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Effect of nitrogen concentration on nano-structure and high-temperature strength of 9Cr-ODS steel

Hiroshi Oka*, Takashi Tanno, Satoshi Ohtsuka, Yasuhide Yano, Takeji Kaito

Japan Atomic Energy Agency, 4002 Narita-cho, Oarai-machi, Ibaraki 311-1393, Japan

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ABSTRACT

The objective of this study was to investigate the effect of nitrogen concentration on mechanical properties and nano-structure of 9Cr oxide dispersion strengthened (ODS) ferritic/martensitic steel. 9Cr-ODS specimens with the wide range of nitrogen concentration, from 0.004 to 0.110 wt%, were systematically investigated by hardness and tensile tests and several microstructural characterization methods. Hardness and tensile strength at 973 K were significantly decreased as nitrogen concentration increased, due to the decrease in the amount of the residual α-ferrite phase. Coarse inclusions containing Y and Ti, which could negatively affect creep strength and processability, were formed, and that suggested degradation of the nano-particle distribution. The technical knowledge obtained in this study will contribute towards the setting of a reasonable nitrogen concentration specification for 9Cr-ODS steel.

1. Introduction

Oxide dispersion strengthened (ODS) ferritic/martensitic steels are attractive for use in nuclear applications under extreme conditions due to their excellent high-temperature creep properties and irradiation resistance [1–5]. For 9Cr-ODS steel, their excellent creep strength is attributable to a ferritic/martensitic dual phase structure and nano-sized oxide particles uniformly dispersed in a matrix. In past studies, it was found that the concentration of excess oxygen [6] and titanium [7] in the 9Cr-ODS steel had a large influence on its nano-structure and creep strength. The specifications of the concentration range of these alloying elements were determined on the basis of the strength.

On the other hand, nitrogen can be found anywhere in the air, and can be included in the 9Cr-ODS steel through several possible ways during the manufacturing process, e.g. from nitrogen impurity in the raw material powder, as contaminant introduced during mechanical alloying, and as contaminant introduced due to extrusion capsule breakage. In the 9Cr-ODS steel specification, the tentative upper limit of the nitrogen concentration is 0.07 wt%. This value was determined based on knowledge about the ferritic/martensitic steel developed by Japan Atomic Energy Agency for use as the wrapper tube material of a fast reactor, where the nitrogen concentration ranged from 0.03 to 0.07 wt% [8]. However, the effect of nitrogen concentration on the material property of the 9Cr-ODS steel has not been investigated.

In recent manufacturing test of 9Cr-ODS steel, which used the fully pre-alloyed method [9,10] for manufacture, significantly softened extrusion bars were confirmed. From the composition analysis, the nitrogen concentration of these bars was found to be relatively high. The presence of nitrogen contaminant was thought to result from breakage of the mild steel capsule in the extrusion process.

From the viewpoint of quality stability of materials, it is desirable to strictly define the nitrogen concentration range, but from the viewpoint of production yield and cost, the concentration range should be defined with the minimum necessary specification. To define the concentration range reasonably, an enlargement of technical knowledge about the nitrogen concentration effect on 9Cr-ODS steel is important. Therefore, to enlarge the technical knowledge so that a reasonable nitrogen concentration specification for 9Cr-ODS steel can be set, the influence of nitrogen concentration on the strength and nano-structure of 9Cr-ODS steel was systematically investigated in this study.

For evaluating the ferrite/martensite dual phase structure in 9Cr-ODS steel, the distribution of tungsten was utilized in this study. Tungsten is a ferrite stabilizer having a higher partitioning ratio into ferrite compared with austenite, thereby preferentially partitioning into ferrite matrix at the temperature higher than Ac3 temperature [11–13].

2. Experimental

Pre-alloyed powder (Fe-0.13C-9Cr-2W-0.2Ti in wt%) and 0.35 wt% Y_2O_3 powder were alloyed mechanically with an attritor ball mill for 48 h using the ball/powder ratio of 15. 9 batches of mechanically-alloyed (MA) powder were produced and then combined into 1 batch.

* Corresponding author.
E-mail address: oka.hiroshi@jaea.go.jp (H. Oka).

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Table 1
Chemical composition (wt%) of the MA powder and extruded bars.

Specimen type	ID[a]	C	Cr	W	Ti	Y	O	N	Y_2O_3[b]	Ex.O[c]
MA powder	–	0.11	9.0	1.9	0.20	0.28	0.14	0.004	0.36	0.07
	2401M	0.11	9.14	1.97	0.21	0.27	0.15	0.031	0.34	0.07
	2405M	0.11	9.07	1.95	0.21	0.27	0.15	0.004	0.34	0.07
	2409M	0.11	9.09	1.95	0.21	0.27	0.15	0.069	0.34	0.07
	2410M	0.11	9.05	1.95	0.21	0.27	0.14	0.004	0.34	0.07
	2414M	0.11	9.09	1.96	0.21	0.27	0.14	0.004	0.34	0.07
	2418M	0.12	9.10	1.96	0.21	0.27	0.14	0.004	0.34	0.07
Extruded bar	2419M	0.11	9.06	1.95	0.21	0.27	0.15	0.037	0.34	0.07
	2423M	0.12	9.19	1.99	0.21	0.27	0.14	0.110	0.34	0.07
	2427M	0.11	9.09	1.96	0.21	0.27	0.15	0.082	0.34	0.08
	2428M	0.11	8.95	1.93	0.21	0.27	0.14	0.004	0.34	0.07
	2429M	0.13	9.03	1.95	0.21	0.27	0.14	0.004	0.34	0.07
	2431M	0.11	9.08	1.96	0.21	0.27	0.14	0.004	0.34	0.07

[a] Letter M denotes middle part of extrusion bar.
[b] Estimated from yttrium concentration with the assumption that yttrium exists as Y_2O_3.
[c] Excess oxygen, which is defined as the value obtained by subtracting oxygen concentration in Y_2O_3 from the total oxygen concentration in the specimen.

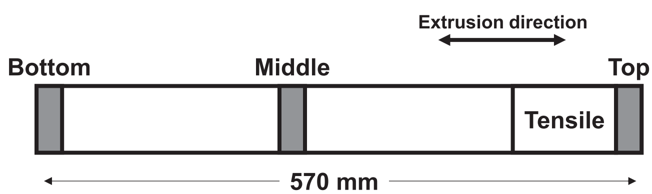

Fig. 1. Positions where specimens were obtained in an extruded bar. The leading side in the hot extrusion process is referred to as Top.

The nitrogen concentration of each batch of MA powder was confirmed to be within the range of 0.003 to 0.004 wt%; there was no notable unevenness in the nitrogen concentrations of MA powder. Table 1 shows the chemical composition of the combined MA powder. The combined MA powder was then canned into mild steel with degassing and subjected to hot-extrusion at 1423 K. The extruded bar was subjected to hot-forging at 1373 K for straightening, then annealed at 1323 K for 1 h followed by cooling at a rate of 70 K/h for the purpose of softening. In all, 16 extruded bars of 9Cr-ODS steel were produced.

The specimens for chemical composition analysis and hardness test were taken from the top, middle and bottom parts of each bar, as shown in Fig. 1. The obtained chemical compositions for the middle specimens of 12 randomly chosen extrusion bars are shown in Table 1. The 7 of 12 extruded bars showed no significant difference in composition compared to the MA powder. However, 5 of 12 extruded bars showed the increment of nitrogen concentration, indicating nitrogen contamination during the hot-extrusion process. The hardness test with a load of 1kgf at room temperature was performed for all hardness test specimens (top, middle and bottom parts of 16 bars, i.e. 48 specimens). The uniaxial tensile test at 973 K was performed for 7 extruded bars with a cylindrical tensile specimen having the gauge length of 30 mm and diameter of 6 mm. Normalized-and-tempered specimens were used for the tensile test. Moreover, an additional chemical composition analysis of Y, O, and N was carried out for some of the hardness test specimens and a gauge part of the tensile specimens. The hardness test results and chemical composition results for all specimens can be found in the supplementary data.

Elemental distribution maps were obtained by electron probe micro analysis (EPMA) using the JEOL JXA-8900RL operated at 15 kV. The purpose of the EPMA analysis was to investigate the distribution of tungsten for evaluating the fraction of ferrite phase in the ferrite/martensite dual phase structure. The specimens subject to EPMA analysis were annealed at 1323 K for 1 h followed by rapid cooling in order to retain the equilibrium tungsten distribution that had been present at 1323 K. The area fraction of the tungsten-partitioned area, i.e. ferrite phase, was estimated by image analysis of the EPMA mapping views. At least three images with a size of 80 × 80 μm were used for the analysis of each specimen. Another purpose of EPMA analysis was to observe the distribution of submicron-sized precipitates such as oxide and nitride precipitates. Therefore, the distributions of oxygen, nitrogen, titanium,

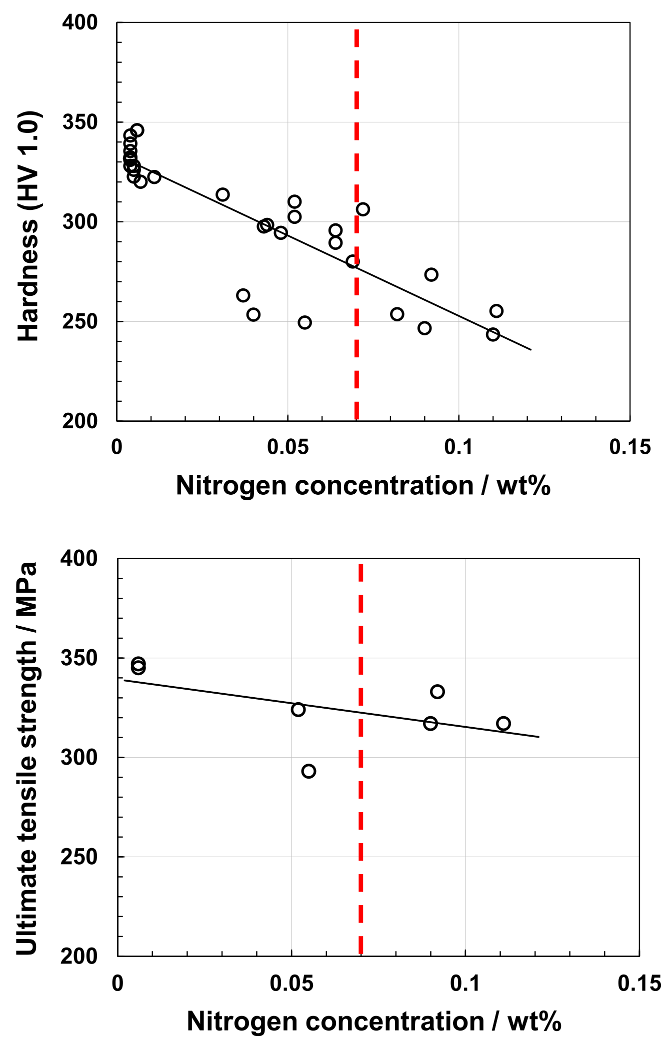

Fig. 2. Hardness and ultimate tensile strength as a function of nitrogen concentration. The dashed line shows the current upper limit of nitrogen concentration (N ≤ 0.07 wt%).