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Creep rupture properties of nitrogen added 10Cr ferritic/martensitic steels

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Abstract

The effect of nitrogen on creep rupture strength and microstructure evolution in 10Cr–N steels has been studied. Creep testing was carried out at 600 and 650 °C under constant load conditions. The prior austenite grain size and martensite lath width were decreased by addition of nitrogen. The Cr_2X precipitates were stabilized at 750 °C as the nitrogen content increased. The 0.08 wt% N steel had a minimum martensite lath width and finer Cr_2X precipitates in the as-tempered state. Creep rupture strength increased with increasing nitrogen content. The optimum nitrogen content for creep rupture strength was 0.08 wt% in 10Cr ferritic/martensitic steels, and Cr_2X precipitates were not dissolved after creep deformation. These fine and stable Cr_2X precipitates may contribute to the increase of creep rupture strength.

1. Introduction

Ferritic/martensitic 9–12% Cr–Mo steels are widely used as high temperature materials in power plants and chemical industries, with high strength and thermal conductivity, low thermal expansion, and good resistance to corrosion. Due to the better irradiation properties (e.g. excellent irradiation swelling resistance) than austenitic alloys [1], they have been receiving attention for application as fuel cladding or core structures of various advanced nuclear reactors. One of the most important challenges in fusion technology research is the development of low-activation materials. Presently ferritic/martensitic steels, vanadium alloys and SiC/SiC composite materials are considered as promising candidates. Of these candidates, low-activation ferritic/martensitic steels are recognized as the most advanced and developed materials [2,3]. However the creep rupture strength of ferritic/martensitic steels abruptly decreases during long term creep exposure at high temperature [4]. In order to increase operating temperature and power plant life, an optimum balance between fracture toughness and creep rupture strength should be achieved.

Nitrogen is an element of precipitation hardening. The nitrides are more stable and less soluble than the corresponding carbide because the enthalpy of formation of nitrides is higher than that of carbides. The movement of free dislocation may be effectively suppressed by the addition of nitrogen [5]. The creep rupture strength of ferritic/martensitic steel at about 600 °C is largely influenced by the stability of precipitates, and the nitrogen may contribute to the increase of the creep rupture strength.

In the present work, nitrogen up to 0.10 wt% is added and the effect of nitrogen on the creep rupture strength of 10Cr ferritic/martensitic steels has been studied.

2. Experimental procedures

The chemical compositions of materials investigated in this study are shown in Table 1. Nitrogen up to 0.10 wt% was added in 10Cr steels. Five 30 kg ingots were melted in vacuum and hot rolled at 1150 °C to a final plate thickness of 15 mm. All specimens were austenitized at 1050 °C for 1 h and tempered at 750 °C for 2 h.

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Table 1
Chemical composition, prior austenite grain size and lath width of 10Cr ferritic/martensitic steels (wt%)

	C	Cr	Mo	V	Nb	Si	Mn	Ni	N	Prior γ grain size (μm)	Lath width (nm)
N1	0.13	10.17	1.20	0.20	0.20	0.07	0.48	0.50	0.003	15.3	433
N2	0.15	9.94	1.27	0.20	0.20	0.08	0.48	0.49	0.020	16.3	371
N3	0.15	10.00	1.28	0.20	0.20	0.08	0.48	0.50	0.045	14.5	315
N4	0.15	10.01	1.29	0.20	0.21	0.06	0.47	0.45	0.079	11.5	280
N5	0.14	9.96	1.27	0.20	0.21	0.06	0.48	0.47	0.093	11.7	412

After austenitizing and tempering, creep tests were conducted at 600 and 650 °C under constant load conditions. Creep specimens of 6 mm diameter and 30 mm length in gauge section were taken from plate transverse to the rolling direction.

The precipitates were observed by using a transmission electron microscope (TEM) equipped with an energy dispersive X-ray spectrometry (EDS) for carbon extraction replicas. Lath width was also measured with TEM micrographs. The number of laths evaluated for each material was about 250.

3. Results and discussion

3.1. Microstructure in the as-tempered state

The variation of prior austenite grain size with nitrogen content is shown in Table 1. As nitrogen content increased the prior austenite grain size decreased. The prior austenite grain size has a good relationship to the size and content of NbX precipitates. NbX precipitates effectively inhibit austenite grain growth because NbX precipitates remained undissolved during the austenitizing treatment. The content of NbX precipitates increased with increasing nitrogen content. Until the nitrogen content reached 0.08 wt%, the number densities of NbX precipitates increased, but the size of NbX precipitates was not changed greatly. Both content and size of NbX precipitates increased with the next increase in N, to the 0.10 wt% N steel. Some very large NbX precipitates were formed in N5 steel. These precipitates may not effectively restrict austenite grain growth, and N4 and N5 steels had a similar prior austenite grain size. The martensite lath width also changed with nitrogen content. Martensite lath width showed a tendency to decrease as nitrogen content increased. As shown in Table 1, 0.08 wt% N steel had the minimum martensite lath width.

The most stable carbide formed in these steels was $M_{23}C_6$, and small quantity of other carbides, nitrides, and carbonitrides such as MX (V-rich and Nb-rich) were produced after austenitizing and tempering. Spherodised primary NbX particles were present randomly dispersed in the matrix. Intragranular precipitation of finer particles of VX phases was found. These precipitates were formed in all test materials regardless of nitrogen content. But precipitation behavior of Cr_2X precipitates was different with nitrogen content. In general fine needles of Cr_2X precipitates nucleate primarily on the dislocations within the martensite lath structure during tempering at 450–500 °C [5], and Cr_2X precipitates are replaced by $M_{23}C_6$ phases at higher tempering temperature. The Cr_2X precipitates remained undissolved after tempering at 750 °C in the case with nitrogen content was above 0.08 wt%. This result was consistent with the observations [6] that the increase of nitrogen content from 0.05 to 0.112 wt% stabilized Cr_2X precipitates, thus unlike in the low nitrogen steels, Cr_2X precipitates were not replaced by $M_{23}C_6$ precipitates. The average size of Cr_2X precipitates formed in N5 steel was lager than that in N4 steel.

3.2. Creep properties

Fig. 1 shows the creep rupture strength at 600 and 650 °C. Creep rupture strength increased with increasing nitrogen content and showed a maximum value when the nitrogen content was 0.08 wt%. In short term tests, N3 steel exhibited a higher creep rupture strength than N4 steel at 600 °C. In long term tests, N4 steel exhibited a higher creep rupture strength than N3 steel and the difference may be increased with increasing the time to rupture. In contrast, N4 steel showed the highest creep rupture strength at 650 °C both in short and long term tests. It showed that the improvement of microstructural stability by addition of nitrogen appeared more distinctly at 650 °C. Creep tests at lower stress are continuing for N4 steel to confirm exactly the effect of nitrogen on creep rupture strength.

The creep rupture elongation at 600 and 650 °C was also shown in Fig. 1. As the time to rupture increased the creep rupture elongation decreased, but the creep rupture elongation did not change with the testing temperature. N5 steel had the highest creep rupture elongation regardless of test temperature. N1, N2, N3,

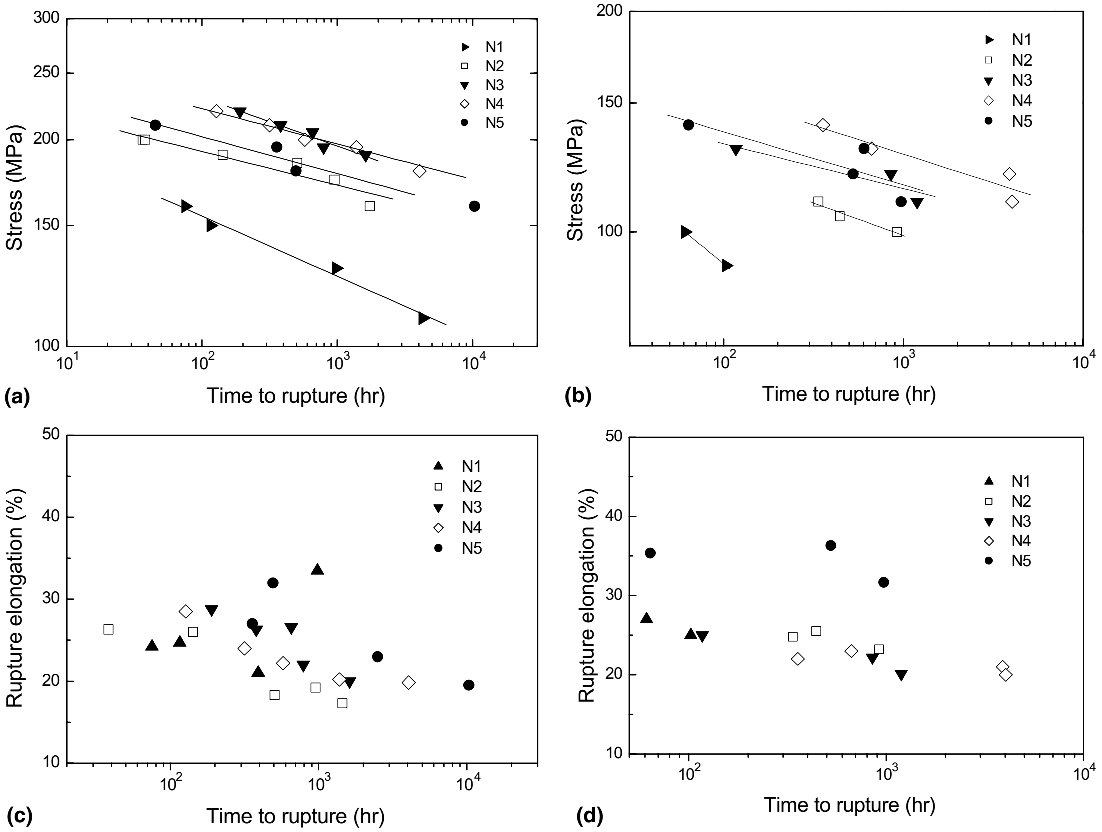

Fig. 1. Creep rupture strength of 10Cr steels: (a) tested at 600 °C, (b) tested at 650 °C and creep rupture elongation of 10Cr steels, (c) tested at 600 °C and (d) tested at 650 °C.

and N4 steels had a similar creep rupture elongation at 650 °C. The creep rupture elongation of N4 steel was above 20% for all completed tests.

3.3. Microstructural changes after creep deformation

Softening is the main physical phenomenon observed in materials after creep tests. All the creep specimens show pronounced strain softening in the gauge length, measured as a decrease in hardness. Thermal softening in the ends of creep specimens is lower. Dislocation recovery and carbide coarsening are the primary causes of material softening. The original martensite lath structure becomes coarser and round-shaped, with formation of dislocation cells and subgrains, while analysis of the precipitates show carbide coarsening and Laves phase formation. This process leads to progressive reduction in both the hardness and creep rupture strength of these steels.

The growth curve of martensite lath width is shown in Fig. 2, where the mean width of martensite laths is plotted as a function of time to rupture. Lath width in the tested specimens increased with increasing time to rupture. The lath width grew rapidly with time to rupture up to 10^3 h, after that time the growth rate slowed.

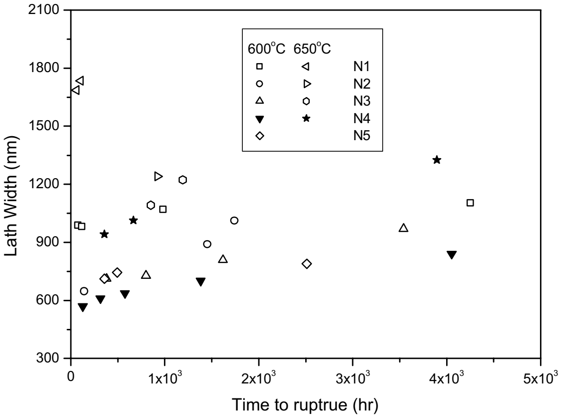

Fig. 2. Variation of martensite lath width with time to rupture.

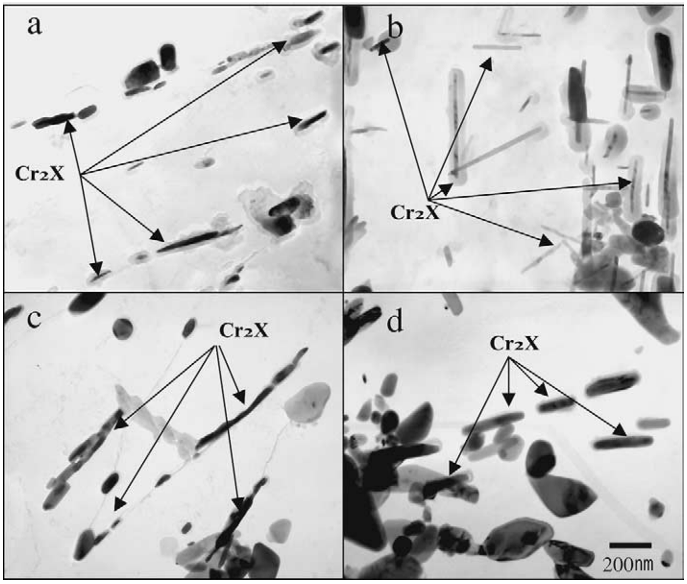

Fig. 3. Morphology of Cr_2X precipitates: (a) before creep in N4, (b) after creep at 600 °C for 1619 h in N4, (c) after creep at 600 °C for 1384 h in N5 and (d) after creep at 650 °C for 4045 h in N4.

N4 steel which showed the highest creep rupture strength had the smallest lath width for all values of the time to rupture. In other words, it took longer to reach the same lath width in N4 steel at the same creep temperature. This means that the softening during creep deformation was restricted by the addition of nitrogen in ferritic/martensitic steels. Here the optimum content of nitrogen was 0.08 wt%.

Fig. 3(b) and (c) shows the morphology of Cr_2X precipitates after creep at 600 °C for 1619 h in N4 and 1384 h in N5 steel. In N4 and N5 steels, Cr_2X precipitates were not dissolved during creep deformation at 600 °C. The Cr_2X precipitates may act as an effective dispersoid against dislocation glide during creep at 600 °C, so these fine, stable Cr_2X precipitates may contribute to the increase of creep rupture strength. It is expected that if more fine, stable Cr_2X precipitates were uniformly distribute in the as-tempered state, the creep rupture strength may be further increased. Fig. 3(d) shows the morphology of Cr_2X precipitates after creep testing at 650 °C for 4045 h in N4 steel. These were partially dissolved and coarsened after creep at 650 °C for 4045 h. It showed that the stability of Cr_2X precipitates at 650 °C during the creep testing became deteriorated.

The VX precipitate forms preferentially on dislocations inside martensite laths during creep deformation and plays an important roll in the excellent creep resistance of ferritic/martensitic steels with higher nitrogen content. VX precipitates are very stable and grow slowly. However, the precipitation behavior of VX precipitates was not distinctly changed with nitrogen content when nitrogen content is over 0.02 wt%.

The creep rupture strength of ferritic/martensitic steels is improved by three major factors, i.e. grain refinement, solution hardening and precipitation hardening. There are two possible explanations for the higher strength of N4 steel. First, the creep rupture strength of ferritic/martensitic steels is correlated inversely with the martensite lath width [7]. N4 steel had smaller martensite lath width and prior austenite grain size, so N4 steel had higher creep rupture strength. Second, the coarsening of precipitates should be minimized to maintain the precipitation hardening effect during creep testing. The stability of precipitates increases as their enthalpy of formation increases. Nitrides are more stable and less soluble than the corresponding carbide. Thus the use of enhanced nitrogen content in ferritic/martensitic steels is soundly based to improve microstructural stability. The fine, stable Cr_2X precipitates formed in N4 steel had a good effect on improving the creep rupture strength of 10Cr ferritic/martensitic steels. In the future, it is necessary to investigate the exact behavior of Cr_2X precipitates in creep tests lasting tens of thousands of hours.

4. Summary

The effect of nitrogen on the creep rupture strength of 10Cr steels was investigated. The following conclusions were obtained:

1. The prior austenite grain size and martensite lath width were decreased by increasing the nitrogen content. Minimum prior austenite grain size and martensite lath width were 11.5 μm and 280 nm in 0.08 wt% N steel, respectively. As the nitrogen content increased, the dissolution of the Cr_2X phases was delayed, so Cr_2X precipitates remained undissolved after tempering at 750 °C in high nitrogen steels. Coarse Cr_2X precipitates were formed in 0.10 wt% N steel, but only fine Cr_2X precipitates were formed in 0.08 wt% N steel after tempering at 750 °C.
2. Creep rupture strength increased with the addition of nitrogen and showed a maximum value when the nitrogen content was 0.08 wt%. The improved properties results from the finer Cr_2X precipitates and the smaller lath width formed in the as-tempered state.

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