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Improvement of 9Cr-ODS martensitic steel properties by controlling excess oxygen and titanium contents

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Abstract

The effects of different percentages of oxygen and titanium on the mechanical properties and microstructure of 9Cr-ODS steel were investigated. It was shown that the high-temperature strength was drastically improved by controlling the atomic ratio between excess oxygen and titanium (x in TiO_x) around 1.0. When x is around 1.0, the elongated alpha-grains containing the ultra-fine and close oxide particle dispersion were generated in addition to equiaxed martensite grains. Furthermore, the number density of oxide particle in the martensite grains increased. The control of phase transformation and oxide particle dispersion by adjusting oxygen and titanium contents should be a key technology to achieve superior high-temperature strength.

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1. Introduction

Martensitic steel presents excellent swelling resistance, however, high-temperature strength has to be improved to utilize this steel for fission and fusion reactor application. Oxide dispersion strengthened (ODS) martensitic steel has the potential for both excellent high temperature strength and swelling resistance, and it is considered as one of the most promising candidates for advanced fast reactor (FR) core and fusion reactor blanket.

Japan Nuclear Cycle Development Institute (JNC) has successfully produced cladding tubes with 9Cr-ODS martensitic steel [1]. It was also revealed that increase of excess oxygen (defined as total oxygen contents in steel minus oxygen contents in Y_2O_3) and lack of titanium lead to particle coarsening and high-temperature strength deterioration [2–4].

The present paper describes the optimization of titanium and excess oxygen contents in 9Cr-ODS martensitic steel, based on the microstructure and the mechanical properties. The excess oxygen content was varied from 0.026 to 0.17 wt% in this study.

2. Experimental

2.1. Manufacture of 9Cr-ODS martensitic steels

Mixtures of iron (Fe), chromium (Cr), carbon (C), tungsten (W) and yttrium oxide (Y_2O_3) powder, together with different amounts of iron-yttrium intermetallic compound (Fe_2Y) and iron oxide (Fe_2O_3) powder were mechanically alloyed in a high purity argon (Ar) atmosphere (99.99 wt% Ar) for 48 h with the rotation speed of 220 revolutions per minute (rpm). Y_2O_3 powders consisted of clusters composed of 20 nm diameter particles. Mechanical alloying (MA) was performed using an attrition-type ball mill with 10 kg batch. The alloyed powders were sealed in mild-steel cans and degassed at 400 °C in 0.1 Pa vacuum. The powder-filled can was made up into 10 mm diameter rod through the

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process of 1150 °C hot-extrusion and air-cooling. The final heat treatment was conducted in three different ways: normalizing (1050 °C×1 h, air-cooling (AC)), normalizing and tempering (1050 °C×1 h, AC⇒780 °C×1 h, AC), or else furnace-cooling (1050 °C×1 h, AC ⇒ furnace-cooling at 30 °C/h).

Excess oxygen (Ex.O) was controlled by changing the mixture ratio of Fe_2Y and Fe_2O_3 powders based on the standard mixture ratio of Fe–9Cr–0.13C–0.2Ti–2W–0.34Y_2O_3. Higher amount of titanium of 0.46 wt% was added in T5. Base steel without Y_2O_3 addition was also manufactured (B0) in order to investigate the effects of oxide particle on mechanical properties and microstructure.

2.2. Properties evaluation

Metallographic examinations were carried out using an optical microscope, where the normalized steels were observed. Oxide particle distributions were observed using a 200 keV transmission electron microscope (TEM). The images of the oxide particles were obtained from the furnace-cooled steels. EDS analyses of yttrium and titanium contents of the oxide particles were performed using extracted replica technique.

Vickers hardness tests with 1 kgf loading were conducted for furnace-cooled steels. Uni-axial creep tests and uni-axial tensile tests at 700 °C for the normalized-and-tempered steels were carried out with the gage section of 6 mm diameter and 30 mm length. The stress of the creep tests ranged from 100 to 180 MPa. By fitting the derived rupture data to a logarithmic curve with method of least squares, 1000 h creep rupture strength was estimated.

3. Results and discussions

3.1. Effect of excess oxygen and titanium on transformation behavior

Chemical analysis results are summarized in Table 1. The excess oxygen and titanium approximately stay in the target levels. A parameter 'x in TiO_x', which is defined as the atomic percentage ratio of excess oxygen to titanium, was estimated in each steel and shown in Table 1.

The optical micrographs are shown in Fig. 1, where the horizontal direction corresponds to the direction of the hot-extrusion. It is considered that the elongated grains in Y2, Mm11 and T5 are delta-ferrite, which remained untransformed without transforming to gamma when the temperature is increased from room temperature to 1150 °C for hot-extrusion [3]. In this study, we call this untransformed delta-ferrite the residual alpha-phase. If all grains perfectly transform from alpha to

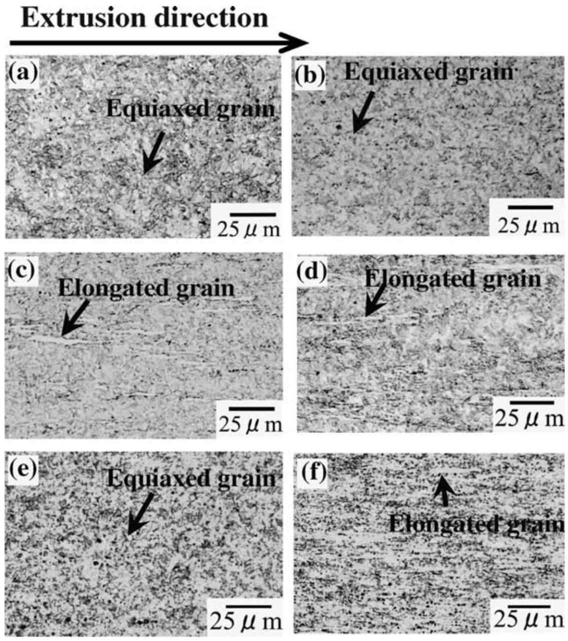

Fig. 1. Metallographic photographs of manufactured steels after normalizing: (a) B0, 0.080 wt% Ex.O, 0.18 wt% Ti; (b) Y1, 0.026 wt% Ex.O, 0.20 wt% Ti; (c) Y2, 0.044 wt% Ex.O, 0.21 wt% Ti; (d) Mm11, 0.070 wt% Ex.O, 0.20 wt% Ti; (e) T3, 0.15 wt% Ex.O, 0.21 wt% Ti; (f) T5, 0.17 wt% Ex.O and 0.46 wt% Ti.

Table 1
Chemical composition of manufactured steels

	Chemical composition (wt%)								
	C	Cr	W	Ti	Y	O	Y_2O_3	Ex.O	x in TiO_x
Y1	0.13	8.9	1.93	0.20	0.27	0.099	0.34	0.026	0.4
Y2	0.13	8.9	1.96	0.21	0.28	0.12	0.36	0.04	0.6
Y3	0.14	8.9	1.97	0.21	0.28	0.18	0.36	0.10	1.5
Mm11	0.14	9.0	1.92	0.20	0.28	0.15	0.36	0.08	1.2
E5	0.13	8.9	1.97	0.21	0.28	0.16	0.36	0.07	1.0
T3	0.13	8.8	1.93	0.21	0.27	0.22	0.34	0.15	2.1
T5	0.13	8.8	1.93	0.46	0.27	0.24	0.34	0.17	1.1
B0	0.13	9.1	1.95	0.18	0.01	0.08	0.01	0.08	1.3

gamma during the 1150 °C hot-extrusion and from gamma to martensite at subsequent air-cooling, the microstructure would be composed of only equiaxed grains. Normally, the Fe–9Cr–2W–0.2Ti–0.13C alloy should transform to gamma during the 1150 °C heat treatment, referring to the phase diagram [3]; however, the 9Cr-ODS steel shows a peculiar transformation behavior that the alpha-phase remains even at 1150 °C. On the other hand, base steel without Y_2O_3 addition (B0) shows the normal transformation behavior that no residual alpha-phase are generated at 1150 °C as seen in Fig. 1.

The carbon depletion in matrix due to titanium carbide formation should decrease the driving force for the alpha to gamma transformation because titanium is added in 9Cr-ODS. The pulling force against gamma grain boundary migration by oxide particle dispersion (Zener effects [5,6]) should make the driving force consume while the grain boundaries are moving over oxide particles These two factors would restrict the alpha–gamma transformation and cause the residual alpha-generation at 1150 °C in 9Cr-ODS.

Comparison of microstructures in Y1 with 0.026 wt% Ex.O, Y2 with 0.04 wt% Ex.O and Mm11 with 0.07 wt% Ex.O shows that the increasing excess oxygen generates the residual alpha. Volume fraction of oxide particles should increase as excess oxygen increases, as described later in Section 3.3. For the formation of Y–Ti complex oxide ($Y_2Ti_2O_7$), required amount of excess oxygen is 0.1 wt%. Y1 contains too little excess oxygen (0.026 wt%), that is 1/4 of required amount to convert the mixed Y_2O_3 powders to complex oxide ($Y_2Ti_2O_7$). This lower excess oxygen in Y1 would result in lower volume fraction of oxide particles and lower consumption of the driving force than higher excess oxygen-containing steel (Mm11[2] and Y2), which would lead to the complete transformation in Y1. On the other hand, the transformation was incomplete in Mm11[2] and Y2 where larger part of the driving force would be consumed for grain boundary migration over the higher number density oxide particles.

T3 with higher excess oxygen of 0.15 wt% should contain as much volume fraction of oxide particles as Mm11, nevertheless, it does not contain the residual alpha-grain. It has been reported that the reduction of carbon and oxygen inside grains occurs by the strong strain-induced diffusion to grain boundaries during mechanical alloying [7,8]. The depletion of oxygen inside grains would cause more titanium carbide formation instead of titanium oxide, which is considered to promote the local carbon depletion inside grains. In T3, the carbon depletion would be suppressed by the formation of more titanium oxide instead of carbide, because T3 contains higher oxygen. This lower carbon depletion should lead to enough driving force for alpha to gamma transformation in T3. T5 with 0.46 wt% titanium also contains residual alpha, even though it contains as much excess oxygen as T3. Higher titanium is considered to promote residual alpha-generation by causing higher carbon depletion in matrix.

3.2. Effect of excess oxygen and titanium on oxide particle distribution

Oxide particle observations using TEM were performed in both elongated residual alpha-grains and equiaxed grains as shown in Fig. 2. The oxide particles in residual alpha-grains showed significantly finer and closer distribution than in equiaxed grain of both Mm11 and T5, which implies that residual alpha-grains have extremely higher strength than equiaxed grains.

Oxide-particle diameter was estimated from image analysis, and the results are summarized against the ratio between atomic percentages of excess oxygen to titanium (x in TiO_x) with the Vickers hardness test results in Fig. 3. The furnace-cooled steels were used for Vickers hardness test to estimate the oxide dispersion strengthening without high density of dislocations.

As seen in Fig. 3, hardness becomes a maximum when x is around 1.0, where oxide particle diameter becomes the finest in equiaxed grain and elongated residual alpha-grains containing ultra-fine oxide particle dispersion are formed. The increase of x, namely higher excess oxygen against titanium, induced the decline of hardness. This would be caused by the coarsening of oxide particle dispersion in equiaxed grain as well as diminution of residual alpha-grain. Lowering of x less than 1.0 also makes specimens soften. This is caused by both the reduction of oxide particle number density due to the lack of excess oxygen and the lowering of residual alpha-grains.

3.3. Identification of oxide particles and estimation in total amount of oxide particles

The EDS analysis of yttrium and titanium in oxide particles were performed in equiaxed grains and summarized against excess oxygen, as shown in Fig. 4. The atomic ratio of yttrium to titanium (Y/Ti) in oxide particles is 9.0 in Y1. Therefore, the particles are thought to be Y_2O_3 type containing solute titanium. As for Y2, Y/Ti is around 2.5, which oxide particle might be a non-stoichiometric oxide similar to Y_2TiO_5. Higher excess oxygen-containing steel than 0.07 wt% (Mm11, Y3, T4, T3) has the Y/Ti ratio of from 1.1 to 1.3 in oxide particles. It is inferred that oxide particles in these steels may be non-stoichiometric oxides similar to $Y_2Ti_2O_7$.

If we assume that Y_2O_3 powders were converted to $Y_2Ti_2O_7$ particles in the higher excess oxygen-containing steel (Mm11, Y3, T4 and T3), the amount of oxide

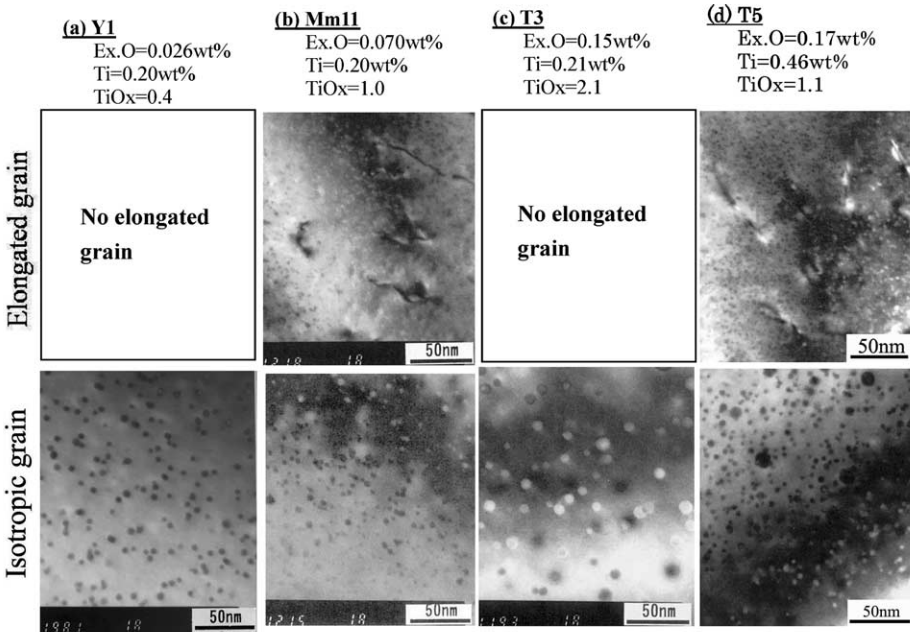

Fig. 2. TEM observation result of manufactured steels (after furnace-cooling).

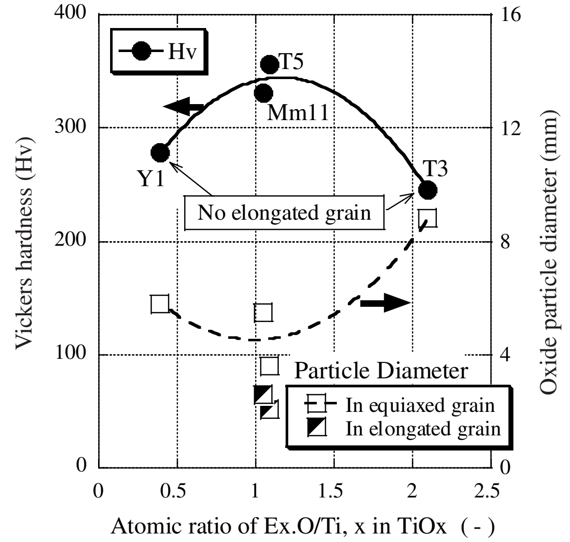

Fig. 3. Vickers hardness and oxide particle diameter of manufactured steels.

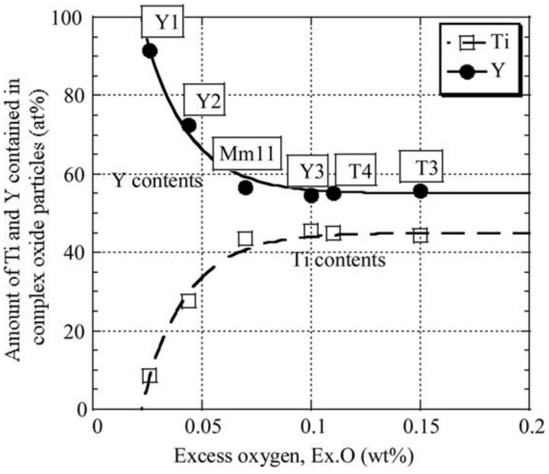

Fig. 4. EDS analysis result of oxide particles in transformed alpha-grain by extracted replica/EDS method.

particles are estimated to be ~0.6 wt%. The mixed Y_2O_3 powder would approximately remain as Y_2O_3 in Y1. Therefore, the amount of oxide particles in Y1 would be estimated to be 0.34 wt%, which is half as much as the amount of oxide particles in Mm11. This difference in amount of oxide particles between the higher excess oxygen-containing steel and Y1 would cause the difference of Zener effects.

3.4. High-temperature strength

The creep rupture strength and tensile properties at 700 °C are evaluated and plotted against x as shown in Fig. 5. It should be noticed that creep strength as well as short-term strength (0.2% proof stress, tensile strength) becomes a maximum when x is around 1.0, where elongated residual alpha-grains are formed and oxide particles in equiaxed grain are most finely and densely distributed. Uniform elongation shows similar tendency

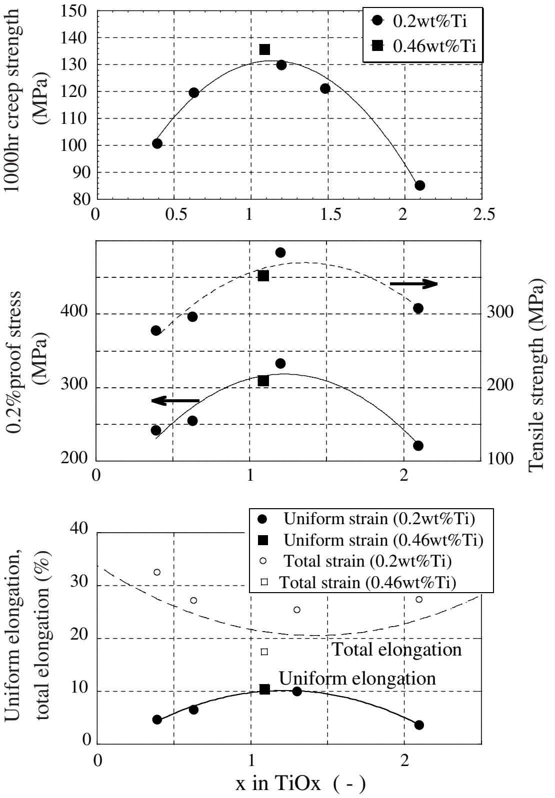

Fig. 5. Mechanical properties of manufactured steels.

as the strength alteration with x. It is considered that the improvement of uniform elongation around $x \sim 1.0$ is caused by the promotion of work-hardening due to denser oxide particle dispersion.

4. Summaries

The effects of different percentages of excess oxygen and titanium on the mechanical properties and microstructure of 9Cr-ODS steel were investigated. The results can be summarized as follows:

(1) Controlling the atomic ratio between excess oxygen and titanium (x in TiO_x) to around 1.0 produces elongated residual alpha-grains, which possess ultra-fine and close oxide particle distribution.
(2) It is considered that the number density of oxide particles in equiaxed grains would be maximum when x in TiO_x is around 1.0, where oxide particles are most finely distributed and the required amount of excess oxygen for Y–Ti complex oxide is maintained in the steel.
(3) It is indispensable for achieving the superior high-temperature strength to control x around 1.0 and promote the formation of residual alpha-grains and high number density of oxide particles in equiaxed grains.

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