Intergranular brittleness studies in
W using Auger Spectroscopy

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Abstract

The present investigation was aimed at understanding the problem of brittleness in powder metallurgy tungsten by utilizing Auger Electron Emission Spectroscopy as a tool for direct chemical analysis of fracture surfaces. Substantial segregation of P to the grain boundaries was observed in tungsten and the concentration of P can be related to the ductile-brittle transition temperatures. The amount of segregation was dependent upon the grain size - the larger the grain size, the greater the concentration of P at the grain boundary and the associated embrittlement.

P4462

INTRODUCTION

A major limitation in the usefulness of tungsten is its tendency to be brittle. This difficulty is especially acute when it is in the polycrystalline form. Inspection of the fracture surfaces reveal that polycrystalline tungsten often fractures along the grain boundaries.

It has been postulated that a major cause of grain boundary fracture is due to the segregation of oxygen to the grain boundaries resulting in embrittlement. However, there is no direct evidence that oxygen is responsible for the brittleness and therefore in an effort to examine this hypothesis different grades of tungsten were prepared with various amounts of carbon additions in the powder stage. The added carbon was expected to interact with oxygen present in the material and thus control the brittleness. The measured ductile-brittle transition temperatures (DBTT), however, bore no relation to the additions of carbon thus indicating that either carbon did not react as expected or oxygen is not the cause of the observed brittleness in tungsten.

The frequent occurrence of intercrystalline fractures in these materials suggested the usage of Auger Electron Emission Analysis for direct determination of segregants at the grain boundaries. This technique has proved its effectiveness in directly identifying certain segregants in the grain boundaries of temper embrittled low alloy steels,^(1,2) and therefore it might be useful in study of embrittlement of tungsten.

MATERIALS

Three powder metallurgy tungsten targets that had been formed for use in

x-ray tubes and a zone refined tungsten rod were selected for the study of embrittlement in W. All the three targets were made by the General Electric Company from pressed and sintered W billets and then high energy rate forged. After coining to the target angle they were recrystallized in hydrogen at 1600°C. The targets differed by the amount of carbon added in powder stage in order to react with and decrease oxygen during the sintering operation. The estimated ductile-brittle transition temperatures and the carbon additions are indicated in Table I. The DBTT values were determined using three point beam test and using the 50% ductility value of beam deflection. (The values were determined at the General Electric Research and Development Center).

TABLE I

<u>Material</u>	<u>DBTT (°C)</u>	<u>Remarks</u>
Code 10	250	carbon added in powder stage
Code 41	800	carbon added in powder stage
Code 50	estimated at 600-800	no carbon added
Zone refined W	estimated at 0 - 100	

AUGER SPECTROSCOPY

The technique of Auger Electron Emission Spectroscopy is a relatively new experimental tool and, hence, a brief description of it will be given. When an atom is struck by an energetic electron, the electrons in the shells are excited to higher energy states. Vacancies in the electron shells so created

are unstable and will be immediately filled by drop back of higher energy electrons. This causes an emission of energy which may be given off either as a photon i.e., characteristic x-radiation, or transferred to another electron which is then ejected from the atom, i.e., Auger emission. Auger electrons, thus, carry energies characteristic of the emitter and to be identified so, they must escape from the material without suffering any inelastic collisions thereby retaining the discreteness of their energy. This escape depth depends upon the material and on the energy of the Auger electrons. Since the energy is usually small and often less than 1000 ev, the escape depth is limited to a very small distance from the surface, on the order of 10^1 . This aspect makes the Auger spectroscopy a very attractive tool for surface ^(3,4,5) and segregation studies.

Fig. 1 shows a schematic of the electronics and electron optics used for analyzing the Auger electrons. The specimen is bombarded with primary electrons in 2000-3000 e.v. range from an electron gun. The Auger electrons, after passing through the control grids, are collected by a hemispherical collector. They are then analyzed in the associated phase sensitive electronic circuit and displayed as the second derivative of number of electrons emitted $\frac{d^2 N}{dE^2}$ versus energy, E, on the x-y recorder.

All possible Auger emissions could be calculated for any given element from the available tables of electron binding energies. For example, oxygen with binding energies of 532 ev (k state), 24 ev and 7 ev (L states) would be expected to give Auger peaks at 527, 508 and 17 ev. However, only the 508 ev peak is seen. This illustrates that not all transitions are equally probable.

At this time Auger transitions are not well enough understood to predict which of the transitions will occur, therefore it is usually necessary to run spectra on pure elements or materials with known compositions to determine the exact spectra for each element.

The system for doing the Auger Electron Emission Analysis was designed and assembled in the physical electronics laboratories of the University of Minnesota. A vacuum system provided by Varian Associates, Inc. is used for housing the electron optics and is capable of pressures below 10^{-9} torr. Provisions for cooling the specimens, if necessary, and breaking them by impact were made. The system is also equipped with a thermocouple to measure the temperature of the specimen and a sputtering gun to D. C. sputter the fracture surface of specimen using Xe gas. Close control of the amount of sputtering was obtained by controlling the ion current and the time of sputtering. The amount of material sputtered away in a given time was calculated from the published data of Wehner ⁽⁶⁾.

Auger Analysis of the Refractory Metals

In preparation for the analysis of the fracture surfaces the system was pumped down to a pressure of approximately 10^{-9} torr with all the specimens fixed in it and baked at 180°C for approximately 36 hrs. It was observed in earlier experiments that upon baking the system the carbon and oxygen contamination of fracture surfaces was considerably reduced. Each of the specimens was fractured under vacuum and immediately analyzed. Figure 2 shows the Auger spectra of three of the four tungsten specimens analyzed. Spectra B and C belong to specimens code 10 and 41 respectively. Spectra A of zone refined tungsten was determined in a separate run and hence the oxygen and

carbon peaks could not be directly compared with the others. Fresh fracture spectra of code 50 was very similar to that of code 41 and hence, is not shown. The Auger spectra of the fresh fractures of the various W specimens did not indicate any noticeable variations in C or O peaks (275 ev and 510 ev respectively). The peaks at approximately 170, 180, 210, 220 and 350 ev all correspond to W and can be explained from the electron binding energies. The only prominent peak whose height varied considerably from material to material is that at 120 ev which corresponds to phosphorous. (P has electron binding energies corresponding to 2149, 186, 136, 135, 16 and 10 ev). The existence of peak at 120 ev is confirmed by Auger analysis of a P doped iron ⁽⁷⁾ and by comparing to Auger spectra of steels ⁽²⁾. It may be noticed that the 120 ev peak is more prominent in the spectra of code 41 and code 50 (which have a high DBTT 600-800^o C) than in that of code 10 (DBTT = 250^o C). The peak disappeared upon sputtering, indicating that it is only concentrated at or in the close vicinity of fracture surface. The peak (at 120 ev) is entirely absent in the spectra of zone refined W.

Another specimen of code 41 was chosen to study the concentration profile of P in the direction away from the boundary. This is obtained by stepwise Auger analysis followed by sputtering in small steps. The result of such a study are shown in Figure 3. It is evident from the figure that the P is concentrated in a few layers at the fracture surface, essentially the first three layers. Beyond 8 to 9 layers no detectable signals were present indicating that either P was absent beyond that distance or the technique is not sensitive enough to detect the existing but very small concentrations.

An assumption made in the interpretation of these results is that sputtering removes the atoms from the surface with no selection.

FRACTOGRAPHY

The fracture surfaces of the specimens under investigation are examined under the light and scanning electron microscopes.

Figures 4 and 5 show the scanning microscope photographs of the fracture surfaces of code 10 and code 41, tungsten specimens. Fracture surface of code 50 appeared very similar to that of code 41 and all the materials exhibited primarily intercrystalline fracture with over 95% intercrystallinity on an average. Another interesting feature that can be noticed from these photographs is that code 10 possessed a much finer grain size than either code 41 or code 50 (not shown).

DISCUSSIONS

The fractographic examination in view of the results of Auger analysis reveals two important aspects. They are

(a) the fracture surface of tungsten specimens is primarily intercrystalline.

The indication is that P segregates to the grain boundaries in these materials.

(b) the variations in the grain sizes. Code 10 has a much finer grain size than either code 41 or 50. Since a finer grain size results in an overall large grain boundary area, a fixed quantity of P distributed over large areas would hence, as observed in Code 10, be expected to give low concentrations at the boundary. Thus the additional embrittlement observed in the target materials is a result of P at the grain boundaries and the amount of embrittlement is

controlled by the concentration of P in the boundaries.

A plot of the P peak height against the estimated DBTT is shown in Figure 6. This demonstrates the correlation between P concentration in the grain boundaries and the observed embrittlement.

Assuming all the phosphorus in these materials is segregated to the grain boundaries a rough estimate of the overall or bulk concentration of phosphorus may be made. In a material like code 41, containing approximately 100 grains per square centimeter, the total grain boundary surface per c.c. of material equals about 30 sq. cm. Assuming the grain boundary has a layer of pure phosphorus with a thickness of about $10\text{\AA}$, the phosphorus concentration in the material is estimated to be about 6 ppm. This amount thus represents an estimated upper limit of P needed if complete segregation occurs and shows how minute quantities of P present in the material can give rise to such highly damaging effects.

CONCLUSIONS

1. Segregation of P to the grain boundaries is the primary cause of embrittlement in the powder metallurgy tungsten materials that have been under investigation.
2. The amount of embrittlement is in direct relation to the P peak height observed by Auger analysis and hence can be directly correlated to the P concentration in the fracture surface of the powder metallurgy tungsten materials.
3. P in the grain boundaries of W is primarily located in the few atomic monolayers. Auger spectroscopy does not indicate the presence of P beyond

about 20 Å from the grain interfaces.

4. P concentration in the boundaries of W (i.e., amount of phosphorus per unit area of grain boundary) can be controlled by controlling the grain size. The larger the grain size, the smaller is the overall grain boundary area and hence the concentration of P and associated embrittlement are larger. Minute quantities of P, of the order of a few parts per million, present in the material can give rise to such large changes in the transition temperatures.

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Figure Caption

- Fig. 1 Schematic of electronics and electron optics used for Auger Electron Emission Analysis.
- Fig. 2 Comparison of the Auger spectra of tungsten specimens under investigation. (A) zone refined tungsten, (B) tungsten - code 10, (C) tungsten - code 41.
- Fig. 3 Variation in phosphorus concentration with distance from the intergranular fracture surface of tungsten code 41.
- Fig. 4 Scanning electron fractograph of the tungsten, Code 10. Same material as in Figure 2 (B). Magnification X 1000.
- Fig. 5 Scanning electron fractograph of the tungsten, Code 41. Same material as in Figure 2 (C). Magnification X 1100
- Fig. 6 Effect of phosphorus segregation to the grain boundaries on the ductile-brittle transition- temperature of tungsten.

SIMPLIFIED SCHEMATIC OF THE ELECTRONICS

Fig 4

Fig 5

DUCTILE-BRITTLE TRANSITION TEMPERATURE