Hydrogen Absorption in Metals: A Field Ion Microscopy Study

Progress Report for the Period

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MASTER

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ABSTRACT

During the first year of this project, we have made progress in many areas: (1) sample preparation, (2) computer interfacing for automated data acquisition and (3) computer simulation of ion optics of atom-probes, in addition to the actual chemical compositional analysis of the Fe-Ti alloy samples and observations on hydrogen-induced microcracking. It is found that Ti segregates at the surface and grain boundaries when heated to and above 800°C. Some of the Ti atoms form clusters with carbon, nitrogen and oxygen as a nucleus. The formation and propagation of a microcrack involving hydrogen was documented for the first time on a truly atomic scale.

In the first year, research work has begun in the following areas:

- (1). Establishing the technique to prepare specimens of various alloys for field ion microscopy.
- (2). Interfacing atom-probes with a DEC MINC-11 computer.
- (3). Computer simulation of ion optics of atom-probes.
- (4). Compositional analysis of iron and Fe-Ti alloys.
- (5). H absorption in Fe-Ti alloys.

There are four graduate students who participated in this research, two of them working full time for this project and two others working partially for this project.

- (1) Establishing the technique to prepare specimens of various alloys for field ion microscopy.

It is very important for systematic investigation of alloy systems that we should be able to make alloys of desired compositions and to process them into fine wires (less than 0.1 mm diameter) from which needle-shape field ion emitter specimens are made. We have successfully made a number of alloys (Fe-Ti and Ni-Cu alloys) using a standard laboratory-type induction furnace for melting. We have designed our own automatic wire-drawing device which enables us to reduce the wire diameter successively from approximately 3 mm to 0.1 mm. This device has been just completed and is ready for use. For improved quality control in the ingot melting process, we are currently designing a small-size vacuum induction furnace suitable for our work. Since atom-probe study only requires very small amounts of materials, the furnace can be made in a relatively small size but should achieve high vacuum in order to avoid unwanted reaction with residual gases during the melting process.

(2) Interfacing atom-probes with a DEC MINC-11 computer.

The unique, superb feature of atom-probes--that individual atoms can be analyzed one by one precisely-- is accompanied with the hardship that collection of the high quality data is time-consuming and tedious. At each evaporation event triggered by a high voltage pulse during the data acquisition, at most one layer at the surface is probed. Therefore, tens of thousands of pulse evaporations are necessary to accumulate statistically meaningful data. This cannot be achieved without incorporating an automated data acquisition system. A DEC MINC (Modular Instrument Computer)-11 was chosen for this purpose, since this computer was designed primarily for controlling laboratory instruments. Interfacing this computer with the time-of-flight atom-probe is currently being carried out and is expected to be completed in the middle of March. The interfacing with the other atom-probe, the magnetic-sector, has just begun and will be completed before this summer.

(3) Computer simulation of the ion optics of atom-probes.

It was realized soon after our attempt of automated data acquisition that computer interfacing with the atom-probes requires much more information on the ion trajectory of atom-probes than that needed for manual operation. It has also become clear that the present time-of-flight atom-probe may not have the detection efficiency satisfactory for study of some systems and interfaces. In order to solve these problems we are currently undertaking computer simulation for the ion optics. In the case of the time-of-flight atom-probe, there are several major questions, such as (a) the effect of the shape and width of the nanoseconds high voltage trigger pulse, (b) The focusing efficiency of a Porschenrieder electrostatic lens and (c) the effect of the alignment of the tip with respect to

Porschenrieder electrostatic lens optical axis. Our preliminary computer results suggest that the size of a Porschenrieder electrostatic lens should be increased considerably in order to achieve higher detection efficiency. Now that many groups over the world are planning to build atom-probes similar to our high-resolution ones, the results we obtain through computer simulation is extremely valuable not only to our own project but also to the Field Emission Community in general. Computer simulation of the magnetic-sector atom-probe is about to be completed and this new result will be incorporated in the interfacing program being prepared.

(4) Compositional analysis of iron and Fe-Ti alloys.

In the initial stage of our study on Fe alloys and hydrogen interactions in them, we have found a persistent oxide formation at and near the surface. This is not peculiar to Fe-Ti alloys since we concurrently have observed the same feature for stainless steel and Ni-Cr alloys. It was also noticed that other impurities, such as carbon and nitrogen, concentrated at the interface more than expected. Realizing that there have been few successful investigations on these subjects on an atomic scale, we focused our attention on the compositional analysis of Fe and Fe-Ti alloys under various conditions.

In the case of pure iron, we have detected various forms of iron-oxide ions. Undoubtedly some of them are byproducts (artifacts) of the dissociation process under high electric field as pointed out in our original proposal. In order to understand the dissociation processes, and to document them quantitatively, various iron-oxide emitters (FeO , Fe_3O_4 and Fe_2O_3) are currently being prepared for atom-probe study.

In the case of Fe-Ti alloys, we have so far studied several alloy

samples (Fe - xwt.% Ti; $x = 0.005, 0.15, 0.29$, and 1.5). Although preliminary, some of the samples ($x = 0.15$ and 0.29) yielded several interesting observations. Ti atoms segregate to the surface and grain boundaries when heated to and above 800°C . A decreasing titanium concentration profile extends over several atomic layers and even at 20 atomic layers from the surface, the Ti concentration is above the nominal bulk value. In the outermost surface layer and in the grain boundaries, Ti is present in the oxide form, mainly TiO and TiO_2 , whereas in the near-surface bulk, it is present as randomly dispersed Ti atoms and to a lesser degree as cluster of Ti atoms around C, N, and O. The observation of stable Ti clusters with C and N is most exciting since their existence has been hypothesized as the main cause of hardening at slightly elevated temperatures in the case of iron and its alloys containing small amounts of titanium. These results are as such worthy of publication on their own merit. (Preprint is attached.)

(5). Hydrogen absorption in Fe-Ti alloys.

A striking observation was made using a Fe-0.29wt% Ti sample when it was exposed to hydrogen. A small microcrack (approximately 200 Å in length), which accidentally came into the field of view of a field ion image, became noticeably large when the tip was heated to 950°C for 5 min. in the presence of hydrogen (1 Torr). This crack could be easily reduced in size by gradually field-evaporating the surface area. The propagation of this crack was repeated several times and reproducible results were obtained. It was also found that the microcrack grows when heated to 950°C but not when heated to lower temperatures (less than 800°C). Formation and propagation of the microcrack are expected to have occurred during the cooling following the $\gamma \rightarrow \alpha$ phase transformation. Residual

stresses and the actual (supersaturated) hydrogen concentration associated with a lower solubility limit for hydrogen in bcc α -iron, compared to that in fcc γ -iron which is the stable phase at the hydrogen charging temperature, 950°C, (40ppm H dissolves in γ -iron at 950°C vs. 1ppm in α -iron at 900°C for $P_H = 1$ Torr.) are reasoned to be the main contributing factors leading to crack formation and growth.

After approximately 30 min. of the above-mentioned temperature cycling a portion of the tip along the crack path ruptured and became detached from the tip surface.

Large amounts of hydrogen were detected along the crack, but not elsewhere on the surface, suggesting a buildup of hydrogen at the crack site. Almost all Fe atoms in the crack region were in the form of FeH. We believe that this observation of the formation and propagation of a microcrack due to the presence of hydrogen is new, and holds great promise for future experiments investigating the role of hydrogen in metals and the mechanism of hydrogen embrittlement. We are currently preparing a manuscript on this result.

PERSONNEL

Dr. H. W. Pickering, Professor of Metallurgy, and Dr. T. Sakurai, Assistant Professor of Physics, are principal investigators on this project. Dr. Pickering spent approximately 10% of his time for this project throughout the year supervising graduate students in preparing alloys, designing a wire-drawing device and atom-probe work. Dr. Sakurai spent approximately 20% of his time working with four graduate students in computer interfacing, computer simulation and atom-probe studies.

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 the project. Mr. K. Marcantonio, Metallurgy Department, joined this project last September and is working for a M.S. Mr. G. Marlow, Physics Department, began his work on computer simulation last August. Mr. G. Robertson, who will obtain his Ph.D. this spring, also participated in this project by operating the time-of-flight atom-probe and ordinary field ion microscopes.

PUBLICATIONS AND PRESENTATIONS ON THIS PROJECT.

1. H. W. Pickering, Y. Kuk, T. Sakurai, "Atom-Probe Analysis of Segregation in Fe-0.15wt.%Ti," Appl. Phys. Lett. 36, (1980).
2. Y. Kuk, T. Sakurai, and H. W. Pickering, "The Direct Observation of the Formation and Propagation of a Microcrack Associated with Hydrogen by Atom-Probe Field Ion Microscopy," Appl. Phys. Lett. to be submitted.
3. H. W. Pickering, Y. Kuk, and T. Sakurai, "Application of a High-Performance Time-of-Flight Atom-Probe for Analysis of Solute Distribution and of Hydrogen in Metals," Proceedings of an International Conference on Effect of Hydrogen on Behavior of Metals, Wyoming, August, 1980.
4. Y. Kuk, T. Sakurai, and H. W. Pickering, "Propagation of a Microcrack due to Hydrogen by Field Ion Microscopy," Proceedings of an International Conference on Effect of Hydrogen on Behavior of Metals, Wyoming August, 1980
5. H. W. Pickering, Y. Kuk, and T. Sakurai, "Atom-Probe Field Ion Microscopy Study of Fe-Ti Alloys," The Electrochemical Society Annual Meeting at St. Louis, Missouri, May, 1980.

Preprint removed