

## **NANOPRECIPITATES IN STEELS**

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## **ABSTRACT**

The creep strength of ferritic steels is improved by high number densities of nano-scale dispersoids, such as in the oxide dispersion strengthened steels MA956, MA957, and PM2000. The oxide dispersoids in these steels contain Y and Al or Y and Ti. They can be as small as a few nanometers in size. Processing of such steels is traditionally carried out by mechanical alloying of a mixture of elemental or pre-alloyed powders together with  $Y_2O_3$  powder. However, mechanical alloying is an energy-intensive process which is not readily scaled up. The goal of the present research is to identify alternative, more attractive ways of producing ultrafine strengthening dispersoids in steels. Internal oxidation, in which reactive elements contained in a metallic matrix are selectively oxidized may be one such way. Initial internal oxidation experiments were carried out with Fe-Ti-Y solid solution alloys and Fe-Ti-Y intermetallics. In one approach, the oxygen partial pressure was controlled with a mixture of Fe and  $Fe_2O_3$  powders. In another approach, Fe-Ti-Y powders were mixed with an appropriate amount of  $Fe_2O_3$  powder and annealed in vacuum in order to induce a displacement reaction. The size of the precipitates could be reduced by lowering the temperature at which the internal oxidation anneal occurred. With appropriate heat treatments, precipitates as small as 10 nm could be produced. The current work thus shows that internal oxidation has the potential to produce strengthening ultrafine dispersoids in steels.

## **INTRODUCTION**

Based on a minimum rupture life of 100,000 hours at an applied stress of 100 MPa, the creep strength of ferritic steels used in coal-fired power plants is limited to a temperature of about 620°C [1]. At higher temperatures, the creep life of ferritic steels decreases precipitously. For example, increasing the temperature from 600 to 650°C reduces the creep life of the alloy HCM12A (Fe-11Cr-0.4Mo-2W-0.2V-0.05Nb-0.02Al-0.06N-0.1C, wt%) by a factor of 100 [2]. Higher service temperatures may be obtained with austenitic stainless steels (approximately 690°C) or nickel-base alloys (720°C and above) [1].

Oxide dispersion strengthened (ODS) steels produced by mechanical alloying followed by hot extrusion are creep- and oxidation-resistant at temperatures well in excess of the maximum temperatures possible for conventional alloys [3]. Klueh et al. showed that the high-temperature creep strength of ODS steels can

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substantially exceed that of a 9Cr ferritic steel [4]. Ferritic ODS steels contain high number densities of extremely small and stable dispersoids. Kim et al. [5] showed that Ti additions were critical for obtaining nanoclusters with sizes of a few nm in a Fe-12Cr-3W-0.4Ti-0.25Y<sub>2</sub>O<sub>3</sub>, wt% (“12YWT”) ODS steel. Miller et al.’s [6] recent atom probe tomography of a 12YWT ODS steel showed titanium-, yttrium- and oxygen-enriched particles with diameters on the order of 2-3 nm and number densities on the order of  $2 \times 10^{24}/\text{m}^3$ . Annealing for 24 hour at 1300°C increased the particle diameters only by a factor of 3 indicating a high thermal stability. It does therefore not come as a surprise that ODS steels are considered for power plant parts such as heat exchanger pipes.

Although ODS steels have high creep strengths, several issues limit their widespread use [3]. The first issue is joining. ODS steels cannot be joined by fusion welding as this destroys the very microstructure giving them their unique properties. Less conventional joining techniques such as plasma-assisted pulsed diffusion bonding and transient liquid phase bonding have recently shown promise [3]. The second issue is the anisotropy in the mechanical properties of these materials. The third issue, which may be the most important, is their high production cost. High cost and the ensuing lack of market penetration are a major reason why Plansee GmbH Lechbruck, Germany, is discontinuing its PM2000 alloy.

Ferritic ODS alloys are fabricated by powder-metallurgical (PM) processing involving mechanical alloying of precursor metal or alloy powders with Y<sub>2</sub>O<sub>3</sub> powder, followed by consolidation via hot extrusion. The mechanical alloying, which is carried out in a high-energy ball mill, is required to create a uniform dispersion of nanoscale dispersoids. This PM approach is a rather expensive process which is, in addition, difficult to scale up.

Arguably, the most widely used ODS alloy is GlidCop<sup>®</sup> copper\*, which consists of a matrix of pure copper containing an ultrafine dispersion of Al<sub>2</sub>O<sub>3</sub> particles ranging in size from 3 to 12 nm with an interparticle spacing of 30 to 100 nm and a particle density of  $10^{22}$  to  $10^{23} \text{ m}^{-3}$  [7]. Interestingly, GlidCop<sup>®</sup> copper is not fabricated by mechanical alloying, but by internal oxidation of Cu-Al precursor powders. This suggests that it is worth exploring an internal oxidation route for the processing of ferritic steels. Compared with mechanical alloying, internal oxidation methods are likely to be more economical.

In the present work, preliminary results on the internal oxidation of Fe-Ti-Y solid solution alloys and intermetallics will be presented. While it is by no means clear at this time whether an internal oxidation route is a realistic alternative to the mechanical alloying of ferritic steels with Y<sub>2</sub>O<sub>3</sub> powder we will show that it can produce nanoscale dispersoids with sizes as small as 10 nm.

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\*Formerly produced by SCM Metal Products, Inc., now produced by North American Höganäs High Alloys LLC.

## EXPERIMENTAL PROCEDURE

Fe-Ti-Y alloys and intermetallics were arc-cast from elemental precursor materials in a partial pressure of argon, followed by annealing for 24 hours at 1000 or 1100°C in vacuum. Two approaches were employed for the internal oxidation of the Y and Ti to  $Y_2O_3$ ,  $TiO_2$ , or  $Ti_2Y_2O_7$ . In one approach, the alloys were ground into powder, mixed with an amount of  $Fe_2O_3$  sufficient to oxidize all the Ti and Y, cold compacted, and annealed in vacuum. The purpose of the vacuum anneal was to carry out the displacement reaction between the  $Fe_2O_3$  and the Ti and Y to form (Ti,Y) oxides. In the second approach, coupons of the alloys were ground to a 600 grit SiC finish and encapsulated in an evacuated quartz tube containing a mixture of 0.5 g Fe and 0.5 g  $Fe_2O_3$  (“Rhines pack”). The powder was placed in one end of the tube and separated from the alloy coupon by a constriction and a quartz wool barrier. The quartz tube was then placed in a furnace in order to accomplish the internal oxidation with the partial pressure defined by the Fe- $Fe_2O_3$  mixture which caused oxidation of the Ti and Y, but not the Fe.

The internally oxidized specimens were examined by optical and scanning electron microscopy (SEM) in the secondary electron (SE) and the backscattered electron (BSE) modes, as well as by X-ray diffraction. Internally oxidized coupons were ground and polished at a glancing angle with respect to the surface in order to increase the width of the internally oxidized zone from ~20-50  $\mu m$  to ~1 mm. Hardness measurements were performed with a Nanoindenter XP (MTS Nano Instruments, Oak Ridge, TN) using a Berkovic tip. An indentation depth of 100 nm was chosen resulting in an edge length of the triangular impressions of approximately 750 nm. The hardness values were calculated from individual load-depth data using the standard Oliver-Pharr method [8].

## EXPERIMENTAL RESULTS AND DISCUSSION

### SOLID SOLUTION ALLOYS

An arc-cast alloy with the composition Fe-0.8Ti-0.4Y (at%) was annealed for 24 hours at 1000°C in vacuum, filed into powder, mixed with 2.1 wt%  $Fe_2O_3$  powder, cold-pressed, and annealed for 24 h at 1000°C in vacuum. Figure 1 shows the (Ti,Y) oxide dispersoids present after the displacement reaction. The larger dispersoids have a diameter on the order of 1  $\mu m$ , but smaller dispersoids with diameters on the order of 100 nm are also observed.

Not surprisingly, lower annealing temperatures resulted in smaller oxide particles. Figure 2 shows the oxide particles formed in Fe-0.8Ti-0.4Y after annealing for 4 days at 800°C with an Fe- $Fe_2O_3$  powder mixture. Annealing of a similar alloy at 700°C produces even smaller particles with diameters on the order of 50 nm (note that the scale markers in Figs. 2 and 3 are different).

In order to produce creep-resistant ODS alloys from Fe-based solid solution alloys, even finer dispersoids will have to be created by lowering the temperature of the internal oxidation anneals. The thermal stability of such small dispersoids is not known at this time. Also, it is not clear whether the Cr or Al needed for oxidation protection can be introduced directly as alloying elements, or whether they have to be added at a later stage during the powder processing.

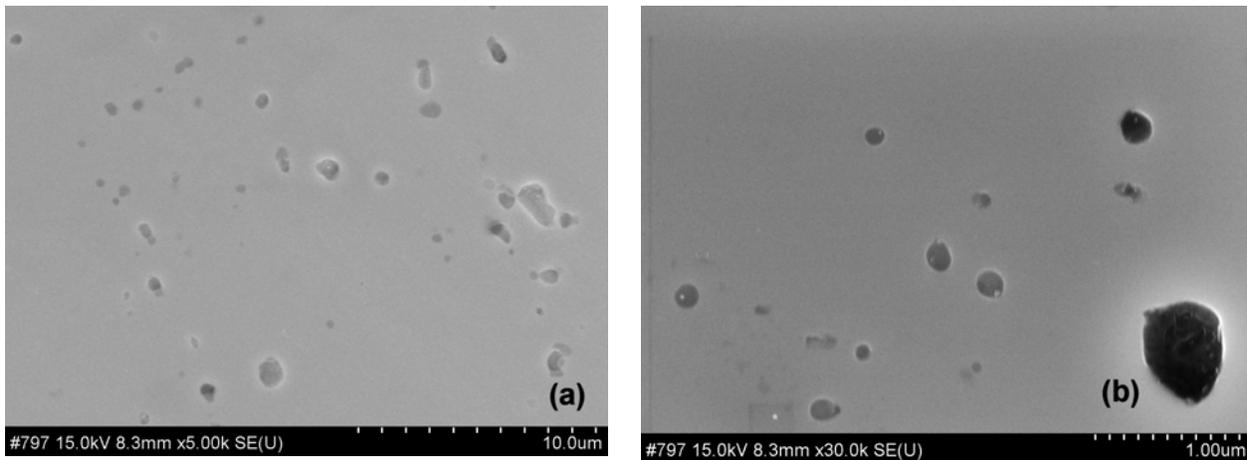


Fig. 1. SEM micrographs of Fe-0.8Ti-0.4Y (at%) after internal oxidation with  $\text{Fe}_2\text{O}_3$  for 24 hours at  $1000^\circ\text{C}$  at (a) 5,000 $\times$  and (b) 30,000 $\times$  magnification.

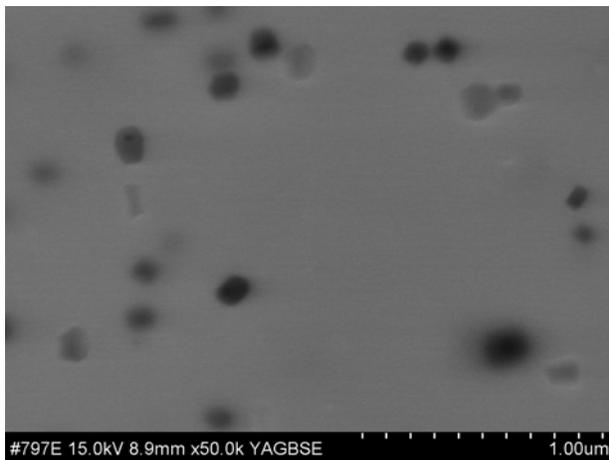


Fig. 2. Oxide particles in Fe-0.8Ti-0.4Y (at%) after internal oxidation for 4 days at  $800^\circ\text{C}$ .

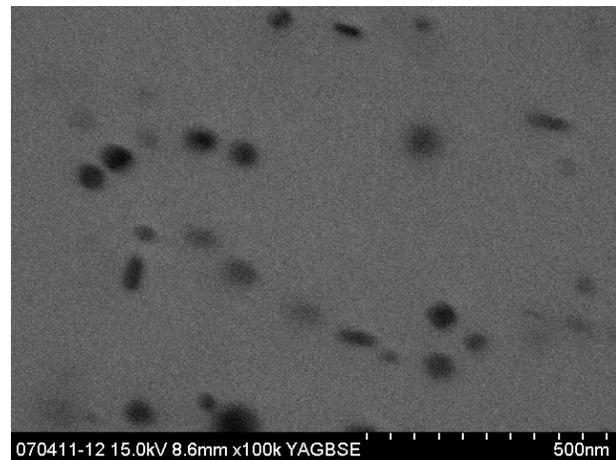


Fig. 3. Oxide particles in Fe-0.42Ti-0.18Y (at%) after internal oxidation for 6 days at  $700^\circ\text{C}$ .

### INTERMETALLIC ALLOYS

An intermetallic ingot with the composition  $\text{Fe}_{17}\text{Y}_2$  (Fe-10.5Y, at%) was ground into -325 mesh powder ( $<45\ \mu\text{m}$ ), blended with  $\text{Fe}_2\text{O}_3$  powder to produce a 87.6 wt%  $\text{Fe}_{17}\text{Y}_2$  – 12.4 wt%  $\text{Fe}_2\text{O}_3$  mixture, and annealed for 1 day at  $1000^\circ\text{C}$  in vacuum. Figure 4 shows large ( $1\ \mu\text{m}$ ) particles, but much smaller particles are also visible.

Similarly, an ingot of  $\text{Fe}_{11}\text{Ti}_1\text{Y}_1$  (Fe-7.7Ti-7.7Y, at%) was ground into -325 mesh powder, blended with  $\text{Fe}_2\text{O}_3$  powder to produce a 81.8 wt%  $\text{Fe}_{11}\text{Ti}_1\text{Y}_1$  – 18.2 wt%  $\text{Fe}_2\text{O}_3$  mixture, and vacuum-annealed for 1 day at  $1000^\circ\text{C}$ . Fig. 5 shows the oxide particles which were identified to be  $\text{Y}_2\text{Ti}_2\text{O}_7$  and  $\text{Y}_2\text{O}_3$  by powder X-ray diffraction, see Fig. 6.

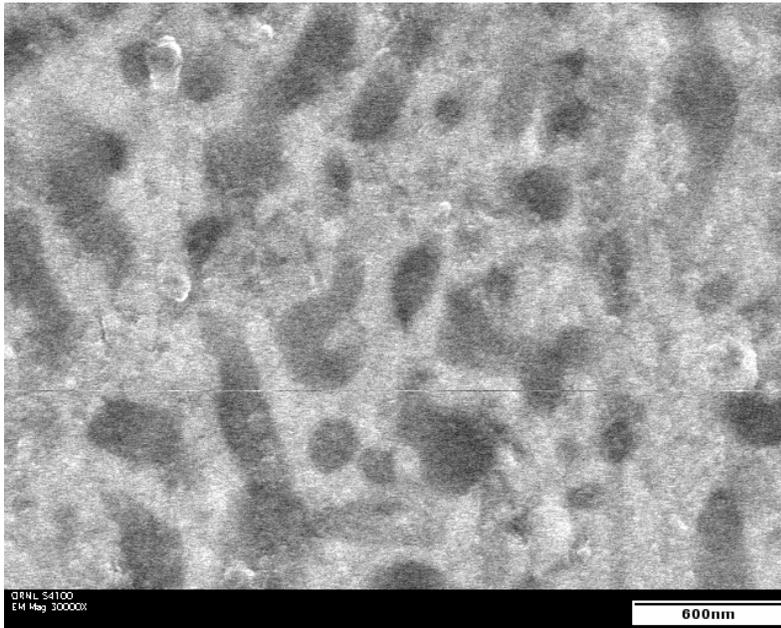


Fig. 5. SEM-BSE image of  $Y_2Ti_2O_7$  and  $Y_2O_3$  particles in  $Fe_{11}Y_1Ti_1$  internally oxidized for 1 day at  $1000^\circ C$

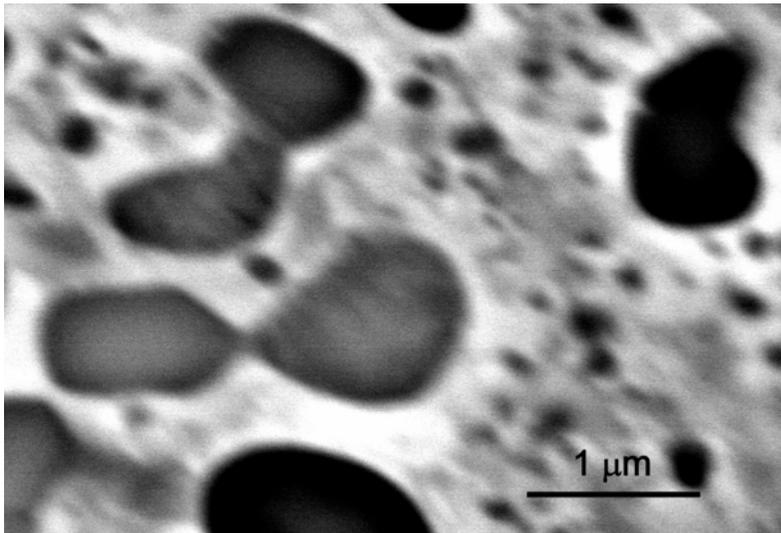


Fig. 4. SEM-BSE image of  $Y_2O_3$  particles in  $Fe_{17}Y_2$  internally oxidized for 1 day at  $1000^\circ C$ .

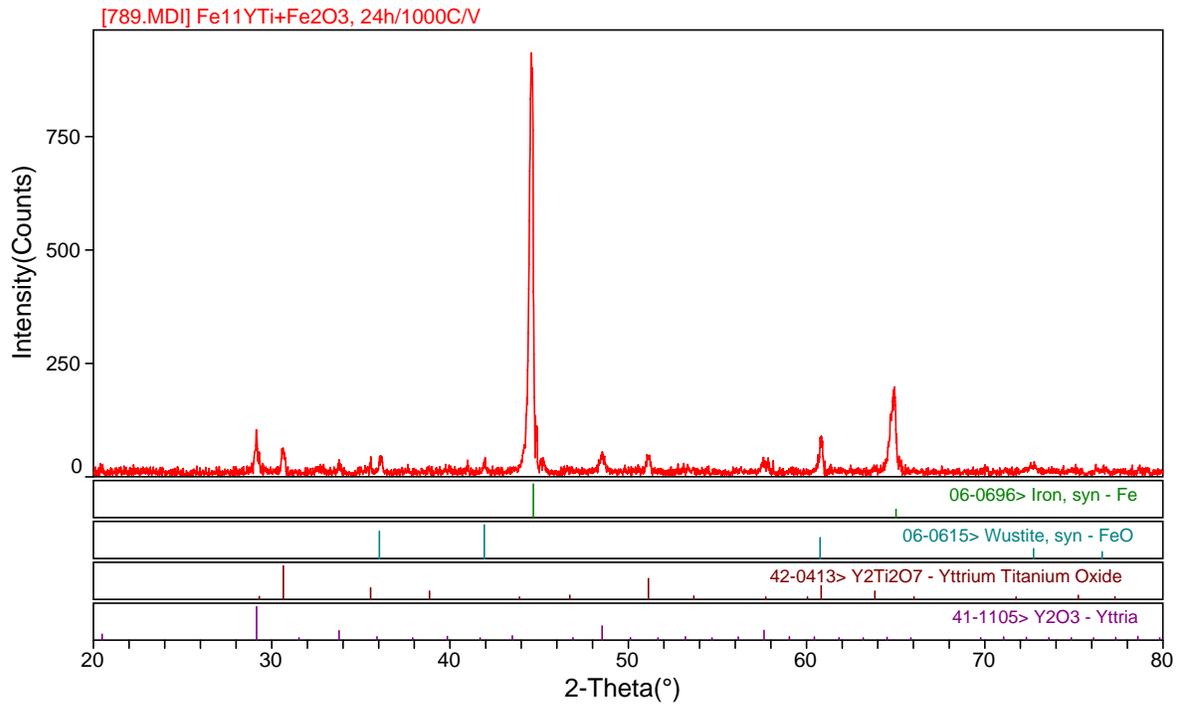


Fig. 6. Powder X-ray diffraction pattern of Fe<sub>11</sub>Y<sub>1</sub>Ti<sub>1</sub> after internal oxidation for 1 day at 1000°C.

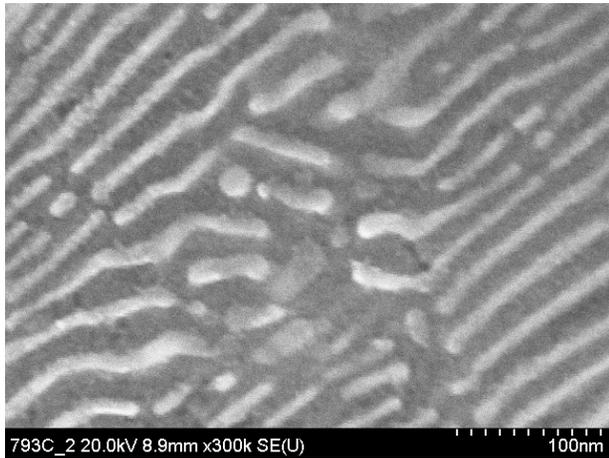


Fig. 7. Y<sub>2</sub>O<sub>3</sub> lamellae (bright) produced by internal oxidation of Fe<sub>17</sub>Y<sub>2</sub> with a Fe-Fe<sub>2</sub>O<sub>3</sub> powder mixture for 3 days at 700°C.

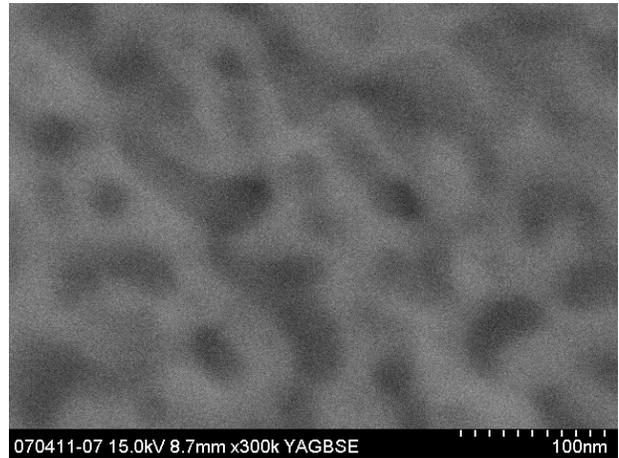


Fig. 8. Oxide particles (dark) produced by internal oxidation of Fe-6.5Ti-6.5Y (at%) with a Fe-Fe<sub>2</sub>O<sub>3</sub> mixture for 3 days at 700°C.

Similar to the solid solution alloys, internal oxidation at reduced temperatures produces much finer oxide particles or lamellae as illustrated in Figs. 7 and 8.

Figure 9 shows hardness measurements for Fe-6.5Ti-6.5Y (at%) coupons which were internally oxidized with Fe-Fe<sub>2</sub>O<sub>3</sub> for 3 days at 700°C and at 600°C, respectively. The figures show the hardness values of the internally oxidized layers and of the intermetallic, with an in-between transition zone. Since the stoichiometric composition of the intermetallic is Fe<sub>11</sub>Y<sub>1</sub>Ti<sub>1</sub> (Fe-7.7Ti-7.7Y, at%), the coupons contained the much softer Fe-Ti-Y solid solution as a second phase. Therefore, a fraction of the hardness measurements indicates soft material – the Fe-Ti-Y solid solution. This is the reason for the large scatter in Fig. 9. The hardness of the internally oxidized Fe<sub>11</sub>Y<sub>1</sub>Ti<sub>1</sub> phase itself is given by the upper bound of the hardness measurements in Fig. 9. The unoxidized Fe<sub>11</sub>Y<sub>1</sub>Ti<sub>1</sub> intermetallic is very hard – its hardness is on the order of 12-14 GPa. Internal oxidation for 3 days at 700°C produces oxide particles with sizes on the order of 20 nm (see Fig. 8). The corresponding hardness is on the order of 9 GPa [Fig. 9(a)]. Annealing for 3 days at 600°C is expected to result in a smaller particle size and thus higher hardness. Consistent with this, the maximum hardness of the internally oxidized zone in Fig. 9(b) is, with a value of approximately 11 GPa, distinctly higher than that produced by annealing at 700°C. While extremely fine oxide dispersoids or lamellae can be produced by internal oxidation of Fe-Ti-Y intermetallics, there are several issues that need to be addressed. First, since the high volume fractions of dispersoids are likely to degrade ductility and fracture toughness, ways to reduce this volume fraction need to be found. Second, it is not clear how and at what point the Cr or Al required for oxidation protection should be introduced. Third, the thermal stability of the dispersoids needs to be examined.

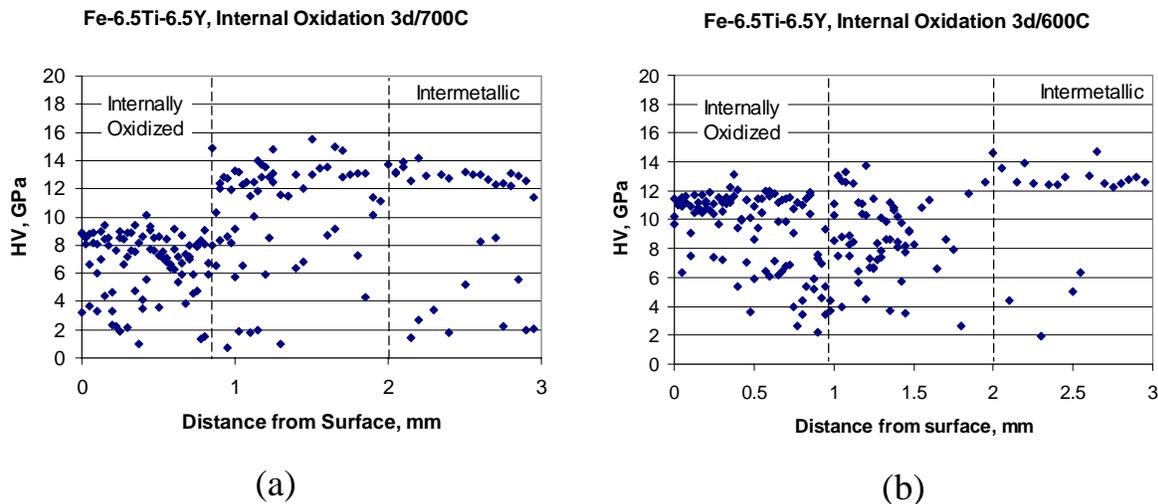


Figure 9. Hardness of Fe-6.5Ti-6.5Y after internal oxidation for 3 days at (a) 700°C and (b) 600°C. The actual thickness values of the internally oxidized layers were on the order of 20-50  $\mu$ m.

Miller et al. have shown that the clusters in ODS steels are substoichiometric oxides with a composition roughly based on (Ti<sub>1-x</sub>Y<sub>x</sub>)<sub>1</sub>O<sub>1</sub> [6]. Fu et al. [9] have performed calculations showing that vacancies are required to stabilize the clusters. These vacancies are presumably generated by the mechanical alloying. While it is unrealistic to expect high vacancy concentrations during internal oxidation anneals, it is interesting to note that Fe-Ti-Y intermetallics may contain substantial concentrations of structural vacancies. Revel et al. [10] claim that the Ti atoms in Fe<sub>8.6</sub>Ti<sub>1.1</sub>Y are restricted to a single type of crystallographic site, but only half of this type of site is occupied by Ti. This suggests a vacancy defect structure. It is tempting to speculate that these vacancies might be exploited to stabilize the ultra-fine dispersoids formed during internal oxidation.

## SUMMARY AND CONCLUSIONS

Internal oxidation experiments were carried out with Fe-Ti-Y solid solution alloys and Fe-Ti-Y intermetallics. With appropriate heat treatments, oxide particles as small as 10 nm could be produced. This shows that internal oxidation has the potential to produce ultrafine dispersoids. However, a number of issues still remain. First, the thermal stability of the dispersoids needs to be examined. Second, ways to introduce Cr or Al into the alloys have to be found. Third, while not only Fe-Ti-Y solid solutions, but also Fe-Ti-Y intermetallics are of interest, it remains to be seen whether the high volume fraction of dispersoids formed during internal oxidation of Fe-Ti-Y intermetallics can be sufficiently diluted to result in alloys with adequate fracture toughness and ductility.

## ACKNOWLEDGEMENTS

This work was sponsored by the Office of Fossil Energy, Advanced Research Materials (ARM) Program, U.S. Department of Energy, under contract DE-AC05-00OR22725 with Oak Ridge National Laboratory managed by UT-Battelle, LLC. A portion of this research was conducted at the SHaRE User Facility, which is sponsored by the Office of Basic Energy Sciences, Division of Scientific User Facilities, U.S. Department of Energy.

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