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

Annual Technical Progress Report - III

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ABSTRACT

The segregation of impurities and the resulting effects on material properties have been measured in several systems. In Al_2O_3 it was found that additives segregated to grain boundaries, with the ions having the largest size misfit segregating the most strongly. The role of additives on the densification of Al_2O_3 and MgO was measured and it was found that the role of Mg ions in Al_2O_3 densification was primarily due to enhanced diffusion rather than restricted grain boundary mobility. In MgO it was found that LiF and NaF promoted densification by the formation of a liquid phase.

Scanning Auger Microscopy has been used to measure segregation of sulfur in nickel, phosphorous in tungsten, and bismuth in copper. In all three cases the segregation measured did not differ from grain boundary to grain boundary on the fracture surface. Therefore it does not appear that segregation occurs preferentially to different high angle grain boundaries.

Work continued on the effect of third element additions for controlling deterioration of properties and on intergranular corrosion in stainless steels. Techniques were developed that will prove useful in the coming year in further developing our understanding of the mechanism of grain boundary segregation, its control, and the effect on properties.

I. INTRODUCTION

This report summarizes the work performed under Contract AT(11-1)-2166 for the year 1973. The program has been directed toward the utilization of Auger Electron Spectroscopy (AES) 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.

Several papers (see attached list) have been published or prepared for publication in the past year. One paper ("Low Temperature Brittleness") is a manuscript prepared as an invited keynote address to the Third International Conference on the Strength of Metals and Alloys, and another is a major review article describing the development and utilization of AES to study grain boundary segregation in solids.

In the past year further development of facilities has occurred. A second vacuum system with the associated electron optics, sputter gun and fracture apparatus has been assembled. This was done with non-AEC money. The same electronics for control of electron optics are used on both systems, but the two systems increase substantially the rate of data acquisition.

II. RESEARCH PROGRESS (1973)

A. Densification of Ceramic Materials

A Ph.D. thesis has been completed on "The Role of Impurities and Additives on Ceramic Densification" by W. C.

Johnson. This study was undertaken to determine the relation between grain boundary hardness and impurity segregation that had been observed in fully dense Al_2O_3 . These fully dense Al_2O_3 bodies were prepared by making addition of MgO and it was thought that the MgO segregated to the grain boundaries and restricted their mobility. The evidence for this was the increase in microhardness measured in the near grain boundary regions. However, direct experiments using AES did not show substantial segregation to grain boundaries. Ca was observed at the grain boundaries at levels as high as 5.5 percent, but the segregation was limited to less than 10 atom layers from the grain boundary. Since microhardness measurements indicate hardening some 5 microns from the boundary, it is clear that the microhardness measurements are not directly related to the chemistry.

The absence of MgO segregation to the grain boundaries posed a question as to its role in densification of Al_2O_3 and to the general role of impurities in promoting densification of oxide materials. The answer to these questions were the more important aspects of Dr. Johnson's thesis. It was concluded that discontinuous grain growth is not inhibited in doped alumina, but rather the material achieves theoretical density before discontinuous grains can nucleate. Because the rate controlling diffusivity is extrinsic due to the MgO introduced vacancies, doped Al_2O_3 sinters faster than pure Al_2O_3 . Therefore, segregation of impurities to grain boundaries is of little if any importance in the promotion of full densification in doped Al_2O_3 .

In the course of the study various impurities were added to Al_2O_3 , such as Y, Ca, Ni, and Mg to test various models of segregation. The size difference of these ions in comparison to aluminum turned out to be an effective way of predicting the segregation to grain boundaries. Using the McLean formula for equilibrium segregation,

$$C_{gb} = \frac{C e^{Q/RT}}{1 + C e^{Q/RT}}$$

where

C_{gb} = grain boundary concentration

C = bulk concentration

Q = misfit energy

T = temperature

R = gas constant

The temperature dependence of the segregation also was consistent with this model, so the evidence strongly supports the Gibbs equilibrium model for segregation of impurities in Al_2O_3 .

B. Scanning Auger Microscopy

In the past year Physical Electronics Industries, Inc. has developed a scanning Auger microscope that they have made available for our use to determine its capability in metallurgical research. Preliminary experiments have demonstrated that segregation of impurities to grain boundaries is not strongly dependent upon grain orientation. The systems studied so far are Ni-S, W-P, and Cu-Bi. The chemistry on the surface of each grain was found to be nearly identical for each material, so either the fracture path is along grain boundaries or nearly

identical mis-orientation or the segregation does not depend sensitively to grain boundary geometry.

Scanning Auger spectroscopy has been used to augment some of the other areas of research also and the results will be described in each section.

C. Non-Equilibrium Segregation

The major effort in this area has been to determine an experimental procedure that would be useful for studying non-equilibrium segregation. It is necessary that a technique be developed for making the grain boundaries brittle without altering the non-equilibrium segregation that has occurred to the grain boundary region. Originally it appeared that the Cu-Zn system would be useful, but it now appears that Ni base materials are better. Nickel can be embrittled at rather low temperatures by sulfur and the previous segregation due to heat treatment can be preserved. Scanning Auger Microscopy has shown that the sulfur is uniformly deposited on all the grain surfaces through which the fracture has passed and therefore it should not interfere with the determination of other solute atoms that have segregated in a non-equilibrium manner at the grain boundaries. Ni-Cu-S alloys have been prepared for this study and preliminary results are encouraging.

D. Stress Rupture in Nickel-Base Alloys

The stress rupture properties of nickel-base superalloys can be markedly affected by very small changes in alloy composition and trace impurity content. High melting point elements such as Hf can markedly improve stress rupture ductility while

low melting point elements such as S, Pb, and Bi have been observed to reduce stress rupture life and ductility drastically. Since stress rupture is typically a grain boundary failure phenomenon, it is important to learn whether the marked effects of these elements are reflected in the grain boundary chemistry of the alloys.

The results to date indicate that Pb (and probably Bi) do not segregate to the grain boundaries in Ni-base alloys. The effect of stress rupture conditions (stress applied at high temperature) did not appear to induce Pb segregation.

Alloys doped with 0.6 a/o Hf were found to have Hf segregated to the grain boundaries in amounts ranging from 3 a/o to 8 a/o. Sputter profiles indicated that the Hf enriched region is on the order of 30 atom layers thick.

In all of the Ni-base alloys observed thus far, S has been observed to segregate strongly to the grain boundaries. Bulk S levels of 50 to 60 ppm are typical of the alloys investigated, however, grain boundary S concentrations of between 0.5 a/o and 2.0 a/o are typically observed in these alloys.

The complexity of the commercial alloys used initially made detailed study of the segregation process difficult in some cases. Work is currently underway on experimental Ni-Al and Ni-Al-Ti alloys in which a more detailed study of S segregation should be possible. The information desired is the variation of S segregation with temperature and bulk S level. Efforts will also be made to determine the rate of S build up at the grain boundaries as a function of time.

E. Porosity in Titanium Powder Metallurgy Components

Porosity in aircraft components produced by a Ti powder metallurgy process has hindered the development of this process which makes use of relatively plentiful Ti alloy scrap. Until recently, the porosity was believed to be the result of entrapped Ar which is used as a shielding gas during the powder processing steps. The responsibility of Ar for the porosity was never conclusively demonstrated, however.

Work under this contract using conventional AES indicated significant amounts of S and Cl on the fresh fracture surfaces of samples heat treated to produce porosity. Inert ion sputtering indicated that the S is present only within a few atom layers of the surface while the Cl which is present in excess at the fracture surface appears to drop off with sputtering, to a constant value, still above the bulk concentration. Sputtering also revealed excess Al at the fracture surface.

Work using the SAM, (Scanning Auger Microprobe), indicates that the Cl and S are located in spots on the fracture surface. These spots are approximately the same size as the pores observed on the fracture surface. AES analysis of the spots indicates that spots contain about 40 a/o Cl. Chemical analysis of the bulk samples indicates that they contain less than 10 ppm Cl or S.

Both Ti and Al form compounds with Cl which have relatively low triple points, 249°K for TiCl_4 and 465°K for AlCl_3 . At the relatively high annealing temperatures, approximately by 1200°K , used to stress relieve the sintered and forged components, these chlorides could be expected to become gaseous and create pressures approaching the yield stress of the alloy, thus causing the pores to develop.

F. Third Element Effects

One of the possibilities for reducing embrittlement in materials is by the addition of a third element. It is known that small additions of Fe to copper containing Bi substantially reduces the amount of embrittlement. However, it is not known if the iron segregates preferentially to the grain boundary or if some other mechanism is responsible for the improvement in ductility.

Since previous work had been done on the Cu-Bi system it was chosen for study with Fe additions. It was found that iron did not preferentially segregate to the grain boundary region, but by some mechanism it substantially reduces the amount of bismuth segregation. This is difficult to understand, since 50 ppm of iron has such a marked effect. Further studies are underway, but the usual explanation of preferred segregation is clearly not correct in this case.

G. Intergranular Corrosion of Ferritic Stainless Steel

These materials are rendered susceptible to intergranular corrosion or embrittlement by various heat treatments. For example, commercial purity alloys are sensitized to intergranular corrosion by quenching from temperatures of 1700° - 2000°F. There is indirect evidence that chromium depletion in areas adjacent to intergranular chromium carbides are responsible for this sensitization.

We have to date studied the intergranular corrosion susceptibility of commercial purity AISI 430. All material is first subjected to 2400°F annealing in order to provide for a

large grain size, quenched, and then held at various intermediate temperatures. Corrosion rates in boiling 65% nitric acid are measured by electrical resistance methods which are substantiated by optical measurements. Susceptibility is induced by 1700°F heat treatments, the rate of subsequent cooling markedly affecting the corrosion rate - rates for air cooled materials exceed those furnace cooled or water quenched. Thermal treatments between 1100°F and 1400°F do not cause intergranular corrosion; however, temperatures of 900°F - 1000°F cause greater susceptibility than the 1700°F treatment.

The present task is to determine intergranular compositional changes accompanying the sensitizing heat treatments. The large grained sensitized material can be fractured along the grain boundaries. Work employing Auger spectroscopy to measure compositional profiles near grain boundary fracture surfaces is in progress.

H. Surface Composition of Platinum Electrode-Catalysts

Noble metals serve as electrodes and/or catalysts in many chemical processes of commercial importance. Although platinum is one of these noble metals, it has been known for several years from electrochemical behavior that platinum does react with oxygen during the electrolytic evolution of oxygen at the platinum surface. The nature of the reaction has been difficult to study because the thickness of the product layer is only a few atomic layers. It is important to determine the identity of this surface material since it, and not the metal, is the apparent catalyst for the electrolytic reaction.

We have studied surfaces of platinum anodized in 1 N H_2SO_4 solution and found an extremely stable film of Pto stoichiometry, confirming a postulate based on electrochemical behavior. Platinum anodized in NaCl solution did not form a stable reaction product - chlorine and oxygen are weakly adsorbed on the surface under these conditions.

Detailed results of this study are reported in our recent paper in the Journal of the Electrochemical Society.

III. PUBLICATIONS AND PRESENTATIONS ASSOCIATED WITH CONTRACT

A. Publications - 1973

1. A. Joshi and D. F. Stein, "Impurity Segregation to Grain Boundaries," Journal of Testing and Evaluation, ASTM, Vol. 1, No. 3, 1973.
2. P. V. Ramasubramanian and D. F. Stein, "An Investigation of Grain Boundary Embrittlement in Fe-P, Fe-P-S, and Fe-Sb-S Alloys," Met. TRANS., Vol. 4, July, 1973.
3. W. C. Johnson and L. A. Heldt, "Composition of Pt Anode Surfaces by Auger Spectroscopy," J. Electrochem. Soc.: Electrochemical Science and Technology, Vol. 121, No. 1, January, 1974.
4. W. C. Johnson, Ph.D. Thesis, "A Study of the Role of Impurities and Additives on Ceramic Densification," Michigan Technological University, October, 1973.

B. Accepted for Publication

1. W. C. Johnson and D. F. Stein, "A Study of Grain Boundary Segregants in Thermally Embrittled Maraging Steel," MET. TRANS.
2. D. F. Stein, W. C. Johnson, and C. L. White, "Experimental Techniques for Studying Grain Boundary Chemistry," manuscript of Invited Keynote Lecture, International Summer School on Grain Boundaries, Ecole Polytechnique, Montreal, Canada, July, 1973.

3. D. F. Stein, "Low Temperature Brittleness," manuscript of Invited Keynote Lecture, Third International Conference on the Strength of Metals and Alloys, Cambridge, England, August, 1973.
4. D. F. Stein, W. C. Johnson and C. L. White, "Study of Grain Boundary Segregation using Auger Electron Spectroscopy," to appear in book, Grain Boundary Structure and Properties.

C. Invited Presentations

1. W. C. Johnson, Application of AES to Studies of Grain Boundary Segregation, Pratt and Whitney Aircraft, July, 1973.
2. W. C. Johnson, Role of Impurities and Additives on Densification of Oxides, University of Illinois, July, 1973.
3. W. C. Johnson, Application of AES to Studies of Grain Boundary Segregation, Republic Steel, July, 1973.
4. W. C. Johnson, Role of Impurities and Additives on Densification of Oxides, Bell Labs.
5. W. C. Johnson, Role of Impurities and Additives on Densification of Oxides, Ford Scientific Laboratory, July, 1973.
6. W. C. Johnson, Role of Impurities and Additives on Densification of Oxides, General Electric Research and Development Center, July, 1973.
7. W. C. Johnson, Role of Impurities and Additives on Densification of Oxides, Naval Research Laboratory, July, 1973.
8. C. W. White, The Effect of Grain Boundary Chemistry on the Creep Rupture Behavior of a Nickel Base Superalloy, Republic Steel, August, 1973.
9. D. F. Stein, An Overview of New Surface Analysis Techniques, Pittsburgh Chapter, ASM, Educational Seminar, Feb. 20, 1973, Pittsburgh, Pa.
10. D. F. Stein, Brittle Fracture in BCC Metals, North American Rockwell Science Center, March 22, 1973, Thousand Oaks, Calif.

11. D. F. Stein, The Relation of Grain Boundary Chemistry to the Intergranular Corrosion of Austenitic Stainless Steels, Southern California Chapter of AIME, March 22, 1973, Los Angeles, Calif.
12. D. F. Stein, Fracture of Materials, Indiana Institute of Technology, April 18, 1973, Fort Wayne, Indiana.
13. D. F. Stein, Metallurgical Applications of Auger Electron Spectroscopy, Physical Electronics Industries, Inc., Seminar on Applications of AES, May 2, 1973, Minneapolis, Minn.
14. D. F. Stein, W. C. Johnson, C. L. White, Experimental Techniques for Studying Grain Boundary Chemistry, Keynote Lecture, International Summer School on Grain Boundaries, July 2-6, 1973, Montreal, Canada.
15. D. F. Stein, Low Temperature Brittleness, Keynote Lecture, Session on Low Temperature Strength and Ductility, Third International Conference on the Strength of Metals and Alloys, August 21, 1973, Cambridge, England.
16. D. F. Stein, Effect of Grain Boundary Segregation on Material Properties, Carnegie-Mellon University, December 13, 1973, Pittsburgh, Pa.

D. Other Presentations

1. C. L. White and D. F. Stein, The Effect of Certain Elements on Grain Boundary Chemistry of Nickel-Base Alloys, ASM/AIME Abstract Session, Oct. 1, 1973, Chicago, Ill.
2. W. C. Johnson, D. F. Stein, and A. Joshi, The Role of Fe and Bi Impurities in the Embrittlement of Cu, ASM/AIME Abstract Session, Oct. 1, 1973, Chicago, Ill.
3. W. C. Johnson and L. A. Heldt, Composition of Pt Anode Surfaces by Auger Spectroscopy, ASM/AIME Abstract Session, Oct. 1, 1973, Chicago, Ill.
4. W. C. Johnson and D. F. Stein, Role of Impurities on Densification of Al₂O₃, 75th Annual Meeting, Amer. Cer. Soc., Cincinnati, Ohio.
5. W. C. Johnson and D. F. Stein, A Study of Grain Boundary Segregants in Thermally Embrittled Maraging Steel, AIME Spring Meeting, May 29, 1973, Philadelphia, Pa.