MASTERHydrogen Absorption in Metals: A Field Ion Microscopy Study

Progress Report, for the Period

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ABSTRACT

During the second year of this project, we have made progress in several areas: (1) compositional analysis of Ti clusters and H associated microcrack formation in Fe-Ti alloys, (2) grain boundary segregation of phosphorus in a Fe-0.04%P alloy, (3) surface segregation of Cu in Ni-Cu alloys and (4) surface segregation and order-disorder in Ni-Cr alloys. In addition to these achievements, the construction of a new atom-probe is under way, although some delay is anticipated before its completion.

In this second year, our study on Fe-based alloys has made good progress. The initial study of Ni-based alloys has also produced interesting and positive results. We discuss these achievements briefly in the following order since the details are found in the attached materials.

- (1) Cluster formation and formation of a H associated microcrack in Fe-Ti alloys.
- (2) Grain boundary segregation of P in a Fe-P alloy.
- (3) Surface segregation and order-disorder in Ni-Cr alloys.

As to the construction of a new high-performance atom-probe, there is some delay which coincided with the University delay in approving the budget. However, we expect it to be completed in the summer of 1981.

There are currently three Ph.D. graduate students participating on this project.

(1) Fe-Ti alloy system

In the previous year, we started our investigation of hydrogen in metal with a Fe-0.15% Ti alloy. As a first step towards characterizing this alloy on an atomic scale we have documented the surface segregation of Ti at and above 800°C. Characterization of the surface and grain boundary segregation have been studied in more detail this year using Fe-0.29 wt. % Ti, and Fe-0.63 wt. % Ti alloys in addition to Fe-0.15 wt. % Ti, and an attempt to study in more quantitative fashion, Ti cluster formation which we reported briefly last year, has begun. We are also aware of the potential importance of the latter towards an understanding of strengthening mechanisms in some dilute alloy steels. It is now believed that there are two types of stable clusters, one containing Ti atoms and the other without Ti atoms. The ratio between these clusters is roughly 1:1 in the annealing temperature range of 200 to 1000°C. Both types of clusters contain substantial amounts of interstitial impurities, C, N and O. The concentration and distribution of clusters seem to depend strongly on these impurity levels and to less degree on the annealing temperature. In spite of this complication, there is a strong indication that Ti cluster formation is enhanced at approximately 600°C and 1000°C in Fe-0.29% and 0.63% Ti alloys. The total number of clusters observed is still not large enough (~400) to quantify our observations. More experimental study is warranted in order to adequately characterize the Fe-Ti alloy system for understanding the behavior of hydrogen in this system, in particular trapping by the clusters.

In the study of hydrogen in Fe-Ti alloys, we have found that H, H₂, FeH and TiH₂ accumulate at grain boundaries in Fe-0.29 wt. % Ti. The observation of molecular hydrogen by atom-probe FIM is striking and is strong evidence that H₂ gas was trapped in the grain boundary. We have also witnessed for the first time the formation and propagation of a microcrack on an atomic scale when hydrogen was introduced into Fe-0.29 wt. % Ti alloy. When this alloy tip (specimen) was exposed to H₂ gas at elevated temperature, a small crack was noticed at a grain boundary intersection during FI imaging. This was an open crack formed by detachment of metal located between the intersecting grain boundaries. This crack was observed to be much larger after the tip was reheated to 1000°C at a pressure of 1 Torr H₂. The crack could be easily reduced in size by gradually field evaporating the surface, layer by layer. Its propagation was repeated several times and reproducible results were obtained. The grain boundaries and fracture surface were found to be enriched in Ti, O, and C, in agreement with the earlier work for Fe-Ti alloys reported in the first year report.

(2) Fe-P alloy system

In the second year's proposal, we suggested expanding the scope of our research to include the compositional analysis of iron alloys of P, Sb, Sn, B or Te. These alloys are known to be involved in both hydrogen and temper embrittlement of steels. High-purity Fe-0.04% P alloy and others (Sn, S and Sb instead of P) were prepared by Professor H. Grabke's group at the Max-Planck-Institut für

Eisenforschung, Germany. Compositional analysis of these alloys along the grain boundary were performed both by atom-probe at Penn State and by scanning Auger electron spectroscopy at the Max-Planck-Institute. The AES work combined with LEED observation, carried out by Erhart and Grabke showed that phosphorus segregates strongly (~50%) along the grain boundary at room temperature. This result was obtained by in-situ fracture in the AES vacuum chamber. As annealing temperature increases from R. T., the P concentration was found to decrease steadily and reach zero at approximately 700°C. Our atom-probe results agree well with the AES data as to the temperature dependence and even the levels of phosphorus in the grain boundary. The atom-probe work also revealed unexpected enrichment of Ti, Mn and C along the grain boundary (Fig. 1), indicating that the atom-probe specimens were not as pure as originally anticipated. The chemical analysis of the sample after the experiment has subsequently confirmed the existence of those impurities (Ti, Mn and C) in the sample bulk. We believe that these observations clearly demonstrate the power and capacity of the high-performance atom-probe, and help to establish its credibility as a fine microanalytical tool. It is worthwhile to point out that AES cannot be employed for the study of grain boundary segregation unless the grain boundary is embrittled, and thereby made susceptible to grain boundary fracture. Thus, the segregation of non-embrittling elements, such as Ti, C and Mo, to grain boundaries in Fe cannot be studied by AES. Our study of the Fe-Sb alloy is still at a preliminary stage but it shows some degrees of Sb segregation to the grain boundary (~5 atomic %) at 500°C.

Fig. 1. Grain boundary segregation of P, Mn, Ti and C in a Fe - 0.04% P alloy plotted as a function of annealing temperature.

(3) Ni-Cu alloy system

Because of the encouraging initial results of segregation in Fe based alloys, and also of much interest in the surface segregation of Ni-Cu binary alloys, we have chosen Ni-Cu alloys as the first alloy system in the Ni-based alloy project. A series of Ni-Cu alloys (Cu weight % = 9.3, 28.4, 38.1, 48.0, 58.0, 68.3 and 89.3%) were prepared by Prof. K. Watanabe's group, Hokkaido University, Japan. The AES study was performed at Hokkaido University. These alloys were drawn into a wire of 0.25 mm diameter by the wire drawing device we developed last year under this project. The quality of FI images was first tested in a simple FI microscope before attempting atom-probe analysis. Atom-probe data for surface segregation were obtained upon annealing at 600°C for 30 mins. and quenching to liquid N₂ in-situ. This quenching ensures us that atom-probe data correctly reflect the equilibrium composition at the annealing temperature. A result is shown in Fig. 2 although there are several data published for the Ni-Cu system, there is considerable disagreement among them. Our new data obtained with the atom-probe do not agree in detail with any of these including the AES results by Watanabe. Since existing theoretical models do not show complete agreement with the previous results, we are currently applying some of these theoretical models to our own data. The result will be reported soon.

(4) Ni-Cr alloy system

Along with the Ni-Cu alloy study, Ni-Cr binary alloys were also investigated. A series of Ni-Cr alloys (nominal Cr weight % = 5, 10,

Fig. 2. Atomic percentage of Cu on the outermost surface layer is plotted against bulk concentration of Cu in Cu - Ni binary alloys. Our result (●) is compared with our theoretical calculation (CPA) and others (ISM and RSM) for surface segregation.

15, 30, 40 and 50) were prepared in our group. When annealed at 620°C for 30 min. in vacuum these alloys showed no surface segregation. Once exposed to oxygen gas during annealing, Cr tends to be enriched on the surface. As expected from thermodynamics, the O₂ gas pressure required for Cr enrichment is extremely low ($\sim 10^{-10}$ Torr), which makes this experimental study rather difficult.

Another interesting result in the Ni-Cr alloy system is the observation of the order-disorder transformation on an atomic scale. There are some controversies in Ni-Cr bulk phase diagram itself. Since FIM and atom-probe, in principle, allow us to study the geometrical structures of ordered phases and their chemical compositions on an atomic scale, we attempted a study of the phase diagram in a rather low temperature range ($\leq 600^\circ\text{C}$). This exploratory investigation has yielded some interesting results. For instance, annealing at 600°C, Ni-30 wt. % Cr alloy showed two ordered phases, NiCr and NiCr 5. In the cases of Ni-5%, 10% and 15% Cr alloys, we observed a pure Ni fcc matrix with an atomic scale Cr-rich second phase dispersed uniformly.

PERSONNEL

Dr. H. W. Pickering, Professor of Metallurgy, and Dr. T. Sakurai, Assistant Professor of Physics, are principal investigators on this project.

Mr. Y. Kuk, the best graduate student in Physics Department, has been working 100% on this project for his Ph.D. since the beginning of this project. He will obtain his Ph.D. based on the research in this project this spring and plans to continue on this project as a post-doctoral scholar.

Mr. K. Markantonio, Metallurgy Department, left this project last summer to seek a job in industry. Mr. G. Marlow left our project when he changed his major.

Professor T. Inoue, Visiting Scientist from Japan, has spent approximately 75% of his time for this project, helping graduate students and building some of vacuum apparatus to be used for this project.

Mr. G. Bhatt, Physics Department, started to work on this project last summer, though his support came from internal funds. Mr. A. K. Birchenall, Metallurgy Department, has been working for this project for almost a year, being supported by Graduate Fellowship. He is expected to complete his Ph.D. research within a year.

PUBLICATIONS AND PRESENTATIONS ON THIS PROJECT

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3. T. Sakurai, Y. Kuk, H. J. Grabke, A. K. Birchenall and H. W. Pickering "Atom Probe Study of Grain Boundary Segregation in a Fe-0.04% P Alloy", Proc. 27th Intern. Field Emission Symposium, Tokyo (1980)
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