Development of new nano-particle-strengthened martensitic steels

R. L. Klueh, N. Hashimoto, and P. J. Maziasz
Oak Ridge National Laboratory
PO 2008, MS 6138
Oak Ridge, TN 37831-6138 USA

Abstract

Nano-sized precipitates were produced in nitrogen-containing commercial martensitic steels by a new thermomechanical treatment (TMT). A steel with the TMT should have a maximum operating temperature >50ºC over the steel given a conventional heat treatment. A >100ºC increase should be possible for a steel developed for the TMT.

1. Introduction

Ferritic and martensitic steels are preferred structural materials for elevated-temperature applications for fossil-fired [1,2] and future nuclear fission [3] and fusion [3,4] power plants. Their major advantage is good thermal properties relative to other elevated-temperature alloys (e.g., austenitic stainless steels and superalloys). A major shortcoming is their high-temperature strength [5,6], which places a limit on the maximum service temperature.

The commercial chromium-molybdenum steels 2¼Cr-1Mo (nominally Fe-2.25Cr-1.0Mo-0.1C) and 9Cr-1Mo (Fe-9.0Cr-1.0Mo-0.10C) steels (all compositions are in weight percent) were introduced in the 1940s for power-plant applications [7,8]. Upper-use temperature for these steels was about 540ºC. In the 1970s, Nb, V, and N were introduced into the composition of 9Cr-1Mo steel, and this modified 9Cr-1Mo, which is still used today, has a maximum operating temperature of ≈593ºC. This steel was used as a benchmark for development of steels with upper-use temperatures of 600-620ºC [1,5].

It is doubtful these steels can be pushed to much higher temperatures. Therefore, to continue to exploit the advantages of ferritic steels, oxide dispersion-strengthened (ODS) steels [9-12], first introduced in the 1960s [13], are being pursued. ODS steels are strengthened by small oxide particles, but they are produced by complicated and expensive mechanical-alloying, powder-metallurgy techniques. Despite being around for about 40 years, they are still in the development stage because of mechanical-properties anisotropy [14,15].

In this paper, we present preliminary information on the science and technology of the development of dispersion-strengthened steels produced by conventional processing techniques.

2. Experimental procedure

The new TMT on nitrogen-containing commercial and experimental steel plates involved (1) austenitizing for 1-5 h at 1000-1400ºC to transform the low-temperature body-centered-cubic ferrite into face-centered-cubic austenite and dissolve existing precipitates, (2) cooling to the hot-rolling temperature (600-1000ºC), (3) hot rolling 20-50%, (4) annealing 0-4 h at the hot-rolling temperature, and (5) air cooling to ambient temperature to transform the austenite to martensite. If necessary, the steel was tempered at 650-850ºC to improve ductility and toughness.

The new TMT was applied to 25.4-mm-thick plates of a commercial 9Cr (modified 9Cr-1Mo, nominal composition Fe-9.0Cr-1.0Mo-0.20V-0.07Nb-0.05N-0.10C) and commercial 12Cr (HCM12A, Fe-10.5Cr-1.89W-0.8Cu-0.35Mo-0.20V-0.05Nb-0.06N-0.12C) steels.

Five new 9Cr steels (labeled 9Cr-MoNiVNbN and nominally Fe-9.0Cr-1.0Mo-1.0Ni-0.30V-0.07Nb-0.05C with different nitrogen concentrations) with compositions designed to exploit the TMT were produced as 400-g vacuum arc-melted ingots and processed by the TMT.

For comparison with steels given the new TMT, the commercial steels were also studied after a conventional normalizing-and-tempering treatment: austenitizing 1 h at 1050ºC, air cooling, and tempering 1 h at 750ºC. Comparison was also made with two ODS steels: PM 2000 (Fe-19Cr-5Al-0.45Ti-0.37Y-0.25O), a commercial product of Metallwerk Plansee GMbH of Germany, and 12YWT (Fe-13.0Cr-0.60Mn-0.35Ti-0.16Y-0.16O-0.05C), an experimental alloy produced in Japan by Kobe Special Tube.

Precipitate microstructures were observed by transmission electron microscopy (TEM). Tensile tests were performed on miniature specimens taken from steels after a conventional heat treatment or the TMT. Creep tests were conducted at constant load at 650ºC.

3. Results and discussion

3.1. Rationale for TMT

After normalizing and tempering, commercial 9Cr and 12Cr steels are essentially 100% tempered martensite, which consists of martensite laths (elongated subgrains with average width ≈0.25-0.5 μm) with a high dislocation density (10^{13}-10^{15} m^{-2}) and precipitates. Dominant precipitates are "large" (60-200 nm) $M_{23}C_6$ particles located mainly on lath boundaries and prior-austenite grain boundaries. If vanadium and/or niobium are present, smaller (20-80 nm) MX forms at a lower number density.

Since small MX precipitates have the highest elevated-temperature stability, steel with a high number density of fine MX particles should have elevated-temperature properties superior to current steels. Creep strength could also be enhanced if $M_{23}C_6$ formed as a high density of small particles, or if the amount of $M_{23}C_6$ was minimized. The latter is probably the best alternative, as this phase has a minimal effect on elevated-temperature strength. One way to meet these conditions is to change processing procedures of commercial steels containing nitrogen so MX forms before $M_{23}C_6$, thus making carbon available for MX rather than $M_{23}C_6$.

The new TMT was designed to produce a dispersion of nano-sized particles by providing nucleation sites for MX precipitates. Nucleation sites chosen were dislocations introduced by hot working. To define TMT conditions, calculations were made using the computational thermodynamic program JMatPro [19] to determine kinds and amounts of stable vanadium and niobium nitrides and carbonitrides that could be developed. In addition to determining conditions for commercial steels, calculations were made to delineate new steel compositions.

3.2 Microstructures

The microstructure of the normalized-and-tempered commercial 9Cr steel had estimated average particle size and number density of $M_{23}C_6$ of 130-150 nm and 3-6 x 10^{19} m^{-3}, respectively, with MX precipitates estimated at 30 nm and 7-8 x 10^{18} m^{-3}, respectively [(Table 1 and Fig. 1(a)]. The smaller MX precipitates are credited with the major elevated-temperature strengthening role, although the number density and size limit their strengthening capability. For nitrogen-containing commercial steels with vanadium and niobium, MX precipitates have been identified as vanadium and niobium rich, with the vanadium-rich particles being nitrides and the niobium-rich particles being carbides and/or carbonitrides [20,21].

After a 25.4-mm-thick plate of commercial 9Cr steel was processed by the new TMT, the microstructure differed dramatically from normalized-and-tempered steel [Fig 1(b)]. Many MX precipitates formed during the TMT. Essentially all the fine precipitates form on dislocations introduced by hot rolling, but because of electron-diffraction conditions, most dislocations are not imaged. The MX particle size was four-times smaller (7-8 nm) after TMT, and number density was three orders of magnitude greater (2-9 x $10^{21}$$m^{-3}$) than for this steel given the conventional normalizing-and-tempering treatment (Table 1).

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

The commercial 12Cr steel was given two TMTs (Table 1). One involved hot rolling at 750ºC, the other at 800ºC. In contrast to observations on the 9Cr steel, no fine precipitates were visible. However, after tempering 1 h at 750ºC, fine precipitates (4.2 nm, 2.4 x $10^{21}m^{-3}$) were detected in the one rolled at 800ºC (Table 1). Because they were extremely small, they could only be resolved easily by dark-field electron microscopy. Evidently the higher vanadium and nitrogen concentrations in this steel promoted extremely fine precipitates that were too small to observe by TEM. During tempering, the precipitates coarsened in the steel rolled at 800ºC to the point they could be observed.

Based on thermodynamic calculations, small (400-g) heats of new compositions were produced to maximize the effect of the TMT. 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, the average MX precipitate size was smaller and number density greater than for the commercial steels (Table 1): about 4.0 nm, 1.0 x 10^{22} m^{-3} and 3.3 nm, 7.2 x 10^{22} m^{-3} for 9Cr-MoNiVNbN4 and 9Cr-MoNiVNbN5, respectively. Again, the precipitates could only be viewed easily in dark field (Fig. 2). The “necklace-like” appearance of aligned precipitates in the dark-field micrographs indicates they formed on a common dislocation line. Less $M_{23}C_6$ will form in these steels because of the lower carbon, which should improve creep properties.

3.3. Mechanical properties

The most important properties for these steels are elevated-temperature tensile and creep. Tensile tests were conducted on the commercial 9Cr steel after a TMT (TMT2 in Table 1) and after the TMT plus a 1 h temper at 750ºC and compared to average values for the normalized-and-tempered steel. After the TMT, the 0.2% yield stress and ultimate tensile strength from room temperature to 800ºC were greater than for the normalized-and-tempered steel, with the difference increasing with increasing test temperature. For tests at 600 and 700ºC, yield stress after the TMT was 61 and 88% greater than for normalized-and-tempered steel. After tempering, the yield stress was 7 and 69% greater at 600 and 700ºC, respectively. Given the normal trade off of strength and ductility, the total elongation after the TMT was less than for normalized-and-tempered steel. Nevertheless, ductility was excellent, with total elongation of 16 and 22% at 600 and 700ºC, respectively, and increasing further after tempering at 750ºC to 24 and 30%.

The commercial 12% Cr steel after two TMTs and temper (Table 1) showed large increases in yield stress relative to the normalized-and-tempered condition: 47 and 64% increases occurred at 600 and 700ºC, respectively, with little difference between the two TMTs. An increase of 22% was observed for tests at 800ºC.

The yield stress of the commercial 12Cr steel with TMT plus temper was greater than that of the 9Cr steel with just a TMT (Fig. 3), a reflection of the smaller precipitates at a higher number density in the 12Cr steel, as discussed above. As Fig. 3 shows, the strength up to 700ºC was also greater than that of PM 2000—the best commercial ODS steel available [22].

To demonstrate the excellent strength properties of the new steel compositions developed to take advantage of the TMTs, yield stress of 9Cr-MoNiVNbN (0.042% N) was compared to the experimental ODS steel 12YWT [23], a steel with superior strength to any commercial ODS steel. The TMT of 9Cr-MoNiVNbN produced yield stress values much higher than those of the normalized-and-tempered commercial steels and for the commercial steels after a TMT. The strengths were comparable to those of 12YWT up to 700ºC—the highest temperature that 9Cr-MoNiVNbN was tested (Fig. 4). Total elongations for 9Cr-MoNiVNbN in the TMT condition and the TMT-and-tempered condition were also comparable to those of 12YWT [23].

Limited creep tests were conducted; Fig. 5 shows creep curves for tests to rupture for the commercial 9Cr steel after normalizing and-tempering and after the TMT. Rupture life after the TMT was ≈80 times greater than after normalizing and tempering. Even with the big difference in strength, ductility was excellent; total elongation was 21%. Note that the commercial 9Cr steel had a lower yield stress after the TMT than the 12Cr steel and the new 9Cr-MoNiVNbN steels, and therefore these latter steels should have significantly higher creep strengths.

3.4 General discussion

Previous work has sought to exploit nitrogen-containing precipitates [24,25], but the difference in the present work is the TMT. Goecmen et al. [24] produced 9 and 12 Cr steels with about 0.17% N and 0.72% V; After austentization at 1200ºC, the steels were ausaged at 550-700ºC for up to 800 h. Although a dense distribution of precipitates was obtained (no estimate of sizes or number densities were given), the high concentrations of vanadium and nitrogen made it impossible to dissolve all precipitates at 1200ºC. These large precipitates in the matrix and on boundaries led to denuded zones in their vicinity. The hardness of the ausaged steels exceeded that of the normalized-and-tempered steel, but no mechanical properties were presented.

Taneike et al. [25] examined 9Cr-3W-3-Co-0.2V-0.05N with a range of carbon, and for 0.002% C, they found a high density (no value given) of 5-10 nm MX precipitates on or in the vicinity of prior-austenite and lath boundaries after a normalizing-and-tempering treatment.

Although a high number density of matrix precipitates was claimed, only matrix precipitates in the vicinity of the boundaries were shown in TEM photomicrographs. These steels had excellent creep-rupture properties, and the nitrides appeared to have high stability based on TEM of a ruptured creep specimen.

The work presented in this paper is meant to demonstrate the development of new dispersion-strengthened steels using conventional processing techniques. The number density of precipitates produced by the TMT is similar to particle number densities in the best ODS steels produced by complicated and expensive powder-metallurgy and mechanical-alloying procedures [23]. Dispersion strengthening by the nitrogen-rich MX precipitates should allow the steels to be used at 650-700ºC and higher, which is a significant improvement over the upper-use temperature of ≈620ºC for ferritic and martensitic steels now available.

Several questions still need to be answered. The most important involves precipitate stability. This will be addressed by examination of aged and creep-tested material. Optimization of the TMT for optimum elevated-temperature properties is required. Furthermore, since the steels are produced by mechanical processing, the possiblity of anisotropy must be examined. Optical microscopy in the preliminary studies indicates the presence or absence of elongated prior-austenite grains depends on the TMT used.

4. Summary and conclusions

Experimental results indicate that thermomechanical treatments can be devised to produce a dense dispersion of nano-scale MX precipitates in nitrogen-containing commercial steels that also contain vanadium and niobium. Elevated-temperature mechanical properties of the steels are significant improvements over the normalized-and-tempered steels. The new TMT involves three distinct steps, each of which involves a range of experimental conditions that need to be optimized to produce the most favorable precipitate microstructure for elevated-temperature strength. Along with optimization of the TMT, steel compositions that fully exploit the TMT need to be developed further. Initial efforts on the small heats developed for the new processing procedure indicate it should be possible to develop compositions that are significant improvements over commercial steels with a conventional normalizing-and-tempering treatment or with the new TMT.

Acknowledgments

E. T. Manneschmidt conducted the tensile tests, A.M. Kelly conducted the creep tests, and K. A. Yarborough. The manuscript was reviewed by M. A. Miller, J. P. Shingledecker, and S. J. Zinkle.

Research was sponsored by the Office of Fusion Energy Sciences, U.S. Department of Energy, under contract DE-AC05-00OR22725 with U.T.-Battelle, LLC.

References

1. Viswanathan R, Bakker W. J Matls Eng and Perf 2001; 10:81-95.

2. Viswanathan R, Bakker W. J Matls Eng and Perf 2001; 10:96-101.

3. Klueh RL, Harries DR. High-Chromium Ferritic and Martensitic Steels for Nuclear Applications. West Conshohocken, Pennsylvania: American Society for Testing and Materials; 2001

4. Rosenwasser SN et al. J Nucl Mater 1979;85 & 86:177-182.

5. Masuyama F. In: Viswanathan R, Nutting J, editors. Advanced Heat Resistant Steel for Power Generation. London: Institute of Materials; pp. 33-48.

6. Gladman T. In: Strang A, Cawley J, Greenwood GW, editors. Microstructural Stability of Creep Resistant Alloys for High Temperature Plant Applications. London: The Institute of Materials; 1998. pp. 49-68.

7. Strang A. In: Strang A, Cawley J, Greenwood GW, editors. Microstructural Stability of Creep Resistant Alloys for High Temperature Plant Applications. London: The Institute of Materials; 1998. pp. 117-133.

8. Pickering FB. In: Strang A, Gooch DJ, editors. Microstructural Development and Stability in High Chromium Ferritic Power Plant Steels. London: Institute of Materials; 1997. pp. 1-30.

9. Klueh RL et al. J Nucl Mater 2002; 307-311: 455-465.

10. Ukai S, Fujiwara M. J Nucl Mater 2002; 307-311: 749-757.

11. Ritherdon J, Jones AR, Miller U, Wright IG. In: Strang A et al. 'Parsons 2003: Engineering Issues in Turbine Machinery, Power Plant and Renewables. London: The Institute of Materials, Minerals and Mining; 2002. pp. 927-937.

12. Okuda T, Fujiwara M. J Mater Sci Ltrs 1995; 14: 1600-1603.

13. Huet J –J. Powder Metallurgy 1968;10: 108-115.

14. Ukai S et al. J Nucl Mater 1993; 204: 65-73.

15. Alamo A, Regle H, Bechade JL. In: Novel Powder Processing: Advances in Powder Metallurgy & Particulate Materials, Vol. 7. Princeton, NJ: Metal Powder Industries Federation; 1992. pp. 927-937.

16. Krauss G. Steels: Heat Treatment and Processing Principles Materials Park, Ohio: ASM International, 1990.

17. Hashimoto N, Klueh RL. J Nucl Mater 2002; 305: 153-158.

18. Ennis PJ, Zieliñska-Lipiec A, Czyrska-Filemonowicz A. In: Strang A, Cawley J, Greenwood GW, editors. Microstructural Stability of Creep Resistant Alloys for High Temperature Plant Applications. London: The Institute of Materials; 1998. pp.135-144.

19. Saunders N, Li X, Miodownik P, Schillé JPh. Shao J-C et al. Proc Symp Mater Design Approach and Experiences. Warrendale, PA: The Materials Society; 2001. pp. 185-197.

20. Cerjak H, Foldyana V, Hofer P, Schaffernak B. In: Strang A, Gooch DJ, editors. Microstructural Development and Stability in High Chromium Ferritic Power Plant Steels. London: Institute of Materials; 1997. pp. 145-158.

21. Hättestrand M, Schwind M, Andrén H-O, In: Viswanathan R, Nutting J editors. Advanced Heat Resistant Steel for Power Generation. London: Institute of Materials; 1999. pp. 199-211.

22. Material Data Sheet ODS-Superalloy PM 2000, Metallwerk Plansee GmbH, February 1993.

23. Klueh RL et al. J Nucl Mater 2002; 307-311: 773-777.

24. Goecmen A et al. ISIJ Intl 1996; 36: 768-776.

25. Taneike M, Abe F, Sawada, K. Nature 2003; 424: 294-296

Table 1. Precipitate Information for Different TMTs

Steel/Experiment	Austenitization	Hot Roll	MX Precipitates Avg. Size (nm)	MX Precipitates No. Density (m^{-3})
Commercial 9Cr/Control	Normalize & Temper (N&T)		32	7.9×10^{18}
Commercial 9Cr / TMT1	1300ºC/0.5h	750ºC/60%	7.2	8.9×10^{21}
Commercial 9Cr /TMT2	1300ºC/1h	750ºC/20%	7.3	2.1×10^{21}
Commercial 9Cr /TMT3	1200ºC/1h	750ºC/60%	8.0	1.9×10^{21}
Commercial 12Cr/TMT4	1200ºC/1.5h	750ºC/50%	ND	ND
Commercial 12Cr /TMT5	1200ºC/1.5h	800ºC/50%	4.2	2.4×10^{21}
9Cr-MoNiVNbN4/TMT2	1300ºC/1h	750ºC/20%	4.0	1×10^{22}
9Cr-MoNiVNbN5/TMT2	1300ºC/1h	750ºC/20%	3.3	3.3×10^{22}

Figure Captions

Fig. 1. Electron microscopy photomicrographs of the commercial 9Cr steel (a) after conventional normalizing-and-tempering treatment and (b) after the new thermomechanical treatment.

Fig. 3. (a) Low and (b) high magnification of dark-field transmission electron microscope images of fine precipitates in a new 9Cr-MoNiVN steel given a TMT.

Fig. 3. Yield stress as a function of temperature for the commercial 9Cr steel as normalized and tempered (N&T) and after a TMT, for the commercial 12Cr steel after N&T, after TMT and temper. Also shown are data for the commercial ODS steel PM 2000.

Fig. 4. Yield stress of new 9Cr-MoVNiNbN steel after TMT and after TMT and temper compared to commercial 9Cr steel after a conventional normalize and temper (N&T) and the high-strength experimental ODS steel 12YWT.

Fig. 5. Creep curves for the commercial 9Cr steel after the conventional normalizing-and-tempering (N&T) heat treatment and the TMT. Creep tests were at 138 MPa at 650ºC until the specimens ruptured.

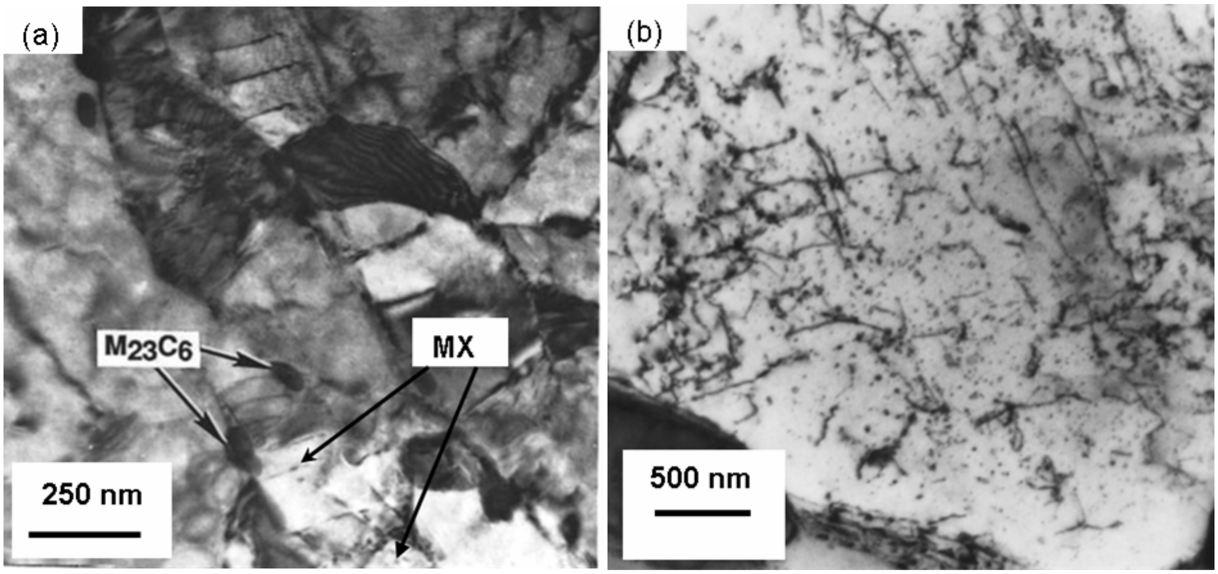

Figure 1

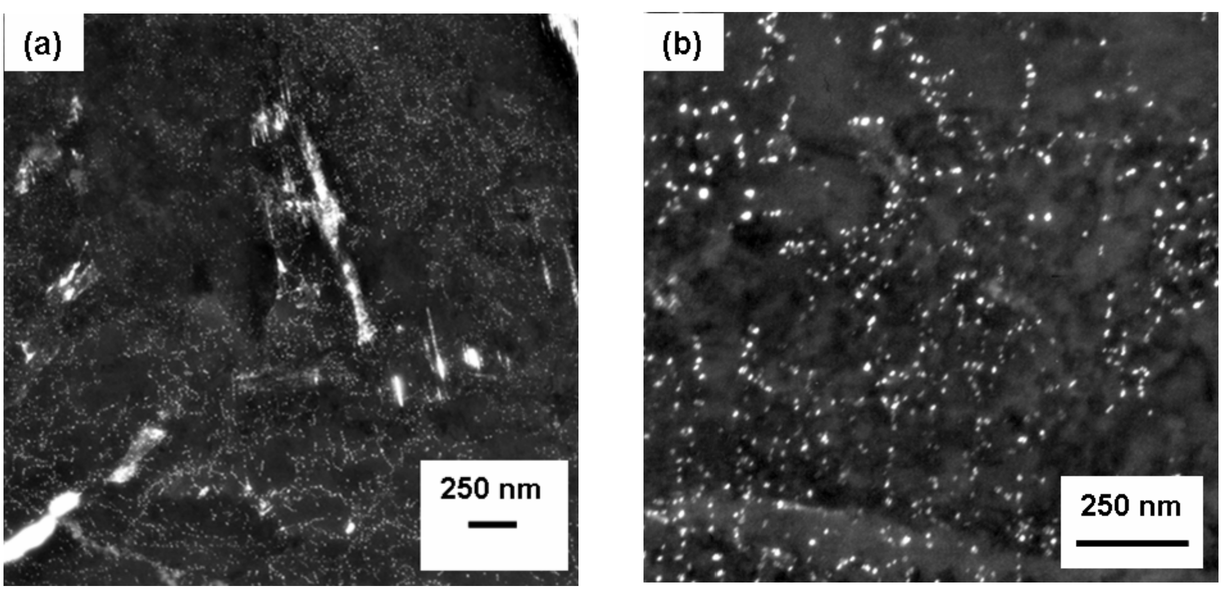

Figure 2

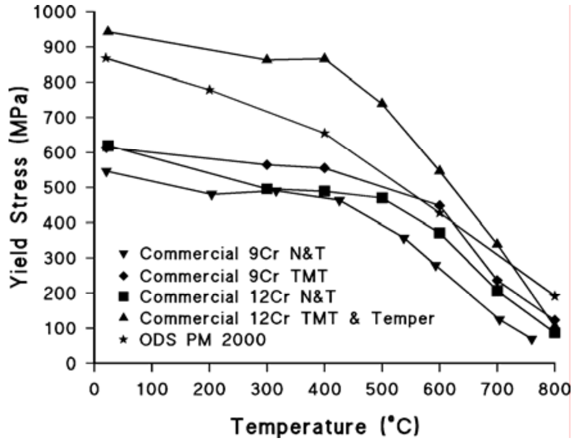

Figure 3

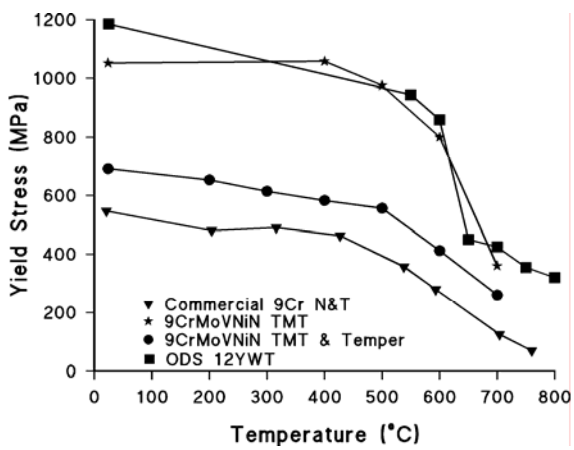

Figure 4

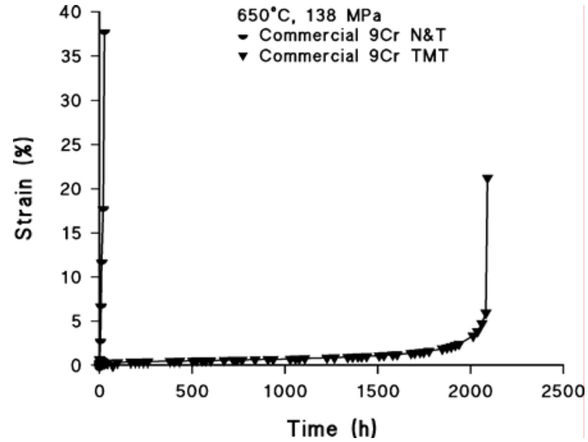
650°C, 138 MPa
Commercial 9Cr N&T
Commercial 9Cr TMT
Strain (%)
Time (h)
0
5
10
15
20
25
30
35
40
0
500
1000
1500
2000
2500

Figure 5