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STUDY OF FERRITE FORMATION IN NEUTRON
IRRADIATED AUSTENITIC STAINLESS STEELS

Progress Report

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ABSTRACT

Magnetization measurements have been carried out on a number of neutron irradiated austenitic stainless steel specimens to determine the total ferrite content of these specimens. Two heats of Type 316 and one heat of Type 321 stainless steel were neutron irradiated at temperatures of 425, 530, and 620°C to fluences of 1.8 and 3.5×10^{22} n/cm² ($E > 0.1$ MeV). However, the field of possible combinations of irradiation conditions and specimen composition and thermo-mechanical history was only partly covered by this investigation. The maximum amount of ferrite (5.6%) was found in the Type 321 irradiated at 530°C to 3.5×10^{22} neutrons/cm². Minimum amount of ferrite (0.08%) was found in one heat of Type 316 irradiated to 3.5×10^{22} neutrons/cm² at 620°C. However, under similar irradiation conditions the other heat of Type 316 contained 1.9% ferrite. A third heat of Type 316 was proton irradiated at 500°C with 1 MeV protons. A maximum of about 21% ferrite was observed in this specimen.

The magnetization curves for these specimens indicate that the ferrite phase is present as fine particles. The temperature dependence of the magnetization curves follows the Curie law for some specimens but Curie-Weiss law behavior is indicated for most of the specimens. Electron microscopy of the Type 321 specimen confirmed the presence of fine ferrite particles.

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PROGRESS REPORT

I. Introduction

In the previous progress report⁽¹⁾ we described difficulties encountered in constructing and calibrating the vibrating reed magnetometer. The difficulties with the magnetometer have all been eliminated and a large number of magnetization measurements have been made in the past twelve months. However, most of the magnetization measurements were made at fields below 1350 oersted because the superconducting magnet that had been obtained on loan from the Physics Department did not have a sufficiently uniform field. The superconducting magnet purchased by the Engineering College was delivered at the end of November, and high field measurements have now been made on all of the available irradiated samples. However, the post irradiation annealing studies planned for this period have been delayed because of the delay in obtaining the high field measurements.

In describing the results of the magnetization measurements we present first just the calculated ferrite content for each of the irradiation conditions and then a discussion of conclusions that can be drawn from these results. The results may seem somewhat unsatisfactory in that we can't answer conclusively a number of important questions such as, what is the effect of neutron fluence on the amount of ferrite formed? However, it must be remembered that we had no choice in the selection of specimens and must make use of the specimens irradiated for other programs, since the neutron irradiations require 2 1/2 to 3 years to obtain the required fluence.

II. Magnetization Measurements

The composition of the alloys used in this study are given in Table 1. Prior to irradiation, the samples were given one of the heat treatments listed in Table 2. A short description of the resulting pre-irradiation microstructure is also given. Table 3 gives results of magnetization measurements in terms of percent ferrite for the various irradiation conditions. Note that the first four entries in this table were determined in an earlier study.⁽²⁾ The irradiation damage is given in terms of calculated displacements per atom, dpa, since we wish to compare neutron and proton irradiations. The number of dpa are calculated according to the recommendations of D. G. Doran⁽³⁾ with 6 dpa for a neutron fluence of $1 \times 10^{22} \text{ n/cm}^2$ ($E > 0.1 \text{ MeV}$). The dpa for the proton irradiated samples were calculated by D. Keefer.⁽⁴⁾ The damage in the proton irradiated specimens is a function of depth as the total range of 1 MeV protons is about 7.3μ . The two damage conditions for proton irradiation were obtained by sectioning a single sample along different parts of the proton range. The first specimen was obtained from the front surface to a depth of 4.8μ and the damage varied from 0.68 dpa at the surface to 1.4 dpa at 4.8μ . The second specimen was obtained from a depth of 4.1μ to 7.4μ and the damage varies from 1.2 dpa at 4.1μ to 4 dpa at 6.7μ to 0.0 at 7.4μ . The damage between 6.7μ and 7.4μ cannot be calculated with any accuracy. The value of 3 dpa given in Table 3 for this specimen is just an educated guess for the average dpa.

What conclusions can be drawn from these results? Firstly, we cannot make any statement about the effect of neutron fluence on the amount of ferrite since the two different neutron fluences occurred at different temperatures. However, for the proton irradiated specimens the amount of ferrite is approximately linear with dpa up to 21 percent ferrite at 3 dpa. The large difference in amount of ferrite between the proton irradiated specimens and the neutron irradiated specimens is probably mainly due to the proton damage being more effective than neutron damage in promoting ferrite formation. However, some of the differences may be due to composition and heat treatment differences.

Composition differences are apparently quite important in determining the amount of ferrite produced for particular irradiation conditions. Comparing items 5, 6, 7 in Table 3 with items 11, 12, 13 we see that for two different heats of 316 stainless all other conditions being identical heat 1 samples had 2 to 3 times the ferrite of heat 2 samples. Again comparing items 8, 9, 10 with 14, 15, 16 in Table 3, the heat 1 samples had 8 to 20 times the ferrite of heat 2 samples. Thus the effect of composition on amount of ferrite is more pronounced for the higher irradiation temperature. Also comparing item 17 with items 5, 6, 7 of Table 3 we see that the 321 stainless steel has 2 to 3 times the amount of ferrite of any of the 316-1 samples. Unfortunately in this case the specimens all have different heat treatments. In order to try to pin down the composition variables we calculated the free energy difference between the austenite phase and the ferrite phase of the same composition using the procedures described by Kaufman and Breedis.⁽⁵⁾

At 700°K the calculated free energy difference between austenite and ferrite is -150 cal/mole for 316-1, -33 cal/mole for 316-2, -26 cal/mole for 321-1, and -114 cal/mole for 316-3. Thus from these calculations 316-1 should have the most stable austenite followed by 316-3, 316-2 and then 321-1. The order of instability of austenite as calculated does not agree with the order of ferrite formation as shown in Table 3 even if we just compare neutron irradiations. Comparing the neutron irradiated specimens at irradiation temperature 530°C we find that the 321-1 specimen has the most ferrite which is in agreement with it having the least stable austenite by calculation. However, the calculation shows that the austenite in 316-2 should have about the same stability as in 321-1 yet 316-2 had the least amount of ferrite of the three different compositions.

The specimens of 316-2 were cylinders 3.8 mm diameter by 3.5 mm long while the remaining specimens were cut from sheet approximately 0.25 mm thick. Since the specimens from 316-2 showed much less ferrite than those from 316-1 under the same irradiation conditions we thought that ferrite formation might be greater near the surface of a specimen. An experiment was performed to determine if this was the case. One of the specimens, item 3, Table 3, was electropolished to remove approximately 1/2 of its volume. The volume removed was distributed fairly uniformly over the surface. After electropolishing the magnetization was remeasured and found to have increased by a factor of about 1.5. Thus, we must conclude that, for this sample at least, the relative amount of ferrite is less near the surface and that surface effects

cannot account for the lower amount of ferrite formation in the 316-2 specimens compared with 316-1 specimens.

The effect of pre-irradiation heat treatment on amount of ferrite formation is shown in comparing items 1, 2, 3, 4 where heat treatment C has approximately 2 times the amount of ferrite of the other heat treatments. For the irradiations at 530 and 620°C the effect of pre-irradiation heat treatment is not significant but unfortunately heat treatment C was not included in these irradiations. According to an article by Weiss and Steckler⁽⁶⁾ the σ phase in 316 stainless is enriched in Cr and Mo compared to the matrix. The heat treatment C causes precipitation of sigma phase and the resulting composition change of the matrix could make the austenite phase less stable.

The effect of irradiation temperature is somewhat obscured by the effects of fluence, composition, and pre-irradiation heat treatment. Comparing items 5, 6, 7 with 8, 9, 10 in Table 3, we see little difference between irradiation temperatures of 530°C and 620°C for 316-1. Comparing item 2 with 5 and 8 we see that irradiation at 425, 530 and 620°C for heat treatment B produces about the same amount of ferrite if we make the assumption that ferrite content is proportional to damage.

For 316-2 samples the effect of irradiation temperature is quite pronounced, the samples irradiated at 530°C having 4 to 7 times the ferrite of samples irradiated at 620°C. The different response to irradiation temperature could be due to differences in composition.

The results discussed above have made use of just the saturation magnetization, i.e., the magnetization at high field, for the various specimens. The shape of the magnetization versus field curves can also be used to gain information about particle size and distribution. In a previous report we stated that the magnetization versus temperature reduced field curves superimposed for measurements made at two different temperatures and that this result verified the assumption that the particles behaved as superparamagnetic particles. The particle size analysis given by Stanley and Garr⁽²⁾ was based on superparamagnetic particles with no interaction between particles, i.e., Curie law behavior. The more extensive measurements made in the past twelve months show that in many cases the Curie law is not obeyed but instead the Curie-Weiss law is obeyed with critical temperatures as high as 300°K. Thus, there is a strong interaction between particles in many of the samples. Since the ferrite volume fraction is less than 10% in all cases except the one proton irradiated sample we expect that the particles will have to be clustered to give a strong interaction. Some of the electron microscopy results show clusters of particles.

The magnetization curves for these samples are rather complex because of the large range of particle sizes present in the samples as well as the clustering effect mentioned above. We haven't yet figured out the best way of analyzing the curves to determine the maximum amount of particle size information. Stanley and Garr⁽²⁾ stated that all samples except one showed zero remnance. However, the more precise measurements at low fields that are possible with

the vibrating reed magnetometer have shown that all of the samples have a small remnance. A hysteresis curve of one sample is shown in Figure 1.

We have also found that the remnance of these samples is time dependent. This is the expected behavior for single domain particles that are nearly small enough to behave superparamagnetically. We have used the relaxation of remnance magnetization to determine particle size distribution in one sample. This particular sample shows approximate Curie law behavior. Figure 2 shows a curve of complementary integrated volume fraction of particles versus particle size for a specimen of item 3, Table 3, after irradiation at 425°C and also for a specimen of the same item after additional anneals at 500°C. In analyzing the remnance relaxation the particle shape is important, and we assumed prolate spheroids with axial ratio 2.5. This makes the maximum particle size about 30 Å diameter x 75 Å long. It seems that the post irradiation anneal produces a relatively greater increase in the population of the smaller particle sizes than in the larger particle sizes. The assumption of spherical particles requires unreasonably large particles to fit the data. The dashed lines in Figure 3 show approximately how the distribution must vary to fit the high field results obtained previously by Stanley and Garr⁽²⁾ for these specimens.

Future work: Magnetization Measurements. In the remaining three months of the present contract we plan to carry out post-irradiation annealing studies on some of the specimens and to perform additional measurements to determine if ferrite content changes near the surface of the specimens. One graduate student is working independently on the problem of analyzing the magnetization curves to obtain maximum particle size information.

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% time to the project during the remaining three months.

III. Electron Microscopy

The presence of ferrite particles in neutron irradiated 321 has been confirmed by electron diffraction. Figure 3 is a bright field image of a region containing portions of four austenite grains. Visible in the most prominent grain are numerous particles which appear dark in the bright field image. A dark field image of the same region is shown in Figure 4. A (110) reflection from the b.c.c. ferrite, determined from analysis of the diffraction pattern shown in Figure 5, was used to obtain Figure 4. The particles, which appear bright in the dark field, appear randomly distributed in general; however two large clusters appear to the left of center in Figure 4.

A selected area diffraction pattern, taken with a 32 μ aperture, is shown in Figure 5. Four austenite grains contribute to the pattern, and are partially responsible for the large number of spots. The pattern was analyzed by determining the camera constant of

the microscope and calculating the ring patterns for both austenite and ferrite assuming lattice parameters of $3.60 \text{ \AA}^{(6)}$ and $2.87 \text{ \AA}^{(7)}$ respectively. Superposing the calculated ring patterns on the diffraction pattern showed that neither pattern could account for all reflections, and, more important, a number of reflections appearing midway between the (220) and (311) rings of austenite fell directly on the (211) ring of ferrite. All other reflections which did not fit the austenite pattern in turn fit the ferrite pattern.

It was possible to determine the reciprocal plane of reflections produced by each austenite grain. The two most prominent are shown in Figures 6 a and b. Furthermore it was possible to assign the ferrite spots to four reciprocal lattice planes; the two most prominent are shown in Figures 6 c and d.

The fact that the diffraction pattern contains distinct spots from the ferrite rather than diffuse rings suggests a strong orientation relationship between the two phases. A preliminary effort to identify this relationship has been made but the results are not complete. The individual patterns shown in Figure 6 suggest that one possible relation is the [110] of austenite aligning with the [111] of ferrite, as can be seen by comparing 6 a with c. However, it has not been definitely established that the ferrite pattern 6c is produced by particles present in the austenite grain 6a.

If in fact an orientation relationship exists, as the data strongly suggest, then the contrast in Figure 3 is probably due to

coherency strains around each ferrite particle. In this situation one would expect to see the so-called line of zero contrast perpendicular to the direction of the diffraction vector if the particles have spherically symmetric strain fields. As can be seen in Figure 3 this line of zero contrast is not present suggesting that the particles do not have spherical symmetry. What can be seen in several particles is a dark band. A possible explanation for their appearance is a magnetic interaction between the electron beam and two closely spaced particles with opposite directions of magnetization, similar to contrast produced at domain walls. Further evidence that the particles are magnetic is the apparent splitting of several diffraction spots which have been identified as being produced by the ferrite particles.

Examination of several samples of 316 stainless have shown the presence of second phase particles which appear similar to those discussed above. However, diffraction studies have not produced results which positively identify the particles as ferrite.

A continued effort will be made to establish the lattice orientation relation between ferrite and austenite through more extensive dark field studies on the sample discussed above. Also efforts to identify the particles observed in the 316 samples will be continued, and additional samples in which magnetic measurements indicate the presence of ferrite will be thinned and examined.

IV. Summary

1. Increased magnetization indicating the formation of the ferrite phase has been observed in proton and neutron irradiated austenitic stainless steel specimens for irradiation temperatures in the range 425-630°C.
2. The important parameters that influence the amount of ferrite formed are pre-irradiation thermo-mechanical history, post-irradiation heat treatment, chemical composition, irradiation temperature, and irradiation damage level.
3. Definite conclusions about the effects of the parameters listed in (2) above cannot be made at present with the following exception: ferrite content is proportional to damage level in proton irradiated Type 316 at least to 21% ferrite at 3 dpa.
4. Ferrite particles have been identified in Type 321 stainless steel and their size, shape and distribution is in approximate agreement with predictions based on the magnetization curves.
5. The magnetization behavior of the specimens is complicated because of a large range of particle sizes and interactions between particles.

Figure 1

Figure 2

Complementary Integrated Volume Fraction
 versus Particle Volume for a specimen
 of 316-1 Heat Treatment C neutron
 irradiated to a fluence of
 3.5×10^{22} neutrons/cm² at 425°C

Figure 3. Bright Field image of specimen
Dark particles in central grain are ferrite.

Figure 4. Dark field image of Figure 3. (110) ferrite
reflection.

←0.1μ→

Figure 5. Selected area diffraction pattern of region shown in Figure 3. 32μ aperture.

Fig. 6. The four most prominent reciprocal lattice planes present in Figure 5. Open circles indicate the location of diffraction spots on Fig. 5 which fit the respective patterns. Note the twin relation between a and b. The straight grain boundary in Fig. 3 is a twin boundary with a (111) twin plane.

- a) $[011]$ zone axis f.c.c.
- b) $[011]$ zone axis f.c.c. (twin of a)
- c) $[111]$ zone axis b.c.c.
- d) $[113]$ zone axis b.c.c.

a) $[011]$ zone axis f.c.c. b) $[011]$ zone axis f.c.c.
twin related to a) c) $[111]$ zone axis b.c.c. d) $[113]$ zone axis b.c.c.

Table 1
Composition of Alloys

Alloy	C	Mn	P	S	Si	Ni	Cr	Cu	Mo	Ti	Co
316-1	0.06	1.68	0.022	0.017	0.51	13.63	17.33	0.075	2.32	----	0.01
316-2	0.037	1.51	0.021	0.015	0.42	11.56	16.65	0.13	2.39	----	0.13
316-3		1.4				13.2	16.7		2.0		
321-1	0.058	1.44	0.022	0.005	0.50	10.47	17.61	0.12	0.15	0.47	

Table 2
Pre-Irradiation Heat Treatments

Designation	Treatment	Preirradiation Microstructure
A	1 hr at 980°C	Solution annealed, no precipitates
B	1 hr at 980°C + 8 hr at 760°C	Carbides, primarily at grain boundaries
C	100 hr at 760°C	Carbides on grain boundaries, carbides and sigma particles in matrix, mostly recrystallized
D	30 min at 1120°C + 25% cold-rolled + 24 hr at 480°C	No precipitates, cold work retained
E	30 min at 1120°C + 25% cold-rolled	No precipitates, cold worked structure
F	Same as B + 22% cold-rolled	Carbides, primarily at grain boundaries; cold worked structure
G	Mill annealed	-----

Table 3
Ferrite Percentages

Item	Alloy	Heat Treat- ment	Irradiation Conditions			Ferrite, percent*
			Particle	Damage, dpa	Tempera- ture	
1	316-1	A	neutron	10.8	425°C	0.5
2	316-1	B	neutron	10.8	425°C	0.8
3	316-1	C	neutron	10.8	425°C	1.3
4	316-1	D	neutron	10.8	425°C	0.6
5	316-1	B	neutron	21	530°C	1.6
6	316-1	E	neutron	21	530°C	2.4
7	316-1	F	neutron	21	530°C	2.0
8	316-1	B	neutron	21	620°C	2.0
9	316-1	E	neutron	21	620°C	1.7
10	316-1	F	neutron	21	620°C	1.9
11	316-2	B	neutron	21	530°C	0.8
12	316-2	E	neutron	21	530°C	0.7
13	316-2	F	neutron	21	530°C	0.7
14	316-2	B	neutron	21	620°C	0.2
15	316-2	E	neutron	21	620°C	0.1
16	316-2	F	neutron	21	620°C	0.1
17	321-1	G	neutron	21	530°C	5.6
18	316-3	G	proton	1	500°C	7.0
19	316-3	G	proton	3	500°C	21.0

*estimated accuracy $\pm 15\%$ x indicated value

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