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

by

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

I. INTRODUCTION

This program is directed toward the utilization of Auger Spectroscopy to study segregation of impurities that result in a deterioration in properties of a material. 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

Work has been carried out with the aim of understanding the phenomenon of temper embrittlement in low alloy steels. Steels with several compositions⁽³⁾ were chosen and the in situ fracture surfaces (fractures made in vacuum) of the steels were analyzed in both the embrittled and non-embrittled conditions. Part of the results were published⁽¹⁾, parts appear in the previous report⁽²⁾ and parts are described in detail in Reference 3. Since steels with varying quantities of alloying elements Ni, Cr and impurities Sb, Sn and As were chosen it became possible to analyse the actual role of these elements. The extent of segregation of various elements in a given steel was found by ion sputtering the fracture surface, in steps, followed by Auger analysis⁽³⁾. It was found that the segregation profiles for Ni and Cr are much wider than for Sb or Sn and that during embrittling treatment the movement of Ni and Sb is complex. A manuscript is in preparation on the findings.

B) Copper-Bismuth Alloys

A program has been completed to determine the role of Bismuth in embrittling copper base materials⁽⁴⁾. 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 3Å 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⁽⁷⁾ 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.

C) Refractory Metal Embrittlement

Part of the work made on the powder metallurgy tungsten has been previously reported⁽²⁾ and a manuscript published⁽⁵⁾ in Metallurgical Transactions. The Auger spectroscopic analysis of these materials 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 under 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 are not responsible for the observed variations in ductile-brittle transition temperature of various materials under investigation.

D) Iron Base

a. Fe-P System

Two alloys: (1) Fe-900 ppm P and (2) Fe-500 ppm were made by mixing appropriate quantities of Johnson-Matthey Fe and an Fe-0.2%P master alloy melting the mixture in vacuum using a high frequency generator.

Experiments were carried out to study the heat treatment conditions under which these alloys showed grain-boundary weakness. It was found that holding at temperatures in the range of 670 to 900°C at very slow cooling (in furnace) from 1000°C caused severe grain boundary embrittlement in these alloys. Water quenching a furnace cooling from 670 to 900°C after holding at these temperatures for an hour did result in embrittlement. The Fe-900 ppm P alloy showed a transition temperature (ductile-brittle) of 145°C while Fe-500 ppm alloy had a transition temperature above approximately 140°C.

The only way the grain boundary weakness in these alloys could be avoided was by water quenching them from temperatures of 1000°C or more. In this case the alloys showed a transition temperature of about 10-15°C and fracture was predominantly by cleavage mode.

Specimens have been made for the Auger Spectral analysis of the fracture surfaces and these measurements are presently being made.

Similar studies are being carried out on an Fe-200 ppm P and an Fe-50-70 ppm P alloys.

Earlier such experiments on Fe-0.2% P alloy (which is used as the master alloy) showed that grain boundary embrittlement prevailed on the alloy under all heat treatment conditions. Auger analysis showed

segregation of P over wide regions after the specimens were 1) water quenched from 700°C after holding at the temperature for 1 hr.; 2) very slowly furnace cooled for 1000°C; and 3) water quenched from 1000°C.

b. Iron-Oxygen-Carbon

There has been considerable difficulty in measuring the segregation of oxygen to grain boundaries in iron because of contamination from residual gases in the vacuum system. The vacuum system has been improved to try and alleviate this problem. The work is continuing.

B) Aluminum

A program to study segregation of germanium to grain boundaries in aluminum was unsuccessful. The difficulty reported in the last progress report in using gallium to produce the necessary embrittlement continued and the possibility of alleviating problems did not appear promising enough to continue the program. The problem is associated with the extensive coverage of the fracture surface with liquid gallium. The only signals received from the surface were due to gallium and these signals apparently covered the germanium if germanium had in fact segregated.

III. CORROSION

A) Sensitization

Two specimens of stainless steels 304 (sensitized) and 321 (titanium stabilized) that were obtained from Prof. K. T. Aust, University of Toronto were fractured for examination using auger analysis. The fractures obtained were primarily transgranular and hence an examination of the chromium depletion theory could not be made.

Considerable amount (of the order of 50%) of intergranular portions in the fracture is required to make a satisfactory analysis and hence experiments are being made to achieve this goal. One of the obvious techniques without extraneously influencing the grain boundary composition is by obtaining large grain size. High temperature annealing under inert atmospheres is being currently used to obtain larger grain sizes.

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 it is expected that a manuscript will be prepared for publication early in 1974.

V. GENERAL TECHNIQUES APPLICABLE TO AUGER SPECTROSCOPY

A) Pure Metal Spectra

In order to use Auger Spectroscopy to study the chemistry of alloys it is necessary that the spectra for pure metals be obtained. Several elements have been studied in cooperation with other groups in the Physical Electronics Laboratory at the University of Minnesota. Pure metal spectra has been obtained for several metals, including Zn, In, Fe, Mo, W, Cr, Bi, Cu, Ni, B and Sb. Some of these spectra and techniques applicable to auger spectroscopy are given in Reference 6.

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