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Journal of Nuclear Materials 367–370 (2007) 48–53

journal of nuclear materials

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New nano-particle-strengthened ferritic/martensitic steels by conventional thermo-mechanical treatment

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Abstract

For increased fusion power plant efficiency, steels for operation at 650 °C and higher are sought. Based on the science of precipitate strengthening, a thermo-mechanical treatment (TMT) was developed that increased the strength from room temperature to 700 °C of commercial nitrogen-containing steels and new steels designed for the TMT. At 700 °C increases in yield stress of 80 and 200% were observed for a commercial steel and a new steel, respectively, compared to commercial normalized-and-tempered steels. Creep–rupture strength was similarly improved. Depending on the TMT, precipitates were up to eight-times smaller at a number density four orders of magnitude greater than those in a conventionally heat treated steel of similar composition.

1. Introduction

Reduced-activation ferritic/martensitic steels are at present considered to be the only viable structural material for fusion power plants [1]. A major shortcoming of the steels is high-temperature strength, which limits the maximum service temperature to 550–600 °C. This has led to the work for developing oxide dispersion-strengthened (ODS) steels [2–4]. These steels, which are strengthened by small oxide particles, are produced by complicated and expensive mechanical-alloying, powder-metallurgy techniques. This paper presents the science and technology of the development of new and different dispersion-strengthened steels using conventional processing techniques for applications at 650 °C and higher.

2. Concept of new steels

For elevated-temperature strength, obstacles to dislocation motion must be built into the metal matrix. In ODS steels, the obstacles are a high number density of oxide particles. A normalized-and-tempered (N&T) reduced-activation or commercial 9–12% Cr steel consists of martensite laths (average width ≈0.25–0.5 μm) with a dislocation density of 10^{13}–10^{15} m^{-2}; obstacles to dislocation motion are provided by ‘large’ (60–200 nm) $M_{23}C_6$ particles located mainly on lath boundaries and prior-austenite grain boundaries and smaller (20–80 nm) MX precipitates in the matrix. Fig. 1 shows the microstructure for N&T modified 9Cr–1Mo steel with average particle size and number density

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doi:10.1016/j.jnucmat.2007.03.001

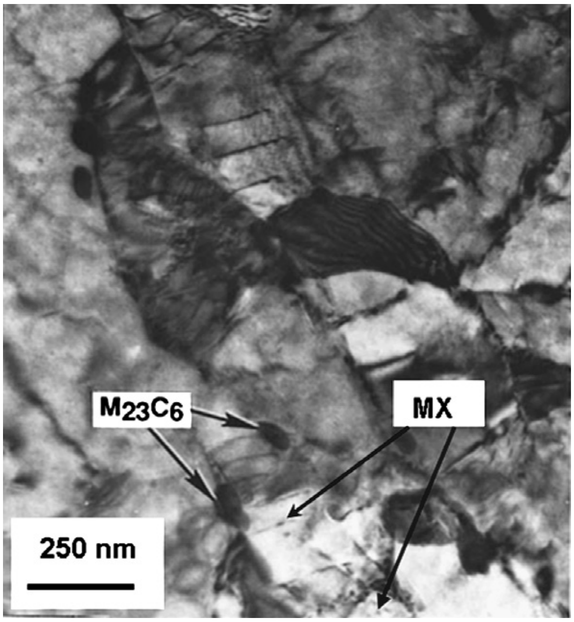

Fig. 1. Transmission electron microscopy photomicrograph of modified 9Cr–1Mo steel after a conventional normalizing-and-tempering heat treatment.

of $M_{23}C_6$ estimated at 130–150 nm and $3–6 \times 10^{19}\ m^{-3}$, respectively, and MX estimated at 32 nm and $7–8 \times 10^{18}\ m^{-3}$, respectively [5].

Most of the precipitation strengthening in 9–12% Cr steels is attributed to MX precipitates [6]. That strengthening effect is limited, however, because of their small number density and relatively large size. In nitrogen-containing high-temperature steels containing vanadium and niobium, MX is a combination of vanadium- and niobium-rich nitrides containing some carbon, and niobium-rich carbides and/or carbonitrides [7,8].

The objective of this work is to develop reduced-activation and conventional nitrogen-containing steels that maximize the strengthening capability of the MX precipitates. Based on computational thermodynamics calculations, steel compositions were identified that have vanadium and nitrogen concentrations to produce a high number density of MX precipitates for increased elevated-temperature strength. To produce such a distribution, a high number density of heterogeneous precipitation sites is required. Dislocations were chosen as nucleation sites, and they were introduced by a thermo-mechanical treatment (TMT).

A similar TMT procedure was previously used to strengthen a steel with TiC as the MX precipitate [9,10]. Strengthening of reduced-activation and conventional nitrogen-containing steels by use of ‘thermo-mechanical controlled processes (TMCP)’ was also studied [11], but the TMCP differed from the TMT of this work. A nitride-strengthened steel without a TMT was recently developed [12].

3. Experimental procedure

A TMT was developed to produce a fine dispersion of nano-sized MX particles in nitrogen-containing steels. The primary objective was the production of reduced-activation and conventional steel compositions that optimize the TMT effect, but because facilities were not available to readily produce nitrogen-containing steels, the TMT was first applied to 25.4-mm plates of nitrogen-containing commercial Cr–MoWVNb steels. The steels included modified 9Cr–1Mo (nominal composition in wt% Fe–9.0Cr–1.0Mo–0.20V–0.08Nb–0.05N–0.10C) and HCM12A (Fe–12.0Cr–2.0W–0.40Mo–1.0Cu–0.30Ni–0.25V–0.05Nb–0.06N–0.10C). Later the process was used on small (400-g) nitrogen-containing heats of Fe–9.0Cr–1.0Mo–1.0Ni–0.30V–0.07Nb–0.05C compositions developed especially for the TMT. Steels with 0.042 (9Cr–MoNiVNbN1), 0.035% N (9Cr–MoNiVNbN2), and 0.065% N (9Cr–MoNiVNbN3) were produced.

The TMT involves heating the steel to 1050–1300 °C to convert ferrite to austenite and dissolve existing precipitates, after which it is cooled to a hot-working temperature (700–1000 °C). Hot rolling the plates used in this work introduces a high density of dislocations that act as nucleation sites for a fine distribution of MX precipitates (vanadium- or niobium-rich nitride and/or carbonitride). Finally, the steel is annealed to grow precipitates to optimum size for hardening. Air cooling converts the austenite to martensite.

4. Results and discussion

4.1. Microstructure

The effect of a TMT on microstructure can be controlled by changing (1) austenitization temperature and time, (2) hot-working temperature, (3) amount of reduction by hot working, and (4) annealing temperature and time.

Application of a TMT to 25.4-mm-thick plates of modified 9Cr–1Mo produced a dramatically different microstructure (Fig. 2) from that of N&T steel (Fig. 1). Transmission electron microscopy (TEM)

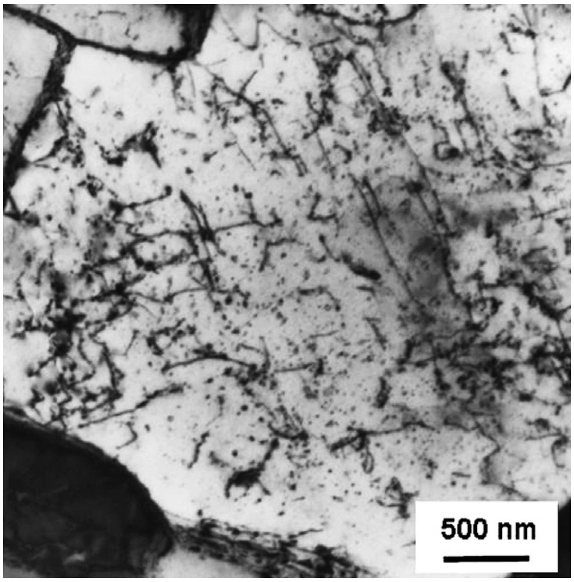

Fig. 2. Transmission electron microscopy photomicrograph of modified 9Cr–1Mo steel after the new thermo-mechanical treatment.

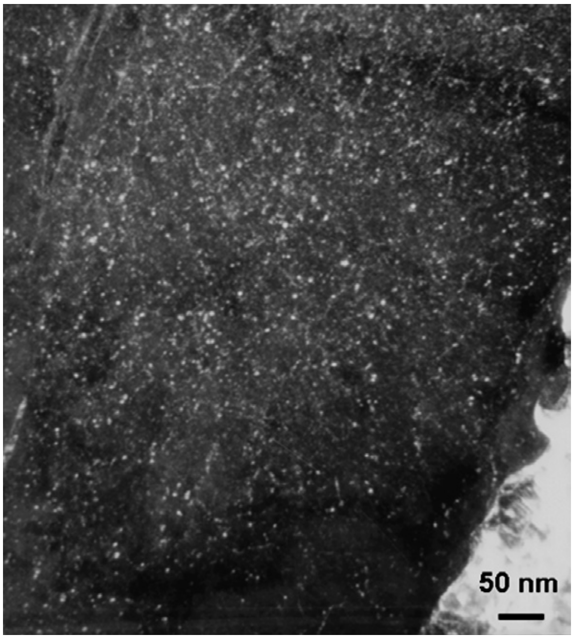

Fig. 3. Dark-field transmission electron microscopy image of the commercial 12% Cr HCM12A steel after a TMT at 800 °C plus a temper (1 h at 750 °C).

indicated that, depending on the TMT, the average MX particle size was up to four-times smaller (7–8 nm) and the number density up to three orders of magnitude greater ($2–9 \times 10^{21}$ m^{-3}) than for N&T steel. Note that precipitates in Fig. 2 are somewhat larger, as they were chosen to demonstrate the high-number density; because of their size they were easily viewed by bright-field TEM.

The commercial 12% Cr steel HCM12A was given two versions of the TMT, one rolled at 750 °C and the other at 800 °C (Fig. 3). In contrast to modified 9Cr–1Mo, no fine precipitates were visible by TEM. After tempering 1 h at 750 °C, however, fine precipitates (4.2 nm, 2.4×10^{21} m^{-3}) were detected by dark-field TEM in the one given the 800 °C TMT. Evidently, the higher nitrogen concentration in HCM12A resulted in precipitates that were too fine to observe by TEM. Tempering coarsened the precipitates in the steel rolled at 800 °C so they were visible by dark-field TEM.

To demonstrate the effect of nitrogen, the 9Cr–MoNiVNbN2 (0.035% N) was compared with the 9Cr–MoNiVNbN3 (0.065% N) after similar TMTs. For both, average MX precipitate size was smaller and number density greater than for the best achieved with modified 9Cr–1Mo given the TMT: about 4.0 nm, 1.0×10^{22} m^{-3} and 3.3 nm, 7.2×10^{22} m^{-3} for 9Cr–MoNiVNbN2 and 9Cr–MoNiVNbN3, respectively – about 8 times smaller at a number density almost four orders of magnitude greater than MX in N&T modified 9Cr–1Mo.

4.2. Mechanical properties

After a TMT on modified 9Cr–1Mo at 750 °C, the 0.2% yield stress and ultimate tensile strength from room temperature to 800 °C were considerably greater than those for N&T steel, with the relative difference increasing with increasing test temperature. At 600 and 700 °C, the yield stress after the TMT was 61% and 88% greater than for the N&T steel. Total elongation after the TMT was less than in the N&T condition, but given the normal trade off of strength and ductility, ductility was excellent with total elongations of 16% and 22% at 600 and 700 °C, respectively.

The 12% Cr steel HCM12A after the TMTs at 750 and 800 °C followed by a temper showed large increases in yield stress relative to N&T HCMA12A: 47% and 64% increases at 600 and 700 °C, respectively, with little difference between the two TMTs. An increase of 22% was observed at 800 °C. The strength of HCM12A with the TMT plus temper was greater than that of modified 9Cr–1Mo steel with just a TMT, a reflection of smaller precipitates at a higher number density in

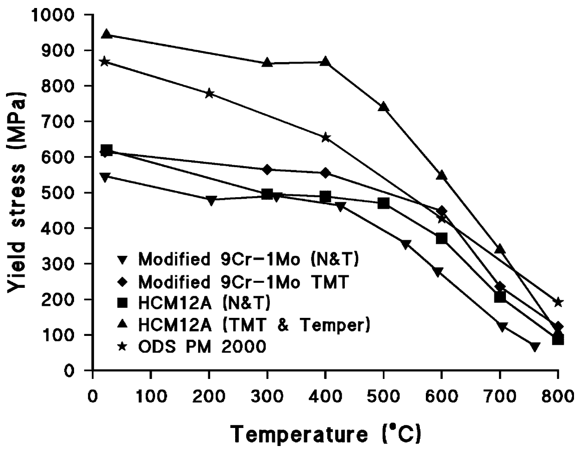

Fig. 4. Yield stress as a function of temperature for modified 9Cr–1Mo steel after a normalize-and-temper (N&T) treatment and a TMT, for HCM12A after N&T and a TMT-and-temper treatment and for the best commercial ODS steel PM 2000.

HCM12A. The strength up to 700 °C of HCM12A was greater than PM 2000, the best available commercial ODS steel (Fig. 4).

The excellent strength properties of new steel compositions developed to take advantage of the TMT are demonstrated by comparing the yield stress of 9Cr–MoNiVNbN1 (0.042% N) with an experimental ODS steel labeled 12YWT (Fe–12.0Cr–2.5W–0.4Ti–0.25Y_2O_3). The strength of 12YWT was superior to that of available commercial ODS steels [4]. The TMT produced yield stress values comparable to those of 12YWT up to 700 °C (Fig. 5(a)). Total elongations for 9Cr–1MoNiVNbN1 in the TMT condition and the TMT-and-tempered condition were also comparable to those of 12YWT (Fig. 5(b)).

In Fig. 6, creep curves for tests at 138 MPa at 650 °C are shown for modified 9Cr–1Mo after a N&T and a TMT. Rupture life after the TMT was ≈80 times greater than for the N&T steel. Even with this large difference in strength, fracture ductility was excellent; total elongation was 21%.

Creep–rupture curves at 650 °C for modified 9Cr–1Mo after a TMT indicated a significant increase in strength relative to N&T modified 9Cr–1Mo [13] and the reduced-activation steels F82H [14] and EUROFER 97 [15] (Fig. 7). After the TMT, rupture life at 650 °C extrapolated to 10 000 h was also about 80 times that of the N&T steel. Extrapolation to 100 000 h gives rupture stresses of ≈60 and ≈40 MPa for the TMT and N&T modified 9Cr–1Mo, respectively. Obviously, the validity of such extrapolations will depend on stability of precipitates produced by the TMT, for which longer-time tests are required. As observed above, HCM12A and the new 9Cr–1MoNiVNbN1 had higher yield stresses and ultimate tensile strengths after the TMTs than modified 9Cr–1Mo with a TMT, so they should have significantly higher creep strengths.

Although the commercial and new steels with TMTs have excellent mechanical properties, it needs to be emphasized that further work is required to validate the materials for future applications. Likewise, larger heats of new reduced-activation and conventional steels with optimum composition are required for the development of the steels to their ultimate potential.

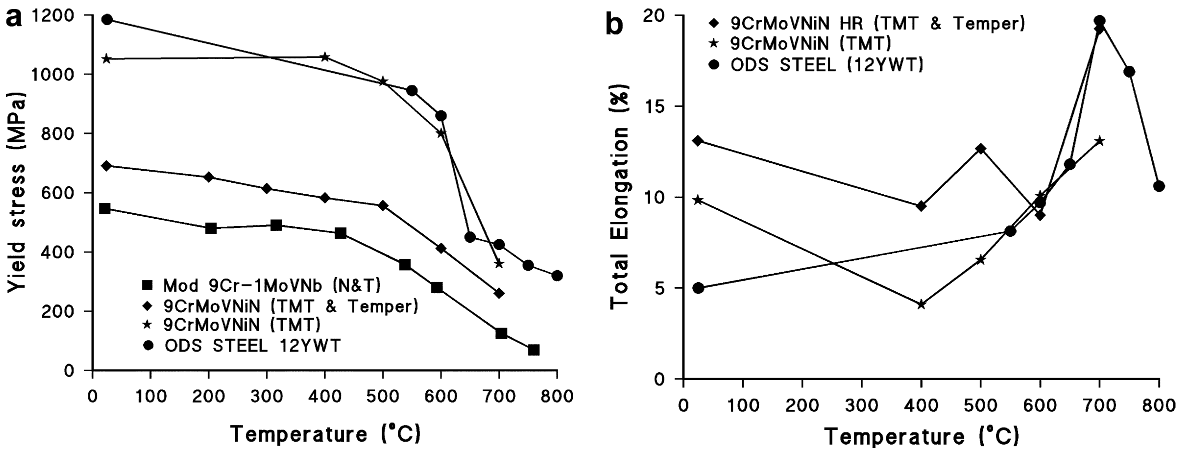

Fig. 5. (a) Yield stress and (b) total elongation of new 9CrMoVNiN steel after a TMT and after a TMT-and-temper treatment compared to normalized-and-tempered (N&T) modified 9Cr–1Mo steel and the high-strength experimental ODS steel 12YWT.

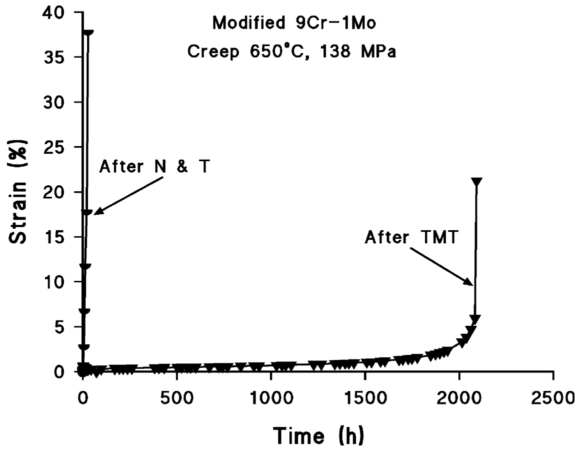

Fig. 6. Creep curves of modified 9Cr–1Mo steel in the normalized-and-tempered (N&T) condition and after a thermo-mechanical treatment (TMT) tested at 138 MPa at 650 °C.

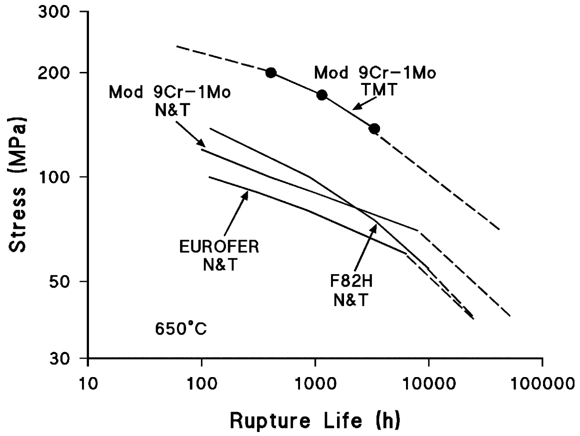

Fig. 7. Creep–rupture curves at 650 °C for modified 9Cr–1Mo steel after a TMT compared to normalized-and-tempered (N&T) modified 9Cr–1Mo, F82H, and EUROFER steels.

5. Summary and conclusions

A thermo-mechanical treatment was devised to produce a dense dispersion of nano-scale vanadium- and niobium-rich MX precipitates in nitrogen-containing 9–12% Cr steels. The new TMT involves three distinct steps, each of which involves a range of conditions that need to be optimized to produce the most favorable precipitate microstructure for elevated-temperature strength. Along with optimization of the TMT process, steel compositions that fully exploit the TMT need to be developed further. The initial efforts on the small heats of new steels demonstrated that it is possible to develop compositions with properties that are significant improvements over the N&T commercial or reduced-activation ferritic/martensitic steels.

The high number density of precipitates produced by the new TMT using conventional processing methods is similar to particle number densities in the best commercial ODS steels produced by much more complicated and expensive powder-metallurgy/mechanical-alloying procedures. Although the nitrogen precipitates will not be as stable as oxides in ODS steels, dispersion strengthening by the MX precipitates should allow such steels to be used at 650–700 °C, a significant improvement over upper-use temperatures of 550–600 °C for N&T commercial or reduced-activation steels now available.

Acknowledgements

K.S. Blakely processed the steels, E.T. Manneschmidt conducted tensile tests, A.M. Kelly conducted creep tests, K.A. Yarborough prepared TEM specimens, and Drs J.M. Vitek, R.K. Nanstad, and S.J. Zinkle reviewed the manuscript. Research was sponsored by the Laboratory Directed Research and Development Program of Oak Ridge National Laboratory and Office of Fusion Energy Sciences, US Department of Energy, under contract DE-AC05-00OR22725 with U.T.-Battelle, LLC.

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