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STUDY OF FERRITE FORMATION IN NEUTRON
IRRADIATED AUSTENITIC STAINLESS STEELS

Progress Report

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ABSTRACT

A vibrating reed magnetometer has been constructed for making magnetization measurements on small irradiated samples as a function of applied field. The magnetometer can be operated at temperatures in the range 4°K to 500°K and can detect a magnetic moment of 4×10^{-5} erg/ O_e with a signal to noise ratio of 20. A simple procedure for calibration of the magnetometer using a small nulling coil has been devised.

The magnetometer has been used to measure magnetization curves of an irradiated type 316 austenitic stainless steel specimen at two different temperatures. The results confirm that the specimen contains numerous small particles of a magnetic phase which is presumed to be ferrite. Transmission electron microscopy of the irradiated specimen has been performed, but the results were not conclusive as to the presence or absence of the ferrite. Further work is in progress to study the effect of post-irradiation heat treatment and irradiation exposure and to fully characterize particle size distribution.

PROGRESS REPORT

I. Introduction

Most of our effort in the past nine months has been devoted to designing, constructing, and calibrating the vibrating reed magnetometer. A number of unforeseen problems have resulted in this phase of the work taking longer than expected. Since the entire program is based on the results of magnetization measurements on the various specimens, we have not been able to carry out experiments in the four task areas identified in the original proposal. We expect to complete some work in these areas within the next three months as the magnetometer is now completed. A brief description of the magnetometer and some of the problems encountered in its construction are given below. In addition, some measurements of the temperature dependence of the magnetization curve and some electron microscopy results are described.

II. Vibrating Reed Magnetometer

The vibrating reed magnetometer used in this work is based on a device described by Zijlstra⁽¹⁾. However, Zijlstra's design is not suited to making measurements at cryogenic temperatures, and thus we were forced to introduce several new features to accomplish all of the objectives of our research. The most important new feature added to Zijlstra's design was the use of a capacitance pick-up to measure vibration amplitude instead of the optical microscope. This modification allows the instrument to be used conveniently at cryogenic temperatures and also reduces the amount of radiation exposure to the experimenter when working on radioactive specimens. There are some other advantages

to using the capacitance pick-up device such as being able to amplify the electronic signal produced and apply it to the gradient coils so that the system is self-resonant. However, the capacitance pick-up has one great disadvantage in that it makes the magnetometer a much more complicated device.

The head of the magnetometer device is sketched in Fig. 1. The most important parts of the magnetometer are the two gradient coils, the capacitor plate, and the reed. The two gradient coils are each mounted on one inch O.D. stainless steel disks that can be adjusted vertically on three 1/8 inch diameter x .010 inch wall stainless steel tubes. The upper stainless steel disk also supports a stainless steel block on which the vibrating reeds are mounted. The specimens, approximately 0.02 inch x 0.02 inch x 0.01 inch, are glued to the end of the (0.002 inch x 0.06 inch x 0.375 inch) copper reed inside the center of a small nulling coil. An electrode extends through the upper gradient coil and terminates in a small capacitor plate that is parallel to the surface of the reed. The variation of capacitance between this plate and the reed produces a signal that indicates the amplitude of vibration of the reed. The two gradient coils are connected in series opposition so that the magnetic field at the midplane between the two coils is zero but the vertical gradient is large. An alternating voltage signal applied to the gradient coils at the resonant frequency of the reed causes the reed to vibrate if the sample attached to the end has a magnetic moment. Separate heaters and thermocouples are attached to each stainless steel disk, so that the temperature of the specimen can be held constant during the measurement. The entire device fits inside a 1.375 inch O.D. by 0.035 inch wall stainless steel tube which can be evacuated and

inserted into a solenoid.

Accurate calibration of the magnetometer proved to be a problem that required much time. The vibration amplitude of the reed is proportional to the magnetic moment of the sample which is affixed to the reed and to the amplitude of magnetic field gradient at the sample. The vibration amplitude is inversely proportional to the internal friction of the reed. The magnetic field gradient at the sample depends on the spacing of the gradient coils relative to the specimen, as well as the amplitude of the current signal supplied to the coils.

The output signal provided by the capacitance pick-up depends on the spacing between the capacitor plate and the reed and on parameters of the electronic circuitry. The initial plan of operation of the magnetometer was to vary the amplitude of current signal to the gradient coils to maintain a constant amplitude of vibration of the reed and thus the magnetic moment of the sample would be inversely proportional to the amplitude of the gradient coil current signal. The proportionality constant was to be determined by measuring the known magnetic moment of a suitable standard.

Procedures were worked out to keep all of the parameters affecting calibration at fixed values. Since capacitor plate spacing can vary with temperature due to differential thermal expansion, a technique was needed to correct this source of calibration error. We observed that the signal generated by the capacitance pick-up device will not be a sinusoid for a sinusoidal variation of vibration amplitude since the capacitance is inversely proportional to the plate spacing. An equation was derived to determine the capacitance plate spacing from the shape of the signal generated. However, in practice, it was difficult to obtain accurate results with this

technique. This problem has been solved by a procedure discussed below.

Internal friction is another parameter that may change considerably with temperature, and thus, the calibration procedure involved measurement of the internal friction of the reed at each temperature of operation. Realizing that each procedure involved in calibration will introduce some error in the final result, it can be seen that the magnetization measurements would have considerable error. Within the past month, we have devised and tested a simple remedy for all of the calibration problems stated above. A small coil consisting of 10 turns of 0.003 inch diameter wire was attached to the end of the vibrating reed so that the sample is mounted in the center of this coil. The magnetic moment produced by passing a current through the coil can be accurately calculated from the coil dimensions and the current. This coil can be used either to produce a known magnetic moment for calibration of the magnetometer or to null out the magnetic moment of the specimen. Since our calculations show that the fields produced by the coil will be negligible compared to the solenoid field used to magnetize the sample, the latter mode of operation will be used. Thus, to make a measurement of the magnetic moment of a sample at any applied field, we simply adjust the current through the nulling coil until the reed stops vibrating and the nulling coil current is a measure of the magnetic moment of the sample. Measurements with this technique have shown that a magnetic moment of 4×10^{-5} erg/O_e can be detected with a signal to noise ratio of 20:1. This magnetic moment corresponds to the saturation magnetization of 0.04% ferrite in our samples.

II. Temperature Dependence of Magnetization Curves

The original proposal for this work was based on magnetization measure-

ments of irradiated stainless steel specimens by Stanley and Garr⁽²⁾. Stanley and Garr interpreted their data using theories of superparamagnetism to show that many fine magnetic particles existed in their specimens. Stanley and Garr were unable to measure magnetization curves at temperatures other than room temperature and were then unable to verify a critical feature of superparamagnetism, i.e., the magnetization curves measured at different temperatures should superimpose when plotted against field reduced by absolute temperature. We have now carried out magnetization measurements on an irradiated specimen at two temperatures. The results are shown in Fig 2 as magnetization (arbitrary scale) versus solenoid current divided by absolute temperature. The magnetic field is directly proportional to the solenoid current. The sample used for these measurements is a portion of a sample previously measured by Stanley and Garr and is the one having the greatest magnetic moment of any tested by them. This sample has some residual magnetic moment, and the residual magnetic moment is greater at lower temperatures. This effect is expected for superparamagnetism of a collection of particles having a range of sizes. Particles above a critical size should no longer exhibit paramagnetic behavior and should have a residual moment after being once aligned with a magnetic field. The critical size for paramagnetic behavior should decrease as the temperature decreases and thus, for a given collection of particles, the residual moment should increase as the temperature decreases. With these considerations in mind, the magnetization curves show very good agreement with the expected temperature dependence for superparamagnetism, as the two sets of data should be shifted vertically to compensate for the different residual moments and thus, the overlap of the two sets of data would be very good.

The results of this test show definitely that the analysis of the magnetization curves in terms of superparamagnetism is basically correct, and that we need not be concerned with the possibility that the shape of the magnetization curves is due to a geometrical effect. There exists the possibility that the particle size determined from the magnetization curves could be in error if the magnetic precipitate was not ferrite but some other magnetic phase with a different saturation magnetization. The equation for particle volume is $\bar{V} = kT/H_h M_s$, where H_h is a parameter determined from experimental measurements, M_s is the saturation magnetization of the particle, k is Boltzmann's constant, and T the absolute temperature. For example, the carbide, Fe_3C , is ferromagnetic with a saturation magnetization about 75% of that of ferrite. This difference in saturation magnetization is not enough to affect the particle size calculations appreciably. Although Fe_3C would not be expected to form in stainless steel, it is possible that some unknown magnetic carbide or other phase forms. However, even if this phase had a saturation magnetization factor of 10 larger or smaller than ferrite, the calculated particle diameter would only be changed by a factor of about 2.2. In view of the uncertainties about the identification of the magnetic phase, it is important to have information from electron microscopy to help in this identification.

III. Electron Microscopy

A technique for preparing thin foils for transmission electron microscopy has been established, and specimens from a control sample and an irradiated sample have been prepared. A preliminary examination of these specimens has been done; however all features of the microstructure have not been completely identified.

Figure 3 shows the typical microstructure of the control sample. No precipitates are visible. Selected area diffraction patterns of this specimen are consistent with what one would expect from single phase austenite. The dark lines in Fig. 3 are dislocations.

A transmission micrograph of the irradiated sample is shown in Fig. 4. A foil thickness of 750 Å, determined from slip traces present, was used to calculate a void density of 1.6×10^{15} , which is in good agreement with published values for this sample⁽³⁾.

Figure 5 is a selected area diffraction pattern of the area shown in Fig. 4. Satellites around the (200) austenite spots are due to double diffraction from an as yet unidentified second phase. Diffuse rings barely visible inside and outside of the (200) spots are further evidence for the existence of a second phase.

The second phase producing the diffraction effects described above may not be resolvable in the bright field image; however contrast within the matrix in Fig. 4 is non-uniform to the extent that dark spots, smaller in size than the voids present, are visible and may be due to diffraction effects from particles of a second phase. Some of these spots can be seen within the voids themselves. It is our intent to continue analysis of this and other samples, using dark field techniques and diffraction pattern analysis in an effort to positively identify the source of contrast in the transmitted bright field image and to identify the second phase particles present.

IV. Future Work

At this time we have obtained 15 specimens of type 316 stainless steel that were irradiated to a fluence of 2.3×10^{22} n/cm² at 425°C. Each of these specimens represents a different combination of pre- and post-irradiation heat treatment, and the magnetization curves of all of these samples have been previously measured at room temperature by Stanley and Garr. In addition, 7 samples that were irradiated to a fluence of 4.2×10^{22} at 500°C and 600°C have been received. One of these samples is type 321 stainless; the remainder are type 316. Also on hand is a proton irradiated sample that has been sectioned into two parts along the proton range so that a different amount of displacement damage is present in each section.

In the remaining three months of this contract we intend to carry out the following work:

1. Perform additional heat treatments followed by magnetization measurements on some of the samples that have been irradiated to 2.3×10^{22} to see if we can increase the amount of magnetic phase on the size of the magnetic particles so that they can be observed more readily in the electron microscope.

2. Magnetization measurements on some of the samples irradiated to 4.2×10^{22} n/cm². Since these samples were irradiated at different temperatures than the lower fluence samples, it will not be possible to determine the effect of fluence directly, but we are hoping that these samples might be more suitable for electron microscopy studies.

3. Measure the magnetization curves of the proton irradiated samples. These measurements should give an indication of how the ferrite formation depends on fluence in the proton irradiation case.

4. Make careful measurements of magnetization versus field at several different temperatures on a few of the samples so that particle size distributions can be characterized more accurately.

5. Additional electron microscopy will be performed on the specimen discussed above to try to identify the phase responsible for the diffuse rings in the diffraction pattern. Any specimens that appear to have large amounts of magnetic phase, as discovered in the work outlined above, will be examined by microscopy.

The principal investigator, J. T. Stanley, has devoted the following percentage of his time to this project: 100% during two summer months, 33 1/3% during the academic year. He expects to devote 33 1/3% of his time to the project for the remaining three months.

Figure 1. Magnetometer Head

Figure 2. Magnetization vs. Temperature Reduced Solenoid Current.
 Type 316 stainless steel irradiated to 2.3×10^{22} n/cm² at 425°C.
 Open symbols represent values obtained with increasing solenoid
 current, filled symbols with decreasing current.

Figure 3: Control sample. No evidence of second phase particles in transmission micrograph. Dark lines in figure are dislocations. Mag. 65,000X.

Figure 4: Sample irradiated to 2.3×10^{22} n/cm², at 425°C. Figure shows voids. Dark regions in matrix may be due to diffraction contrast from unidentified second phase particles. Light bands are slip traces. Mag. 65,000X.

Figure 3

Figure 4

Figure 5: Selected area diffraction pattern of region shown in Figure 4. Satellites near (200) spots are due to double diffraction from second phase particles. Diffuse rings indicate the presence of small random second phase particles.

Figure 5

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