1.2 FABRICATION OF LOW ACTIVATION FERRITIC-MARTENSITIC STEELS CONTAINING ^{54}FE ISOTOPE — Y. Yamamoto (Oak Ridge National Laboratory)

OBJECTIVE

This primary goal is to evaluate the effect on the irradiation microstructure and mechanical properties of the 9Cr base reduced activation ferritic-martensitic (RAFM) steels, such as EUROFER 97 and cast nanostructured alloys (CNA), prepared by using ^{54}Fe isotope reduced from the oxide powder that KIH provided. The ^{54}Fe isotope should accelerate the helium bubble formation during fast neutron exposure at HFIR which allow simulating the high dose conditions within relatively short period of exposure time.

SUMMARY

Reduction of the mixed oxide steel powder consisting primarily of ^{54}Fe was successfully conducted via a combination of a hydrogen reduction process, vacuum-melting, and arc-melting with reactive elements. The arc-melted ingot of ^{54}Fe to date contains 78 wppm oxygen and 70 wppm nitrogen, together with ~1 wt.% of Cr and W, with the total weight of ~200 g. The detailed procedure of each reduction process is summarized in this report. The results were presented in a poster at ICFRM-17.

PROGRESS AND STATUS

Introduction

There are no test facilities available with a neutron spectrum that matches D-T fusion. Various methods are used to simulate fusion reactor conditions and evaluate irradiation effects in structural materials for fusion reactors. For reduced-activation ferritic-martensitic (RAFM) steels doped with B or Ni have been used in fission test reactors to produce helium through (n, α) reactions while the fast neutrons produce displacement damage. However, both B and Ni tend to segregate at grain boundaries, compromising the simulation of uniform irradiation damage. It has been proposed to replace all natural Fe with the isotope ^{54}Fe in selected RAFM steels to expect acceleration of the He bubble formation dispersed uniformly within relatively short period of irradiation time, as previously attempted at High Flux Isotope Reactor (HFIR) with ^{55}Fe by Liu et al. [1]. HFIR neutron irradiation will achieve simultaneous He and dpa production throughout the bulk of specimens in a damage evaluation study.

About 400 g of mixed oxide steel powder was delivered from Karlsruhe Institute of Technology (KIT) which consisted primarily of ^{54}Fe together with small amounts of Cr, W, and other alloying elements. The origin of the powder material was a trial heat of EUROFER 97 with ^{54}Fe made at KIT. However, the heat was accidentally contaminated with high amount of B and C so that the material was fully dissolved into an acid and turned into oxide powders during the recovery process [2]. Reduction process of the oxide powders was applied at ORNL, in order to extract the ^{54}Fe with reasonably low oxygen content. In this report, the efforts on reducing the oxide powders were summarized.

Experimental Procedure

Four bottles containing ^{54}Fe oxide powders (~100 g for each) were delivered from KIT. The oxide powders were reduced by using multiple steps as follows; (1) hydrogen annealing (at 1100°C in a flowing H_2 gas for 24h), (2) cold compaction (to make a pellet, x4), (3) hydrogen sintering (to sinter the pellet, x4), (4) arc-melting (to make a button ingot, x4), (5) vacuum melting (to merge four button ingots into one piece), and (6) arc-melting with reactive elements (to reduce oxygen level by melting with Al). Oxygen content of the ingot at each step was determined by using inert gas fusion analysis (conducted by DIRATS), after the step #6. The step #6 repeated 5 times until the oxygen level became sufficiently low (less than 80 wppm.).

Results

All steps in the reduction process are summarized in Table 1. There were total 10 different steps, and the measured oxygen levels at each step after #6 were also listed. The last arc-melt (the step 6-5) resulted in obtaining the button ingot with 79 wppm oxygen and 70 wppm nitrogen, together with ~1 wt.% of Cr and W, with the total weight of ~200g. The ingot will be sectioned into two pieces, and then mixed with the required elements to fabricate EUROFER97 and CNA steels by arc-melting.

Table 1. List of the reduction process and analyzed oxygen content

Step	Procedure	O, wppm.	Remarks
1	Hydrogen reduction	-	Fluffy powder
2	Cold-press	-	Pressed at 12 ksi to make pellets (x4)
3	Hydrogen sintering	-	Sintered pellets (x4)
4	Arc melting	-	Button ingots with Cr-rich oxides (x4)
5	Melting in a vacuum furnace	-	One large ingot with lots of Cr-rich oxides
6-1	Arc melting	2180	A button ingot with lots of Cr-rich oxides
6-2	Arc melting with reactive elements (I)	1700	A button ingot with scales
6-3	Arc melting with reactive element (II)	741	A button ingot with a few scales
6-4	Arc melting with reactive element (III)	413	A button ingot with a few scales
6-5	Arc melting with reactive element (IV)	79	A button ingot with a few scales
Next	Mix with required element by arc melting	-	Planned

The reduction process was initiated from the hydrogen annealing. The powders were spread on an alumina boat as shown in Figure 1, and kept them in a tube furnace with a flowing hydrogen gas at 1100C for 24h. The powders in four different bottles were reduced separately, and the contents before and after annealing were analyzed by using the powder X-ray diffraction. The obtained spectra are shown in Figure 2. The as-received powder mostly consisted of Fe_2O_3 type oxides with no metal Fe, whereas the hydrogen annealing resulted in reducing the oxides significantly. However, the powders still contained 7~16% of mixed oxides (Fe_2O_3, Fe_3O_4, Cr_2O_3, etc.). Since the majority of the powders were metal Fe, a melt process was proposed in order to separate these mixed oxides from metal Fe.

Figure 1. The powders after hydrogen annealing.

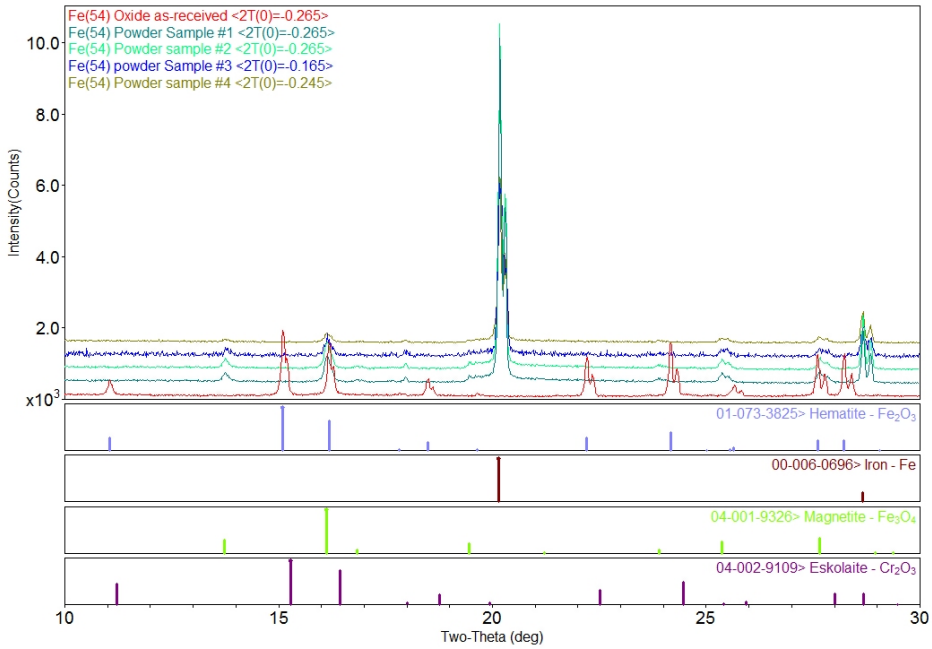

Figure 2. The powder XRD results before and after hydrogen annealing.

The powders were cold-pressed at 12 ksi to make pellets with ~29mm diameter and ~25mm height, and then sintered in a flowing hydrogen gas at 1100C, as shown in Figure 3. This process was applied to prepare the following arc-melting process since the powders would be difficult to arc-melt (e.g. potential explosion during evacuation or melting).

Each pellet was arc-melted several times to make sure to eliminate any residual powders and to form one piece of the ingot. The metal Fe typically showed a spherical shape during arc-melting process, as shown in Figure 4a, together with the agglomerate of the mixed oxides fringed the metal Fe. The resultant button ingots were covered by the mixed oxides, so that they were mechanically separated by using a hammer, as shown in Figure 4b. Some of the oxide pieces could not be removed from the ingots since they were "bitten" inside of the metal ingots. This could potentially be due to lower melting point of Fe-rich oxides compared to that of metal Fe, which resulted in solidifying the metal and oxides almost the same time and difficult to make a clear separation.

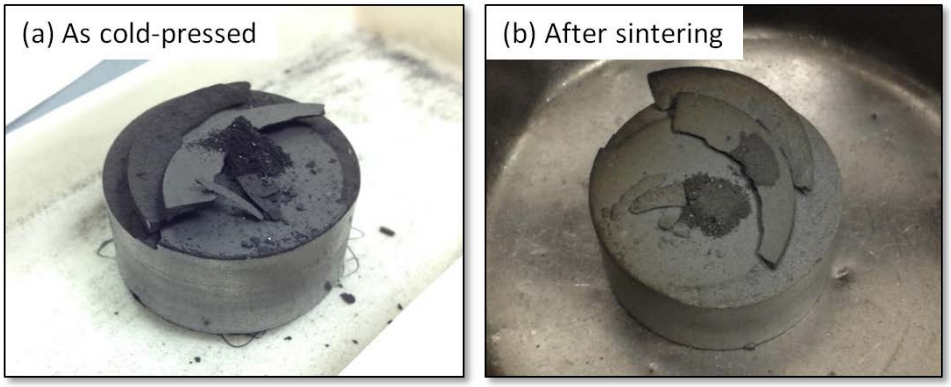

Figure 3. (a) The pellet made from the cold-press powders, and (b) the pellet after sintering.

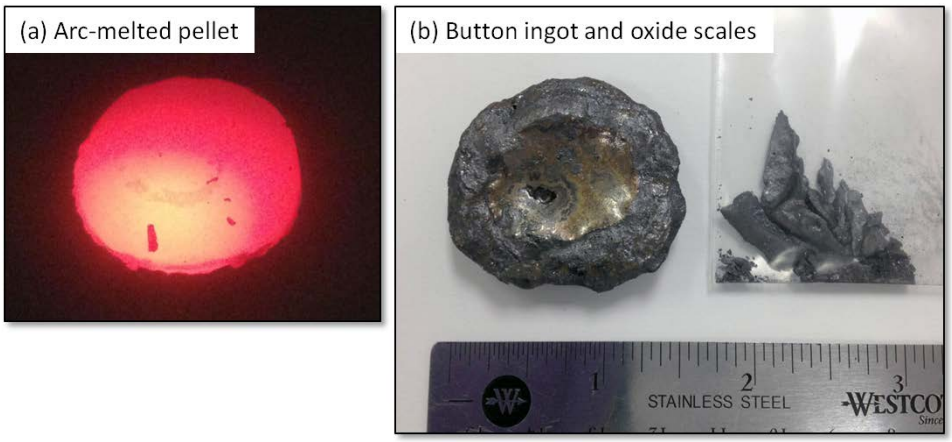

Figure 4. (a) The pellet during arc-melting, and (b) the button ingot and separated oxide scales.

A melting in a vacuum was also attempted. After several trial melt with a dummy (natural) Fe, an MgO crucible was selected for the melting process. Four ingots were melted at once this time in order to make a large ingot. The crucible with the ingots were kept in a vacuum chamber, slowly heated up to 1600C and held for 30min, and then furnace cooled to room temperature. The ingots were fully melted to form one large ingot, although the surface was not smooth and lots of mixed oxides were bitten at the top of the ingot, as shown in Figure 5. After removing the mixed oxides as possible, the ingot was arc-melted again to make a large button ingot. A part of the ingot was accidentally separated from the main body during arc-melting, so that there were two ingots after this process step, as shown in Figure 6. A lot of mixed oxide agglomerates were removed from the arc-melted ingot, and a small piece (~5g) was sectioned from the large ingot for the chemical analysis. The analyzed result indicated that the metal contained not only oxygen with 0.218 wt.% but also 0.93 wt.% of Cr and 0.80 wt.% of W in it.

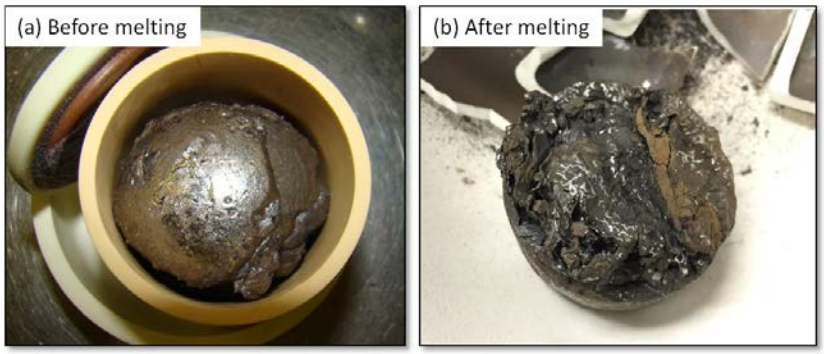

Figure 5. The ingots melted in an MgO crucible in a vacuum; (a) before and (b) after melting

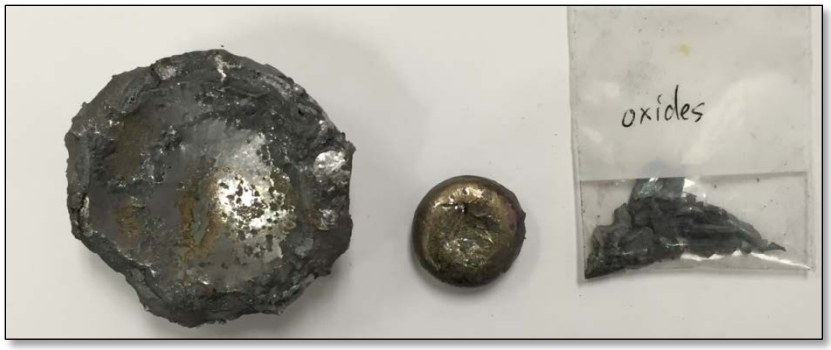

Figure 6. Arc-melted ingots and removed oxide agglomerates

From the chemical analysis result, it was hypothesized that most of oxygen was combined with Cr to form chromium oxide. It would be difficult to separate the chromium oxide from molten Fe, so that another reduction method was proposed; melting the ingot with reactive elements such as Al and/or Si which would form more stable oxides compared to chromia as well as easier to separate from molten Fe because of their higher melting points. Based on this idea, the required amounts of Al and Si (to form Mullite, $Al_6Si_2O_{13}$) or Al (to form Al_2O_3) to compensate the oxygen in the ingot were calculated, and then arc-melted with the ingot.

It was found that the Si addition was not effective to form Mullite but the Al addition was beneficial to separate the oxides from molten Fe, as shown in Figure 7a (after the first mixing, or step 6-2). The Cr content increased after the first mixing, suggesting that the Al successfully captured the oxygen from chromium oxide and increased free Cr in the metal Fe ingot. Since excess Al could be poisons for the fabrication of RAFM steels later (e.g. interfering with the nitrogen addition), relatively small amount of the Al addition was made in the following steps. Total four times mixing of the ingot with Al resulted in reducing the oxygen content up to 78 wppm. together with 1.34 wt.% of Cr. Note that the Al content was below the detection limit (<0.01 wt.%) after the step 6-5.

Step	Cr, wt%	O, wt%
6-2	1.05	0.170
6-3	1.08	0.074
6-4	1.26	0.041
6-5	1.34	0.008

Figure 7. The ingot after mixing with reactive elements; (a) after the step 6-2, (b) 6-3, (c) 6-4, and (d) 6-5.

The ingot after the step 6-5 will be sectioned into two pieces, and then melted with the required elements to fabricate two different RAFM steels. The progress will be summarized in the next semi-annual report.

These contents were presented at the 17th International Conference on Fusion Reactor Materials held at Aachen, Germany on October 12th to 16th, 2015, as a poster presentation entitled "FABRICATION OF LOW ACTIVATION FERRITIC-MARTENSITIC STEELS CONTAINING ^{54}Fe ISOTOPE".

References

[1] H. Liu, M. A. Abdou, L. R. Greenwood, ^{55}Fe effect on enhancing ferritic steel He/dpa ratio in fission reactor irradiations to simulate fusion conditions, Fusion Engineering and Design, 88 (2013) 2860-2864.

[2] M. Rieth et al., EUROFER-Fe54 Specimen Production and Irradiation Proposal, TW4-TTMS-001 D01,TW5-TTMS-001 D02, Karlsruhe Institute of Technology Interner Bericht, Projekt Fusion 31.40.03, Dec. 2010