

An *in situ* Dispersoid Formation in ODS Steels by a Wet Processing

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1. Introduction

Oxide dispersion strengthened (ODS) steels have excellent high temperature mechanical properties due to the presence of thermally stable nano-scale oxides distributed in their matrix[1]. Uniformly-distributed fine dispersoids hinder dislocation motions effectively. Some commercial ODS steels are being used for high temperature structural applications[2]. ODS ferritic martensitic steels (FMS) have been considered as candidate cladding materials for a sodium-cooled fast reactor (SFR) in order to increase an fuel temperature[3]. A mechanical alloying (MA) process or high energy ball milling is a conventional fabrication process of ODS steels. Because the critical problem of the MA process is impurity contamination during milling, innovative fabrication processes which can fabricate clean ODS steels with excellent mechanical properties needs to be developed[4].

In this study, a wet mixing process using yttrium salt precursors was proposed in order to form *in situ* oxide dispersoids by internal oxidation of yttrium salts during the process. One austenitic stainless steel and two ferritic martensitic steels (FMS) were used as matrix alloys. Oxidation reactions of yttrium salts were analyzed by thermodynamic calculations.

2. Experimental Procedures

Yttrium nitrate hydrate, $Y(NO_3)_3 \cdot 6H_2O$, or yttrium chloride, YCl_3 , were dissolved in water or ethanol at room temperature. For an austenitic stainless steel, commercially available 316L stainless steel powder was wet-mixed in the yttrium salt solutions. For FMS, two mixtures (similar to 12YWT and NF616) of elemental powders of Fe, Cr, Mo, W, V, and Ti were wet-mixed in the yttrium salt solutions. After drying the wet mixtures, the powder mixtures were canned and degassed at 500°C before a hot isostatic pressing (HIP) and a hot rolling at 1150°C. Microstructures of the specimens were observed by using a transmission electron microscopy (TEM) and the elemental compositions of the interaction layers were measured by using an energy dispersive X-ray spectroscopy (EDS). Crystal structures of dispersoids were measured by neutron diffraction, X-ray diffraction (XRD) and selected area diffraction of TEM. High temperature tensile tests were carried out up to 700°C to measure the mechanical properties.

3. Results and Discussion

Among yttrium salts, yttrium nitrate has the lowest Y_2O_3 formation temperature as shown in Table 1. It has been reported that yttrium nitrate was decomposed to yttrium oxide below 500°C[5]. Therefore yttrium oxide is expected to form during the degassing process which has been carried out at 500°C. Chemical analyses of wet-processed ODS steel powders before and after a degassing showed that oxygen content was decreased due to decomposition. When yttrium chloride was used as an yttrium salt for a wet processing, the oxygen content was reduced further because chlorides do not contain oxygen in their chemical formula. When the variation of free energy of Y_2O_3 formation from yttrium salts was calculated by using thermodynamic data as shown in Fig. 1, it is apparent that Y_2O_3 formation is favorable with increasing temperature.

The non-MA process resulted in much lower carbon content because a contamination from the milling balls and jar was not incorporated. It has been known that the excess oxygen dissolved in the matrix steel has a detrimental effect on the formability of ODS steels. Excess oxygen content was lower in the wet-processed ODS steels when compared with the MA ODS steels using the same 316L powder as shown in Table 2.

Various oxides were observed from microstructural analyses of a hot rolled specimen by using TEM. Selected area diffraction pattern (SADP) analyses revealed that $Y_2Si_2O_7$, and SiO_2 were formed after HIP and a hot rolling as shown in Fig. 2. It has been reported that Y_2O_3 reacts with Si to form a complex oxide of yttrium and silicon such as Y_2SiO_5 above 850°C [6]. 316L stainless steel powders in this study had a relatively high silicon content of about 0.8 wt%. However, when a neutron diffraction patterns of ODS samples annealed from 850 to 1150°C for 2 hours were analyzed, Y_2O_3 diffraction peaks were not found whereas $Y_2Si_2O_7$ diffraction peaks were observed.

High temperature tensile tests of a hot-rolled specimen at 700°C showed that the non-MA processed ODS steels have larger tensile elongations when compared to the MA ODS steels. Because both steels were processed at the same HIP and hot rolling temperature, the difference of tensile elongation might be due to the impurity contamination during the powder processing. When considering the size of dispersoids in austenitic ODS steel were larger than the reported sizes of FMS ODS steels, more optimized HIP and hot rolling temperatures will result in the improved mechanical properties in high silicon containing ODS steels.

Table 1. Summary of yttrium oxide formations from yttrium salt precursors.

Precursors	Dehydration temperature	Intermediate form	Y ₂ O ₃ formation temperature
Yttrium Acetate	220°C	Y ₂ O ₂ CO ₃	630°C
Yttrium Oxalate	400°C	Y ₂ O ₂ CO ₃	750°C
Yttrium Nitrate	290°C	UONO ₃	460°C

Table 2. Comparison of the minor element content of the mechanically alloyed and the wet-processed 316L-based ODS steel samples.

Process	C	O	N	Y	Ex.O
MA Process	500	2370	770	1700	1911
Wet Process	199	1776	465	1100	1479

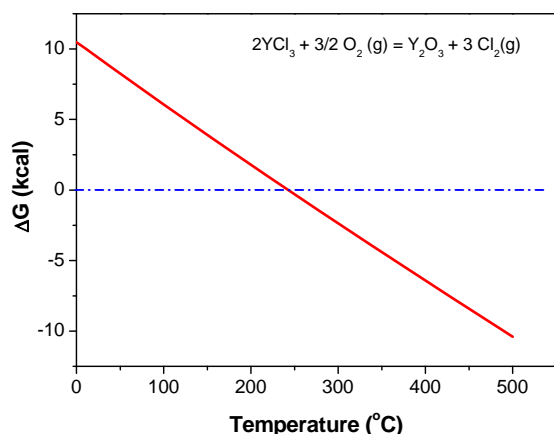


Fig.1. The variation of free energy of Y₂O₃ formation from the YCl₃ and O₂(g) reaction with temperature.

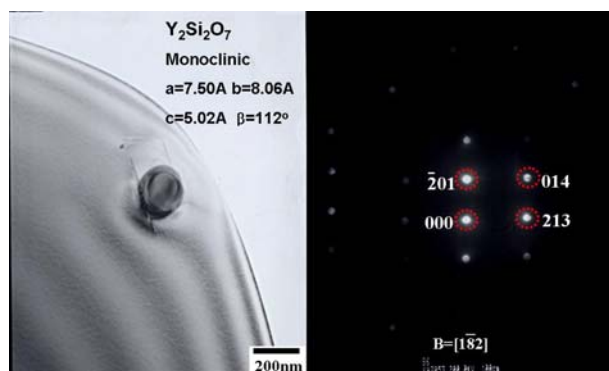


Fig.2. A TEM micrograph and a selected area diffraction pattern of a yttrium silicate dispersoid in a wet processed 316L-based ODS steel sample.

4. Conclusions

In situ dispersoids were formed in non-MA ODS stainless steels fabricated by a wet mixing process using yttrium salt solutions. The wet process resulted in a much lower carbon contamination when compared with the MA process. ODS steels fabricated by a wet process showed larger high temperature tensile elongations when compared to MA ODS steels. Although thermodynamic analyses showed Y₂O₃ forms during degassing process, yttrium silicate were found after a hot isostatic pressing due to high silicon content in 316L.

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