for high temperature filament wires have a very unusual grain structure. The grains have a very elongated structure with the grain being very long parallel to the wire axis. It is suspected that a trace element present in the form of small bubbles is responsible, but there has been no direct evidence identifying the element.

The Westinghouse Corporation has prepared tungsten samples with bubbles in such a way as to produce fracture through the bubbles. Auger analysis of these fracture surfaces clearly shows the presence of potassium. Sputtering the surface with xenon gas demonstrated that the segregation was limited to very narrow regions next to the grain boundary. Further experiments to evaluate the role of other impurities are in progress and a manuscript⁽¹⁰⁾ is near completion.

b) Powder Metallurgy Iron

In iron compacts the mechanical properties and rate of densification differs depending upon the type of base metal powder used. We have studied the sintering properties of seven different iron powders with respect to sintered density and in some cases mechanical properties. Fresh fracture surfaces were then prepared in the vacuum system to determine if there was large impurity concentration on the path the fracture took. It was found that large amounts of sulfur, oxygen, and carbon was present in the region of the fracture path. Scanning electron microscopy is now being performed to determine the fracture path. These results are to be presented at the fall meeting of AIME⁽¹¹⁾.