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Correlation between chemical composition and size of very small oxide particles in the MA957 ODS ferritic alloy

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ABSTRACT

ODS (oxide dispersion strengthened) alloys have superior creep properties. As it is well known, these excellent creep properties result from very fine oxide particles dispersed with the matrix. However, there is no common understanding about the nature of the very small oxide particles. Two hypotheses arise from the literature, 1: non-stoichiometric Y-, Ti-, O-enriched clusters and 2: stoichiometric $Y_2Ti_2O_7$. In this work, both chemically extracted residue method and extraction replica method were applied to the commercial ODS ferritic alloy, MA957. These samples were then observed using XRD (X-ray diffractometry) and FEG–STEM (field emission gun–scanning transmission electron microscopy) with EDS (energy dispersive X-ray spectrometer). From the results, it was concluded that the composition of small particles is related to the particle size. They exhibit at least two types of phase, 1: non-stoichiometric Y-, Ti-, O-enriched clusters from ~2 to ~15 nm (Y/Ti < 1) and 2: stoichiometric $Y_2Ti_2O_7$ from ~15 to ~35 nm. Based on the result, it is suggested that the appropriate increase of titanium content compared to yttrium content in oxide particles by modifying the chemical compositions of ODS alloys could be an effective way to obtain a finer dispersion of oxide particles.

1. Introduction

ODS ferritic/martensitic alloys are promising structural materials for attractive fast reactors planned within Generation IV and fusion reactors after ITER. This is due to their excellent creep properties [1–9] and superior irradiation resistance [7,10–18], compared to other conventional heat resistant steels such as 9Cr ferritic/martensitic steels and austenitic steels. These very attractive properties are obtained by means of nanometric oxide particles dispersed in the matrix. These nanometric oxides are believed to be very stable under neutron irradiation and at high temperatures. Consequently, many researches have been conducted in order to finely disperse oxide particles in the matrix by modifying chemical compositions and developing material processing procedures [19–24]. In particular, the precise control of titanium and oxygen levels was found to be one of the effective ways to finely disperse oxide particles in the matrix [19–21,23].

However, there is no common understanding about the nature of the very small oxide particles in the ODS alloys which contain Y, Ti, and O for the formation of oxide, as summarized in Table 1. Some researchers using TEM has reported that they were stoichiometric $Y_2Ti_2O_7$ particles with pyrochlore-type structure [1,4,10,25,28,29]. Other researchers mainly using APT (atom probe tomography) has concluded that they were non-stoichiometric Y-, Ti-, O-enriched clusters [10,12,19,26,27,30,31].

In this work, chemically extracted residues and extraction replicas were carefully prepared from MA957 to realize precise observations of precipitates. The chemically extracted residues were analyzed using XRD system (PANalytical X'pert PRO) and extraction replicas were observed using a FEG–STEM (JEOL JEM-2010F) with EDS system (Oxford Link-ISIS) in order to provide knowledge about the nature of very small oxide particles.

2. Experimental

The specimen used in this study was the commercial ODS alloy, MA957, with nominal compositions of Fe–14Cr–0.3Mo–1.0Ti–$0.25Y_2O_3$ in wt%.

First, a chemically extracted residue was made to obtain useful and statistical information on precipitates obtained from a much larger volume than in the case of TEM observations. The matrix was dissolved in a solution of 1% tetra methyl ammonium chloride – 10% acetyl acetone – methanol solution [32,33]. The reason why this solution was used is that it never dissolves the nanometric oxide particles of interest under well controlled conditions. Tamura et al. reported that Y_2O_3 completely dissolves in hydrochloric acid–methanol, which is traditionally used for chemical extraction of steels, and Y–Ti–O system oxides like $Y_2Ti_2O_7$ are unstable in solutions using hydrochloric acid [34,35]. After

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Table 1
Nature of small particles from the literature

No.	Year	ODS alloy	Stoichiometric	Non-stoichiometric	Reference
1	1990	12Cr-ODS	$Y_2Ti_2O_7$ and/or Y_2TiO_5	–	[1]
2	1995	13Cr-ODS (High Ti and Y_2O_3)	$Y_2Ti_2O_7$ and Y_2TiO_5	–	[25]
3	2000	12YWT	$Y_2Ti_2O_7$ and Y_2TiO_5 (Refer to [2])	Y-Ti-O cluster	[10]
4	2002	12Cr-ODS	$Y_2Ti_2O_7$ and/or Y_2TiO_5	–	[4]
5	2003	12YWT	–	Y-Ti-O cluster (Y/Ti<1)	[26]
6	2004	MA957	–	Y-Ti-O cluster (Y/Ti<1)	[27]
7	2004	9Cr-ODS 12Cr-ODS	–	$Y_2Ti_2O_7$ (Y/Ti>1) with complicated pyrochlore-type structure	[12]
8	2004	9Cr-ODS	–	Nearly $Y_2Ti_2O_7$ or nearly Y_2TiO_5	[19]
9	2004	9Cr-RAFM-ODS	$Y_2Ti_2O_7$	–	[28]
10	2005	9Cr-RAFM-ODS	$Y_2Ti_2O_7$	–	[29]
11	2005	12YWT MA957	–	Y-Ti-O cluster (Y/Ti<1)	[30]
12	2006	14YWT	–	Y-Ti-O cluster (Y/Ti<1)	[31]

dissolution of the matrix, the chemically extracted residue was trapped and separated using a filter with 100 nm pores by percolation. This filter can trap precipitates larger than about 15 nm, because of clogging with precipitates during percolation [34,35]. The extracted residue together with the filter were then analyzed by XRD system using Co Kα ($\lambda = 0.178897$ nm).

Second, extraction replicas were made. An alloy specimen was mechanically polished up to a mirror finish and then electrochemically etched using the same solution as used in the former experiment to make a chemically extracted residue. After etching, carbon deposition was performed in a vacuum better than 4.0×10^{-5} Pa. Then, the deposited carbon layer was carefully and gently removed in the same apparatus using the same procedure as for etching. The removed carbon layer containing precipitates was taken with a butterfly mesh from the solution and observed in a FEG–STEM (spot size: less than about 2 nm) with EDS system.

3. Results and discussion

In the matrix of electropolished thin foils, very small oxide particles dispersed with sizes below 5 nm were revealed, as shown in Fig. 1. They appeared as black or white dots. The analysis of their size distribution will be reported in another work [36]. In general, it is very hard to obtain good signals from very small precipitates in such electropolished thin foil during EDS analysis. This is because the profile of EDS has very high peaks of iron from the matrix. These high iron peaks are very harmful noise for the analysis of the chemical composition of very small precipitates. Therefore, the technique of extraction replica was performed in this work. It is possible to precisely analyse the chemical composition without the noise from the matrix.

Before precise TEM observation of extraction replicas, information on precipitates can be obtained from results of the XRD analysis of chemically extracted residue, as shown in Fig. 2. Though the chemically extracted residue on the filter with 100 nm pores does not include the information on very small precipitates about a few nanometers, it gives helpful information for the identification of precipitates. This is because the chemically extracted residue was obtained from a much larger volume, as compared to TEM observations. In Fig. 2, four types of precipitate can be observed: $Y_2Ti_2O_7$, TiO_2 (Anatase), Al_2O_3, and Fe_3O_4 (Magnetite). Unmarked peaks came from the filter paper and/or the sample holder analyzed together with the extracted residue. The smallest particles were $Y_2Ti_2O_7$ particles with the broadest width at half height. Their size was roughly calculated and estimated to be about 15 nm using Scherrer's relation. Therefore, particles larger than about 15 nm were trapped by the filter. Al_2O_3 and Fe_3O_4 particles are coarse micrometric inclusions, as observed in the other work using EPMA (electron probe microanalysis) [36]. In general, they are hardly observed using TEM, because of their too large micrometric size.

TEM images of extraction replica are shown in Fig. 3. In these replicas, both very small particles less than about 5 nm in size and coarse aggregated particles about 200 nm in size were observed. Fine particles were not lost and successfully trapped in the extraction replicas. Taking into account the results of XRD analysis in Fig. 2, EDS analysis of the replicas confirmed the existence of four types of precipitates, (1) non-stoichiometric very small particles less than about 10 nm, which contain yttrium and titanium (Y/Ti < 1), (2) stoichiometric $Y_2Ti_2O_7$ (Y/Ti ≈ 1) particles about 15 nm, (3) TiO_2 particles with a very low yttrium content, and (4) aggregated coarse oxides about 100 nm, which consist of Y–Ti–O system oxide and Al–O system oxide. The reason why yttrium could be detected from such large TiO_2 particles is possibly that smaller parti-

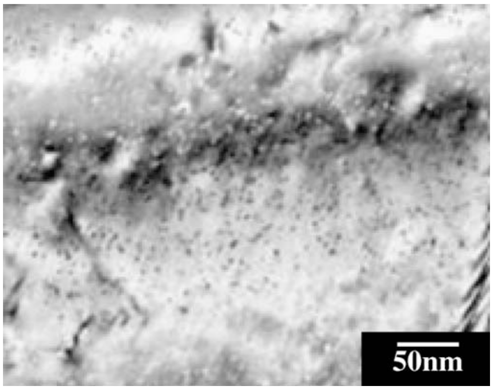


Fig. 1. TEM image of dispersed small particles.

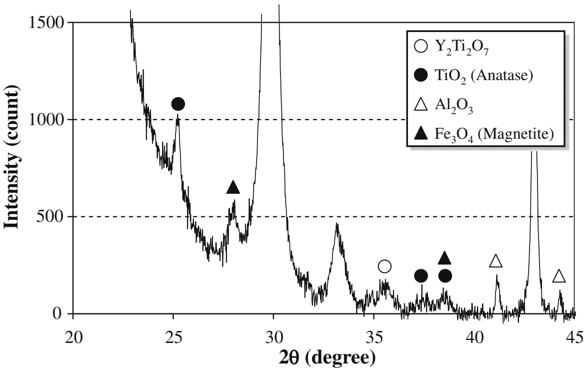
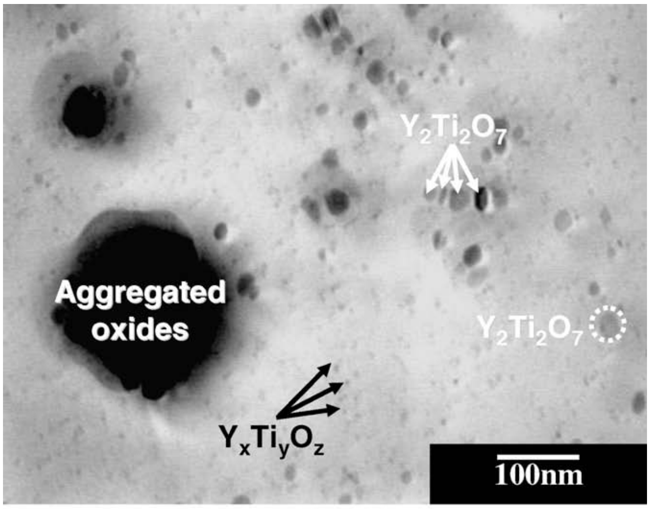
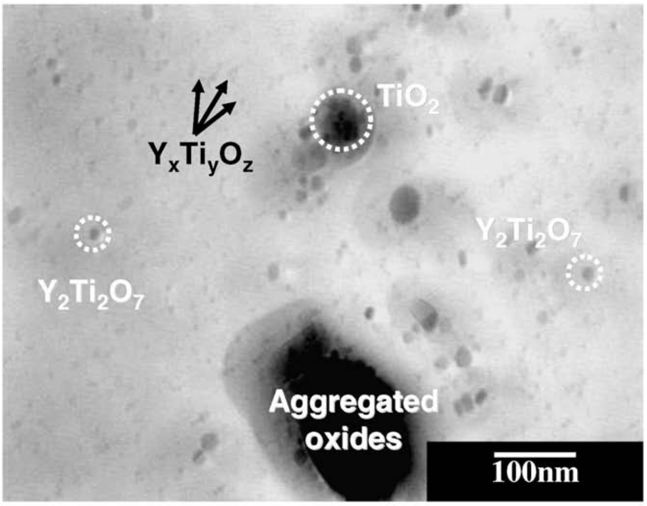


Fig. 2. XRD spectrum of extracted residue.



(a) Area 1



(b) Area 2

Fig. 3. TEM image of extraction replica.

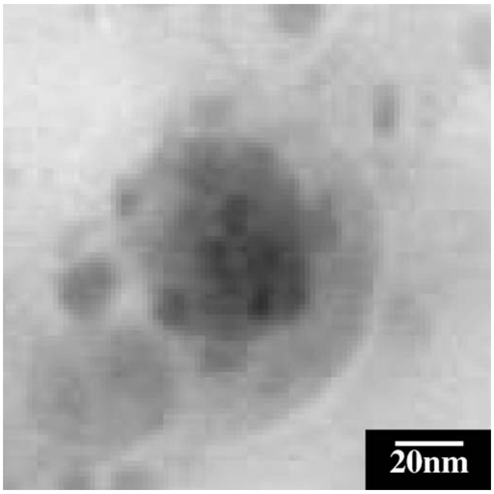


Fig. 4. TEM image of precipitate on large TiO_2 particle with small particles.

cles with more yttrium aggregated and coexisted, as shown in Fig. 4. Such aggregated coarse oxides were already observed and they will be reported in the other work [36].

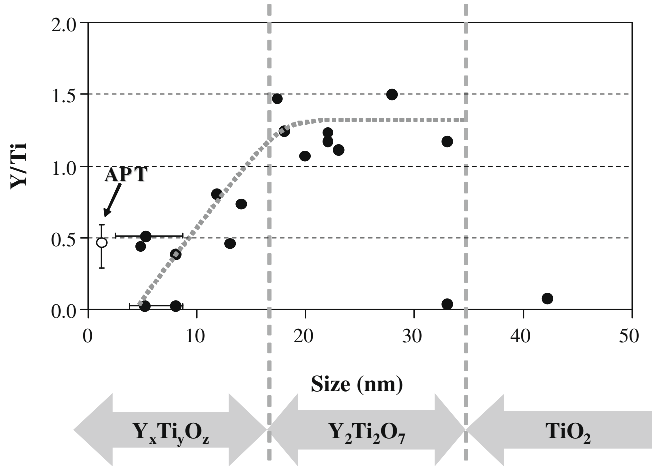


Fig. 5. Correlation between chemical composition and size of oxide particles.

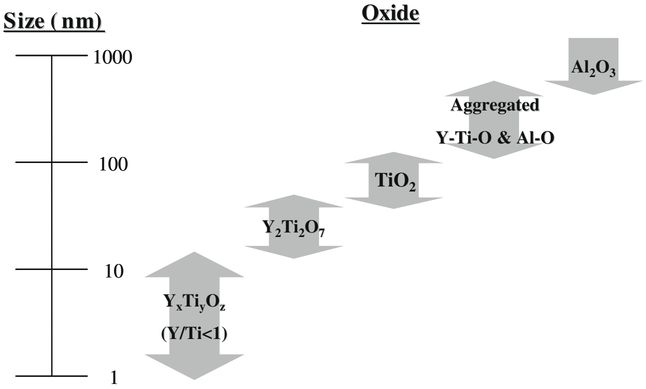


Fig. 6. Size distribution of oxides.

The results of TEM observations together with the results of chemical composition analysis can be summarized, as shown in Fig. 5. In the figure, the filled circles without error bar are the results of point analyses. The filled circles with error bar are the results of area analyses. The area analyses were selectively performed on areas including only small particles less than about 10 nm. The purpose of this area analysis is to statistically confirm the results of point analyses on small particles less than 10 nm, and to avoid misunderstandings caused by drift of the sample during point analysis on very small particles less than 5 nm. The ratio of yttrium level divided by titanium level for small particles less than about 35 nm obviously decreases with decreasing size of the particles. The ratio approaches the ratio calculated from the results of APT conducted by Miller et al. [27,30], as shown as an open circle in the figure. In Fig. 5, three types of precipitates are clearly seen, (1) non-stoichiometric very small Y-, Ti-, O-enriched clusters from ∼2 to ∼15 nm (Y/Ti < 1), which is consistent with the results of APT reported in [10,26,27,30,31], (2) stoichiometric $Y_2Ti_2O_7$ particles from ∼15 nm to ∼35 nm, which is consistent with the results of TEM observations reported in [1,10,28,29], and (3) TiO_2 particles larger than ∼35 nm with a low yttrium content.

In the literature [1,4,10,12,19,25–31], small particles dispersed in the matrix are believed to belong to only one type of phase. However, it was revealed in this work that very small particles belong to at least two types of phase. The disagreement with the past reports is caused by the difference of size of the analyzed particles. APT observations generally focused on very small particles less than a few nanometers, but EDS analysis using TEM mainly focused on larger particles about several tens of nanometers. This is due to the sample drifting during the prolonged analysis on very small nanometric particles. In TEM images like Fig. 1, very small particles less than a few nanometers are clearly visible, but it is very difficult to perform an EDS analysis on them.

The ratio of yttrium level to titanium level of most very small particles is less than about 0.5, as shown in Fig. 5. Based on the result, it can be suggested that the appropriate increase of titanium content compared to yttrium content could be an effective way to increase the number of very small oxide particles by modifying the chemical composition of the bulk. However, all the added titanium did not contribute to the formation of Y-, Ti-, O-enriched particles, as summarized and shown in Fig. 6. TiO_2 particles were also observed and they had larger sizes which are believed to hardly contribute to oxide dispersion strengthening. In 9Cr-ODS alloys, such large titanium oxides were found on the prior particle boundaries which were the surfaces of mechanically alloyed powders before consolidation, and these large titanium oxides degraded the creep property [22,37]. Therefore, the strict control of oxygen in atmosphere during mechanical alloying is all the more essential, as already studied and reported by Ohtsuka et al. [19–21,23].

4. Conclusion

In this work, chemically extracted residues and extraction replicas were carefully prepared from the MA957 ODS ferritic alloy, and then observed using XRD and FEG–STEM, respectively, in order to provide knowledge about the nature of very small oxide particles. From the result, it was revealed that the chemical composition of very small particles relates to their size. They belong to at least two types of phase, (1) non-stoichiometric Y-, Ti-, O-enriched clusters from $\sim$2 to $\sim$15 nm ($Y/Ti < 1$) and (2) stoichiometric $Y_2Ti_2O_7$ particles from $\sim$15 nm to $\sim$35 nm. Based on the result, it is suggested that an appropriate increase of titanium content compared to yttrium in oxide particles by modifying the chemical compositions of ODS alloys could be an effective way to obtain a very fine dispersion of oxide particles for further oxide dispersion strengthening.

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