

NEW NANO-PARTICLE-STRENGTHENED FERRITIC/MARTENSITIC STEELS BY CONVENTIONAL THERMOMECHANICAL TREATMENT—R. L. Klueh and N. Hashimoto (Oak Ridge National Laboratory)

OBJECTIVE

The objective of this work is to develop new ferritic/martensitic steels for fusion applications.

SUMMARY

Martensitic steels are considered for structural applications for fusion power plants, but they are limited by strength to temperatures of 550–600°C. For increased 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 an increase in yield stress of 80 and 200% was observed for a commercial steel and a new steel, respectively, compared to commercial steels after a conventional heat treatment. Creep-rupture strength was similarly improved. Depending on the TMT, precipitates in the steels were up to eight-times smaller at a number density four orders of magnitude greater than those in a normalized-and-tempered steel.

PROGRESS AND STATUS

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 places a limit on maximum service temperature capability of 550–600°C. This has led to work to develop oxide dispersion-strengthened (ODS) steels [2-4]. These steels, strengthened by small oxide particles, are produced by complicated and expensive mechanical-alloying, powder-metallurgy techniques, as opposed to conventional processing. 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.

Concept of New Steels

For high elevated-temperature strength, it is necessary to “build” obstacles to dislocation motion into the matrix. In ODS steels, the obstacles are a high number density of small oxide particles. A normalized-and-tempered (N&T) reduced-activation or commercial 9 or 12% Cr elevated-temperature steel, such as commercial modified 9Cr-1Mo (nominal composition Fe-9.0Cr-1.0Mo-0.20V-0.08Nb-0.05N-0.10C, composition in wt %), consists of martensite laths (elongated subgrains with average width $\approx 0.25\text{--}0.5\ \mu\text{m}$) with a relatively high dislocation density ($10^{13}\text{--}10^{15}\ \text{m}^{-2}$); obstacles to dislocation motion are provided by precipitates on prior-austenite grain boundaries, on lath boundaries, and in the matrix. Dominant precipitates are “large” (60–200 nm) M_{23}C_6 particles located mainly on lath boundaries and prior-austenite grain boundaries. Smaller (20–80 nm) MX precipitates, which are present at a low number density, are thought to provide most of the precipitate strengthening. Figure 1 shows the microstructure for N&T modified 9Cr-1Mo steel with average particle size and number density of M_{23}C_6 estimated at 130–150 nm and $3\text{--}6 \times 10^{19}\ \text{m}^{-3}$, respectively, and MX estimated at 32 nm and $7\text{--}8 \times 10^{18}\ \text{m}^{-3}$, respectively [5].

Since the MX particles are the smallest and form in the matrix, most of the precipitation strengthening effect in 9–12Cr steels is attributed to them [6]. That strengthening effect is limited, however, because of their small number density and relatively large size. In nitrogen-containing high-temperature steels with vanadium and niobium, MX has been determined to be a combination of vanadium- and nitrogen-rich nitrides containing some carbon, niobium-rich carbides, and/or carbonitrides [7,8].

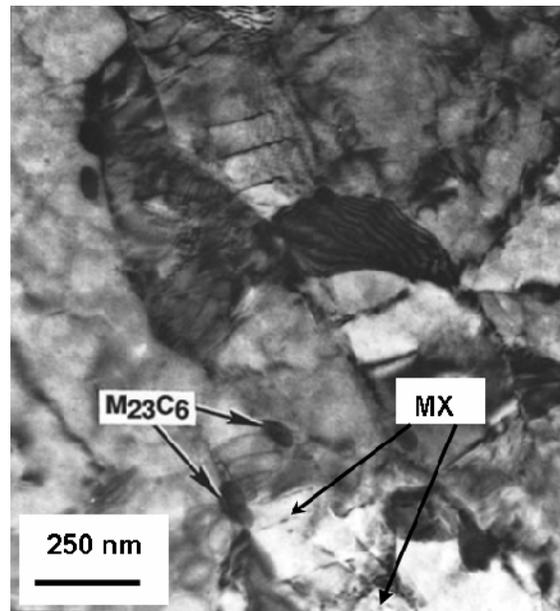


Fig. 1. Transmission electron microscopy photomicrograph of modified 9Cr-1Mo steel after a conventional normalizing-and-tempering heat treatment.

Since a strength contribution in nitrogen-containing steels is obtained from vanadium nitride, the objective of this work was to develop a steel that maximized the MX strengthening capability. Based on computational thermodynamics calculations, steel compositions were determined that have vanadium and nitrogen concentrations to produce a sufficient amount of precipitate for increased strength if precipitates have the correct size and number density. To produce such a distribution, it was reasoned that it would be necessary to provide heterogeneous precipitation sites on which a fine distribution of MX precipitates could form. Dislocations were the chosen sites, and they were introduced by hot working. A similar procedure was previously used to strengthen a steel with TiC as the MX precipitate [9,10].

Experimental Procedure

A thermomechanical treatment (TMT) was developed to produce a fine dispersion of nano-sized particles in nitrogen-containing steels. Because facilities were not available to produce nitrogen-containing steels, the TMT was first applied to 25.4-mm plates of nitrogen-containing commercial Cr-MoVNb-type steels. Later the process was used on small heats of steel compositions developed especially for the TMT.

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 introduces a high density of dislocations that act as nucleation sites for a fine distribution of MX (vanadium- or niobium-rich nitride and/or carbonitride) precipitates. Finally, the steel is annealed to grow precipitates to optimum size for hardening. Air cooling converts the austenite matrix to martensite.

Results and Discussion

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 plate of modified 9Cr-1Mo produced a dramatically different microstructure from the N&T steel (Fig. 2). Transmission electron microscopy (TEM) indicated that, depending on the TMT, average MX particle size was up to four times smaller (7–8 nm) and the number density up to three orders of magnitude greater ($2\text{--}9 \times 10^{21}\text{m}^{-3}$) than for the 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 under bright-field conditions. The commercial 12% Cr steel HCM12A (Fe-12.0Cr-2.0W-0.40Mo-1.0Cu-0.30Ni-0.25V-0.05Nb-0.06N-0.10C) was given two versions of the new TMT, one rolled at 750°C and the other at 800°C (Fig. 3). In contrast to modified 9Cr-1Mo steel, no fine precipitates were visible by TEM. After tempering 1 h at 750°C, however, fine precipitates (4.2 nm, $2.4 \times 10^{21}\text{m}^{-3}$) were detected by dark-field TEM in the one rolled at 800°C. Evidently, the higher vanadium and nitrogen in HCM12A resulted in precipitates that were too fine to observe by TEM. Evidently, tempering coarsened the precipitates in the steel rolled at 800°C so they were visible by TEM.

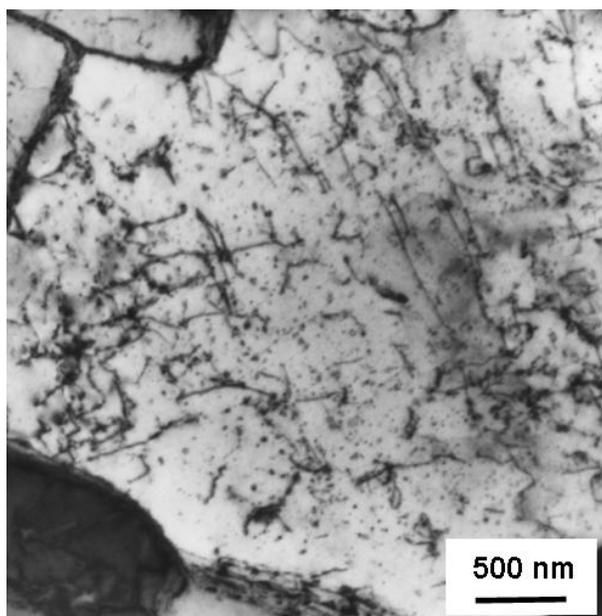


Fig. 2. Electron microscopy photomicrograph of modified 9Cr-1Mo steel after the new thermo-mechanical treatment.

Based on thermodynamic calculations, small (400-g) heats of new compositions were produced in an effort to maximize the effect of the TMT. Besides optimizing the precipitate distribution, another objective of the new steels was minimization of the number of large $M_{23}C_6$ particles lowering carbon. To demonstrate the effect of nitrogen, two new steels with nominal composition Fe-9.0Cr-1.0Mo-1.0Ni-0.30V-0.07Nb-0.05C were compared, one containing 0.035% N (9Cr-MoNiVNbN4) and the other 0.065% N (9Cr-MoNiVNbN5). 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, $1.0 \times 10^{22}\text{m}^{-3}$ and 3.3 nm, $7.2 \times 10^{22}\text{m}^{-3}$ for 9Cr-MoNiVNbN4 and 9Cr-MoNiVNbN5, respectively—about 8 times smaller at a number density almost four orders of magnitude greater than MX in N&T modified 9Cr-1Mo.

Mechanical Properties

Tensile properties were determined on modified 9Cr-1Mo after a TMT at 750°C, and they were compared to average values for N&T steel. After the TMT, the 0.2% yield stress and ultimate tensile strength from room temperature to 800°C were considerably greater than those for N&T modified 9Cr-1Mo 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

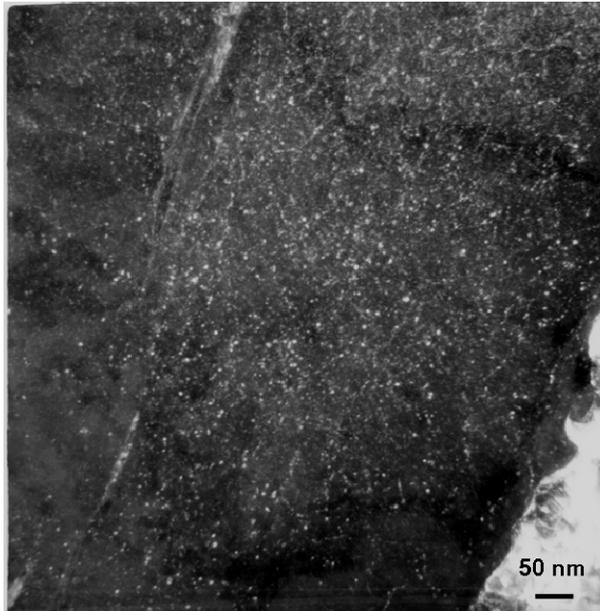


Fig. 3. Dark-field transmission electron microscopy image of the commercial 12% Cr HCM12A steel after a TMT plus temper.

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°C and 800°C followed by a temper showed large increases in yield stress relative to N&T HCM12A: 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 HCM12A. The strength up to 700°C of HCM12A was greater than PM 2000, the best available commercial ODS steel (Fig. 4).

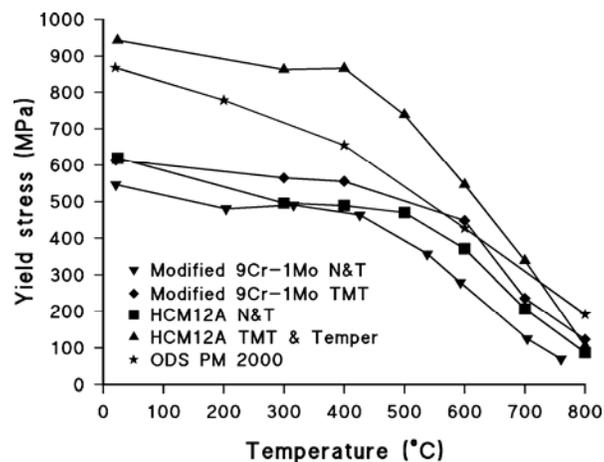


Fig. 4. Yield stress as a function of temperature for modified 9Cr-1Mo steel after a conventional normalize-and-temper (N&T) and a TMT for HCM12A after N&T and a TMT and temper, and for the best commercial ODS steel PM 2000.

To demonstrate the excellent strength properties of new steel compositions developed to take advantage of the TMT, yield stress of the new 9Cr-MoNiVNbN (0.042% N) composition was compared to an experimental ODS steel labeled 12YWT (Fe-12.0Cr-2.5W-0.4Ti-0.25Y₂O₃). The strength of this ODS steel 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-1MoNiVNbN in the TMT condition and the TMT-and-tempered condition were also comparable to those of 12YWT [Fig. 5(b)].

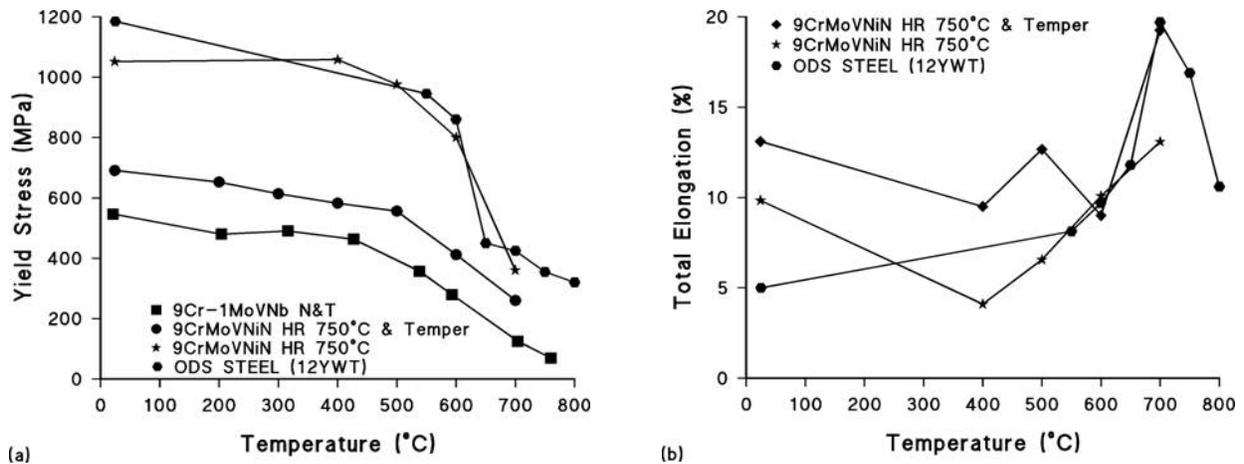


Fig. 5. (a) Yield stress and (b) total elongation of new 9CrMoVNbN steel after a TMT and after a TMT and temper compared to normalized and tempered (N&T) modified 9Cr-1Mo steel and the high-strength experimental ODS steel 12YWT.

In Fig. 6, creep curves for tests at 138 MPa at 650°C are shown for modified 9Cr-1Mo after an N&T and a TMT. Rupture life for the steel with 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%.

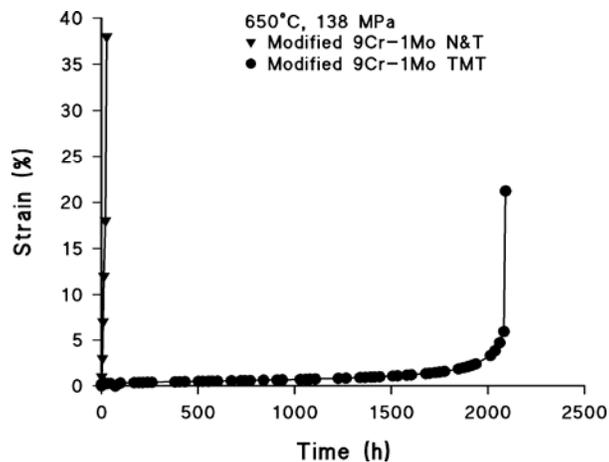


Fig. 6. Creep curves of modified 9Cr-1Mo in the normalized and tempered (N&T) condition and after a thermomechanical treatment tested at 138 MPa at 650°C.

Creep rupture curves for modified 9Cr-1Mo after a TMT indicated a significant increase in strength relative to N&T modified 9Cr-1Mo [11] and the reduced-activation steels F82H [12] and EUROFER 97 [13] (Fig. 7). After the TMT, rupture life extrapolated to 10000 h was also about 80 times that of the N&T steel. Extrapolation to 100,000 h would give 10^5 h rupture stresses of ≈ 60 and ≈ 40 MPa for the TMT and N&T steels, respectively. Obviously, the validity of such extrapolations will depend on stability of the precipitates produced by the TMT, for which longer-time tests are required. As observed above, HCM12A and the new 9Cr-1MoNiVNbN had higher strengths after the TMTs than modified 9Cr-1Mo with a TMT, so they should have significantly higher creep strengths.

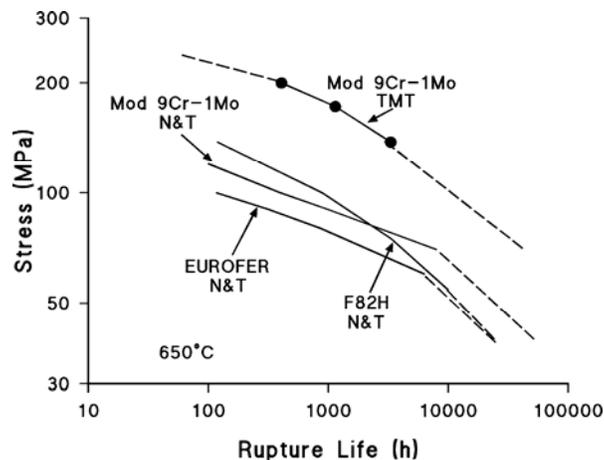


Fig. 7. Creep-rupture curves at 650°C for modified 9Cr-1Mo steel after a conventional normalize and temper (N&T) and after three thermomechanical treatments.

It needs to be emphasized that although it was demonstrated that the commercial and new steels with TMT have excellent mechanical properties, further work is required to validate these materials for future applications. Likewise, larger heats of new steels with optimum compositions are required for the development of the steels to their ultimate potential.

Summary and Conclusions

A thermomechanical treatment procedure was devised to produce a dense dispersion of nano-scale MX precipitates in vanadium- and nitrogen-containing elevated-temperature 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 new TMT process, steel compositions that fully exploit the TMT need to be developed further. The initial efforts on the small heats of new steels indicated 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 the oxides in the ODS steels, dispersion strengthening by the nitrogen-rich 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 reduced-activation steels now available.

References

- [1] R. L. Klueh and D. R. Harries, High-Chromium Ferritic and Martensitic Steels for Nuclear Applications, American Society for Testing and Materials, West Conshohocken, Pa. (2001).
- [2] S. Ukai and M. Fujiwara, *J. Nucl. Mater.* 307–311 (2002) 749.
- [3] A. Alamo, H. Regle, and J. L. Bechade, in *Novel Powder Processing: Advances in Powder Metallurgy & Particulate Materials*, Vol. 7, Metal Powder Industries Federation, Princeton, N.J. (1992) 169.
- [4] R. L. Klueh, P. J. Maziasz, I. S. Kim, L. Heatherly, D. T. Hoelzer, N. Hashimoto, E. A. Kenik, and K. Miyahara, *J. Nucl. Mater.* 307–311 (2002) 773.
- [5] N. Hashimoto and R. L. Klueh, *J. Nucl. Mater.* 305 (2002) 153.
- [6] L. Lundin, S. Fällman, and H.-O. Andrén, *Mater. Sci. Technol.* 13 (1997) 233.
- [7] M. Hättestrand, M. Schwind, and H.-O. Andrén, *Mater. Sci. Eng. A* 250 (1998) 27.
- [8] V. Foldyna, Z. Kubon, V. Vodárek, and J. Purmenský, in R. Viswanathan, W. T. Bakker, and J. D. Parker (eds.), *Proceedings of the 3rd EPRI Conference on Advanced Materials Technology for Fossil Plants*, Gomer Press, Llandysul, Ceredigion, United Kingdom (2001) 89.
- [9] R. F. Buck, *Adv. Mater. Process.* 150 (8) (1996) 27.
- [10] R. L. Klueh, N. Hashimoto, R. F. Buck, and M. A. Sokolov, *J. Nucl. Mater.* 283–287 (2000) 697.
- [11] G. Guntz, M. Julien, G. Kottmann, F. Pellicani, A. Pouilly, and J. C. Vaillant, *The T91 Book*, Vallourec Industries, France (1990) 52.
- [12] K. Shiba, H. Tanigawa, T. Nakata, and Y. Kohno, *Journal of Nuclear Materials* (submitted).
- [13] R. Lindau and M. Schirra, *Fusion Eng. Des.* 58–59 (2001) 781.