C00-2317-4

STUDY OF FERRITE FORMATION IN NEUTRON
IRRADIATED AUSTENITIC STAINLESS STEELS

Progress Report

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March 1, 1975 - February 29, 1976

PREPARED FOR THE U. S. ATOMIC ENERGY COMMISSION
UNDER CONTRACT NO. AT(11-1)-2317

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ERC-R-76007

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Abstract

Magnetization measurements have been carried out on a number of neutron irradiated austenitic stainless steel specimens. The variation of magnetization with field indicates that the magnetic phase particles are very small so that the particles show superparamagnetic behavior. The temperature dependence of the magnetization indicates that more than one ferromagnetic phase may be present in some of the specimens.

Post-irradiation annealing at 500°C increased the quantity of magnetic phase in specimens that had been irradiated at 425°C and annealing in a magnetic field of 33 k Oe has the effect of increasing the total quantity of magnetic phase but reducing the average size of the magnetic particles.

Introduction

Magnetization measurements have shown that a ferromagnetic phase precipitates in austenitic stainless steel during high fluence irradiation at elevated temperatures (1, 2, 3). The shape of the magnetization versus field curves shows that the ferromagnetic phase particles are very small (approximately 20 Å diameter), but they have a high number density (approximately 10^{18} - 10^{19} particles/cm³). The composition and crystal structures of the magnetic phase has not been definitely established, but in a few cases body-centered cubic ferrite particles have been identified in irradiated austenitic stainless steel (2, 4). The ferrite phase is known to be ferromagnetic, and it is known that the ferrite phase can be formed in some austenitic stainless steels by cold working at room temperature or at lower temperatures in some cases. However, the type 316 and 321 stainless steels are not particularly susceptible to formation of the ferrite phase by cold working. A number of precipitate phases have been observed in both irradiated and thermally aged stainless steels (5, 6, 7). However, at this time the ferrite phase is the only ferromagnetic phase that has been identified as forming in austenitic stainless steel. In this report we will present evidence which suggests that more than one ferromagnetic phase forms in irradiated austenitic stainless steel. In past reports we have normalized the magnetization values to give a number equal to the percent ferrite in the specimen. Even though we now suspect the presence of other magnetic phases we have continued the practice of dividing the magnetization values by 14.05 emu/cm³ as this gives a convenient number to work with.

II Specimen materials

Most of the specimens investigated were provided by D. W. Keefer and K. R. Garr of Atomics International and by E. E. Bloom and J. O. Stiegler of the Metals and Ceramics Division, Oak Ridge National Laboratory. These specimens were irradiated for studies of irradiation-induced swelling or of irradiation-induced mechanical properties changes. The chemical composition of the various materials is given in table 1. Also included in table 1 are references to articles where additional information is given about the specimen materials. The various pre-irradiation heat treatments are given in table 2, and the irradiation parameters are listed in table 3.

During the past year we prepared some special samples for proton irradiation. The main objectives of the proton irradiations were to study the effect of damage rate and damage level on the formation of the magnetic phase. The specimens were bombarded with 0.75 MeV protons to a fluence of 2.6×10^{19} protons/cm² at 500°C. The irradiations were carried out by D. W. Keefer, Atomics International at the Boeing Company Dynamitron, Seattle, Washington. The range of 0.75 MeV protons is 5.3×10^{-4} cm in stainless steel⁽¹⁰⁾ and the damage rate varies along the range. Thus for a given proton fluence there will be a variation of damage level from the surface of the specimen to the end of proton range. We plan to measure the magnetization of the specimen and then remove layers of the specimen by electropolishing and measuring the magnetization of the specimens as each layer is removed. In this way we will be able to determine the variation of magnetization as a function of damage. However the damage rate also

varies from the surface to the end of the range so that if the amount of magnetic phase is a function of damage rate and of damage level the two effects are folded together. In our experiment two sets of specimens were irradiated to the same total fluence but at proton fluxes different by a factor of two. By comparing the results of the two irradiations we can separate out any damage rate effects. Also in these proton irradiations the available irradiated area was divided into sections so that the effect of varying other parameters could be tested.

Included in these irradiations was a specimen in which the nickel content was increased by 2% and another in which the silicon content was increased by 1%. The composition modification was produced by evaporating material onto the surface and then diffusing it into the foil in a homogenizing anneal of 24 hours at 1000°C. The unmodified foils were also annealed 24 hours at 1000°C. Specimen homogeneity was checked by electron microprobe scans through thickness and also surface scans. An interesting effect was observed in the first silicon modified specimens. Reagent grade silicon was used for the vapor deposition. The electron microprobe showed that after the homogenization anneal most of the silicon was segregated at the austenite grain boundaries. There was also a high concentration of manganese at the grain boundaries. Specimens were then prepared using semi-conductor grade silicon and these specimens did not show the preferential grain boundary segregation. One half of each of the proton irradiated specimens was injected with helium prior to irradiation. It has been shown that void nucleation is greatly enhanced by the presence of helium and we want to see if helium injection affects the amount of magnetic phase. We have found

that the pre-irradiation heat treatments that give the greatest void formation also give the greatest amount of magnetic phase.

At this time none of the proton irradiated specimens have been tested for magnetization. An electron microprobe scan of the surface was made on each specimen after irradiation but no composition inhomogeneity was detected.

I Magnetization measurements

A. Temperature dependence of magnetization

The analysis of the particle size distribution in the irradiated specimens relies on the theory of superparamagnetism ⁽¹¹⁾. Briefly this requires that the ferromagnetic phase particles be small enough to be single domain particles and also small enough that the total moment of a particle fluctuates rapidly because of thermal energy. If all the particles had the same size then the magnetization versus field curve should obey the Langevin function. However, none of our magnetization curves with one exception discussed later obey the Langevin function. Deviation from the Langevin function is generally interpreted as being due either to a distribution of particle sizes or interaction between particles or composition variation of the particles.

Another feature of assemblies of superparamagnetic particles is that the magnetization curves measured at different temperatures should superimpose when the magnetization is plotted against the temperature reduced field. It should be noted that if the saturation magnetization of the particles changes appreciably with temperature then a correction must be made to both the magnetization values and the temperature reduced field values before superposition will hold. In our case since we assumed the magnetic phase to be ferrite with a Curie temperature of 600°C or greater and all of the magnetic measurements were made below 300°K we did not expect to need a correction for the saturation magnetization. Figure 1 shows results of measurements at four different temperatures.* Clearly

* The specimen designation 1-C-1 indicates alloy 1 (Table 1), heat treatment C (table 2), irradiation condition 1 (table 3).

the superposition rule is not obeyed. Deviations from the superposition rule have been observed for many systems. These deviations are due to interactions between particles in the assembly, or variations of the composition of the particles. Interactions between particles cause deviation from superposition in the low field portions of the magnetization curves. Therefore, the deviations from superposition shown in Figure 1 cannot be entirely caused by interactions between particles but must be at least partly due to variations of chemical composition or of changes in the saturation magnetization of the particles.

Figure 1 shows that the high field magnetization is approximately a linear function of the field. As shown in Figure 1 extrapolation of the linear portion to the axis of ordinates gives a value of magnetization designated $M_0/14.05$. Figure 2 shows a plot of $M_0/14.05$ versus temperature for several different specimens. Not all of our results have been plotted on this graph. All of the as irradiated type 316 specimens that have been measured over a range of temperatures have values that are very close to the lower line in Figure 2. This line shows a linear variation of $M_0/14.05$ with temperature. The as irradiated 321 steel shows no temperature variation of $M_0/14.05$ for the rather limited range of measurements. The type 316 specimen given a post irradiation anneal at 500°C for 3 hours shows a non linear variation of $M_0/14.05$ with temperature. The shape of this curve is similar to curves of saturation magnetization versus temperature for mixtures of two ferromagnetic phases having different curie temperature in the region near the lower curie temperature.

With reference to Figure 2 it is important to note that the magnetization

values are normalized to indicate the percent of ferrite phase present and therefore the value of 11.5 for $M_0/14.05$ at 90°K shown in Figure 2 would indicate a much higher volume fraction of a phase having a curie temperature near 100°K. In general the saturation magnetization of a magnetic phase increases as the curie temperature increases. Thus it is not unreasonable to suggest that as much as 50% of the specimen consists of a magnetic phase with a curie temperature near 100°K. It is known that face centered cubic Fe-Ni alloys are ferromagnetic with curie temperature of about 373°K at 31% Ni ⁽¹²⁾. The curie temperature increases rapidly with increasing nickel content. It is then possible that one of the magnetic phases in the irradiated stainless steel is a nickel rich face centered cubic phase. Obviously magnetization measurements over a wider temperature range are needed. Unfortunately the experimental set-up used to obtain the data shown in Figures 1 & 2 would not allow measurements to be made at temperatures much above 300°K. In order to be able to make magnetization measurements at higher temperatures we replaced the stainless steel specimen chamber of the superconducting magnet with a double walled glass specimen chamber. It was also necessary to redesign the magnetometer to fit in the smaller specimen chamber. We have only recently placed the new magnetometer in operation and have not yet had time to obtain additional data about the effects of temperature on magnetization.

B. Annealing experiments

Stanley and Garr reported that specimens neutron irradiated at 425°C showed significant increases in magnetization when they were annealed at 500°C for one hour ⁽¹⁾. One of the objectives of our research is to study the post-irradiation annealing effects in more detail. Work in this area

has proceeded rather slowly. We have determined that an additional anneal of 2 hours at 500°C produced additional increases in magnetization of the 1-C-1 specimen that had been previously annealed for one hour at 500°C. The value of $M_0/14.05$ increased from 2.4 to 3.4 and the slope of the high field part of the magnetization curve increased by 43%. However, a 30 minute anneal of another 1-C-1 sample at 450°C produced no change in magnetization from the as irradiated value.

Recently we carried out an experiment in which a 1-C-1 specimen was annealed at 510°C for about 6 minutes (total of 10 minutes at temperatures above 450°C) in a magnetic field of 33 k Oe. The magnetization versus field curves obtained on the same specimen before and after the magnetic field anneal are shown in Figure 3. Also shown in Figure 3 is a curve for the 1-C-1 specimen given a 3 hour anneal at 500°C with no magnetic field. The field annealed specimen has higher magnetization at high field but lower magnetization at low field than the zero field annealed specimen. These results indicate that the field annealed specimen has the greater volume fraction of magnetic phase but that the magnetic phase particles are larger in the zero field annealed specimen. In fact the magnetization curve of the field annealed specimen fits a Langevin function rather well as shown by the solid line in Figure 3 which is a Langevin function for 2.8×10^{19} particles/cm³ each particle having a magnetic moment of $534 \mu_B$. This is the only case in which we have obtained a good fit to a Langevin function. The saturation magnetization for this specimen is 140 emu/cm³ which corresponds to a ferrite content of 10%. The ferrite composition we have assumed has magnetic moment of $1.8 \mu_B/\text{atom}$ and therefore each particle

should have about 296 atoms.

C. Oak Ridge specimens

Several irradiated stainless steel specimens were obtained from the Metals and Ceramics Division of Oak Ridge National Laboratory during the past year. The group at ORNL has a large number of specimens covering a wide range of variables such as irradiation temperature, fluence, pre-irradiation treatment, and composition. J. T. Stanley spent three weeks at ORNL selecting specimens for magnetization measurements. A simple sample extraction device was set up and measurements made at Oak Ridge. These measurements indicated that several of the ORNL specimens had significant amounts of magnetic phase. Several of the ORNL specimens were shipped to ASU for further measurements. At this time we have made measurements on only one of the ORNL specimens. This specimen is one of the high purity type 316 stainless steel specimens which was found to have a higher swelling rate than commercial type 316 stainless ⁽⁹⁾. Our magnetic measurements show that this specimen 4-H-2 has a saturation magnetization of 17.6 emu/cm^3 which corresponds to about 1.25% ferrite. This amount of ferrite is similar to what was observed in the specimens obtained from Atomics International ⁽³⁾. This specimen reaches saturation at a temperature reduced field of $40 \text{ Oe/}^\circ\text{K}$ indicating that the magnetic particles should be fairly large, perhaps $70 \text{ \AA}$ diameter.

II Electron microscopy

The electron microscopy results generally show the presence of fine precipitate particles in these specimens. However, with the exception of specimen 321-1-G-3 we have been unable to identify the precipitates. In the case of 321-1-G-3 the precipitates were definitely identified as being ferrite. This information was published in the last progress report ⁽³⁾. The microstructures of the type 316 specimens are very complex. Originally we thought that post-irradiation annealing treatments might cause the particles to grow in size but the magnetization measurements show that annealing tends to produce greater increases in the number of small particles than in the number of large particles and thus the annealing treatment does not reduce the complexity of the microstructure.

III Future work

During the remaining three months of the present contract we plan to carry out additional post-irradiation annealing experiments to compare the results of annealing in a magnetic field to results of annealing in zero field. The magnetization measurements will be made at higher temperatures on specimens that have been previously measured at low temperatures. Additional magnetization measurements will be made on the specimens recently obtained from ORNL. Efforts will continue to attempt to identify the precipitate phases using electron microscopy.

The principal investigation, 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.

IV Summary

1. During the past year additional neutron irradiated stainless steel specimens were obtained from ORNL. Preliminary measurements have established the fact that the high purity stainless steel specimens contain a ferromagnetic phase in quantities similar to the commercial type 316 specimens obtained from A. I.
2. Stainless steel specimens were proton irradiated to test the effects of damage rate, damage level, composition and helium content on magnetic properties.
3. The temperature dependence of magnetization implies that more than one magnetic phase is present in some of the irradiated specimens.
4. Post-irradiation annealing in a magnetic field produces significantly different magnetization curves than annealing in zero field.

Table 1
Composition of Alloys

Alloy	C	Mn	P	S	Si	Ni	Cr	Cu	Mo	Ti	Co	Refer- ences
316-1	0.06	1.68	0.022	0.017	0.51	13.63	17.33	0.075	2.32	----	0.01	(8)
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			
316-4	0.0005	<0.001	0.006	0.002	0.01	14.4	17.5		2.8		N 0.0003 B <0.0001	(9)
321-1	0.058	1.44	0.022	0.005	0.50	10.47	17.61	0.12	0.15	0.47	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	-----
H	1 hr at 1050°C	-----

Table 3

Irradiation Conditions

Irradiation Temperature	fluence E>0.1 MeV n/cm ²
1. 425°C	1.8 x 10 ²²
2. 475°C	3.5 x 10 ²²
3. 530°C	3.5 x 10 ²²
4. 620°C	3.5 x 10 ²²

Figure 1. Relative magnetization vs. temperature reduced field specimen 1-C-1 annealed 3 hours at 500°C . Relative magnetization measurements for unirradiated specimen of 1-C shown for comparison.

Figure 2. Mo/14.05 versus temperature for irradiated specimens of type 316 and 321 stainless steel. Specimen 1-C-1-500°, 3 hr. given 3 hr., 500°C post-irradiation anneal, 1-C-1-450°, 1/2 hr. given 1/2 hr., 450°C post-irradiation anneal.

Figure 3. Magnetization versus temperature reduced field for specimens from 1-C-1. Field annealed specimen annealed 6 minutes at 510°C in 33 k Oe magnetic field. Annealed specimen annealed 3 hours at 500°C in zero field.

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