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Alexandra Fedoseeva
Belgorod National Research University

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Alexandra Fedoseeva and Alexey Fedoseev

Modeling of Thermo-Mechanical Treatment for Formation of Stable Particles in a Low-Carbon 9% Cr Martensitic Steel

Alexandra Fedoseeva[a)] and Alexey Fedoseev

Belgorod National Research University, Belgorod, 308015 Russia

[a)] Corresponding author: fedoseeva@bsu.edu.ru

Abstract. Thermo-mechanical treatment for a low-carbon 9% Cr martensitic steel was modeled with aim to obtain the stable secondary phase particles of Z-phase instead of non-equilibrium MX carbonitrides. Modeling of thermo-mechanical treatment consisting of normalizing at temperatures ranging from 1050 to 1200°C, forging at temperatures ranging from 600 to 680°C with various strains from 10 to 60%, annealing at temperatures ranging from 600 to 680°C with different durations and tempering at 750°C for 3 hrs was carried out using Thermo-Calc and Prisma software. Analysis of phase composition predicted by Thermo-Calc software together with growth kinetic of the Z-phase particles using Prisma software showed that the optimal normalizing temperature of 1200°C, forging/annealing temperature of 680°C and time annealing of 50 hrs must provide the formation of stable Z-phase with a mean size of about 50 nm.

INTRODUCTION

The 9–12% Cr martensitic steels are designed for the manufacture of the elements of boilers and steam pipelines, as well as the elements of rotors and blades of steam turbines operating at ultra-supercritical parameters of steam (temperature of 600–620°C, pressure of 25–30 MPa). A significant increase in the creep resistance of these steels is associated with a dispersion of nanosized MX carbonitrides, where M is a metal (vanadium, niobium, titanium, tantalum, or their combinations) and X is carbon and/or nitrogen. MX carbonitrides precipitate during tempering at temperatures ranging from 720 to 800°C. They are uniformly distributed in the ferritic matrix and act as the obstacles for the rearrangement of free dislocations into low-energy configurations or the embedding of free dislocations into already existing dislocation lath boundaries [1]. Particle hardening due to MX carbonitrides gives a significant contribution to the overall hardening of the 9–12% Cr martensitic steels stabilizing the tempered martensite lath structure under operating conditions [1, 2].

The main disadvantage of a dispersion of nanosized MX carbonitrides in the 9–12% Cr steels is their thermodynamic instability in the temperature range of 600–700°C that leads to the replacement of these MX carbonitrides with the stable large Z-phase particles (CrMN, where M means vanadium, niobium, tantalum or their combinations) during creep at elevated temperature of 650°C. The size of the stable Z-phase particles can reach several microns. This completely eliminates precipitation hardening due to the secondary phase particles [1–3] and sharply reduces the creep resistance of the 9–12% Cr steels [4]. On the other hand, the transformation of a dispersion of nanosized MX carbonitrides into the Z-phase particles does not give a significant contribution to the microstructural degradation of the 9% Cr–3% Co steel during creep, until the mean sizes of the Z-phase particles and MX carbonitrides are comparable as well as the amount of MX carbonitrides exceeds 50% of initial volume fraction [5–8]. Plastic deformation is the main factor provoking the precipitation of the Z-phase particles in the 9% Cr–3% Co steel during creep [6, 7]. In the 12% Cr steel, the precipitation of Z-phase can be revealed even in the tempered or aged states [9–11]. Thus, the problem of precipitation of the large stable Z-phase particles is relevant for the heat-resistant steels containing from 9 to 12% Cr and additionally alloyed with cobalt [3, 5–11]. However, there are all prerequisites to assume that the Z-phase particles can be used to increase the long-term creep strength [9–11].

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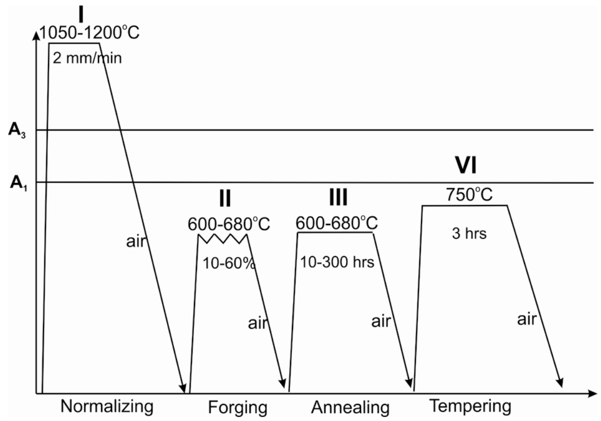

FIGURE 1. Schematic illustration of TMT developed in the present research.

In Ref. [11], the degradation of creep properties is prevented by the precipitation of the Z-phase particles in a 12% Cr steel in tempered state.

The aim of this research is to carry out computer modeling of the phase compositions and kinetics of precipitation and coarsening of the secondary phases for a low-carbon 9% Cr steel alloyed with Co, W and Ta, using the Thermo-Calc and Prisma software to determine the optimal conditions of thermo-mechanical treatment (TMT).

MATERIAL AND METHOD

The low-carbon 9% Cr steel with Co, Cu and Ta doping with the chemical composition (in wt %) of Fe (balance) – 0.02% C – 9% Cr – 3% Co – 2.2% W – 2% Cu – 0.3% Ta – 0.016% N – 0.002% B – 0.2% Si – 0.2% Mn – 0.2% Ni was considered to be material for investigation in the present research. This steel was prepared by vacuum-induction melting as 15 kg. The modeling of TMT regimens for the low-carbon 9% Cr martensitic steel must provide the formation of the fine stable equilibrium Z-phase particles in the initial state instead of non-equilibrium MX carbonitrides. It is assumed that TMT regimens consist of the following stages (represented in Fig. 1):

(I) normalizing at temperatures ranging from 1050 to 1200°C, air cooling;

(II) forging at temperatures ranging from 600 to 680°C with various strains (10 to 60%), air cooling;

(III) annealing at temperatures ranging from 600 to 680°C with various durations (1 to 300 hrs), air cooling;

(IV) final tempering at temperature of 750°C for 3 hrs, air cooling.

The equilibrium chemical composition of various phases was obtained using Thermo-Calc software (Version 5.0.4 75, Thermo-Calc software AB, Stockholm, Sweden, 2010). The particle coarsening kinetics was calculated using Prisma-software on the base of Calphad Database Calculation with the kinetic MOBFE1 and thermodynamic TCFE6 databases. The time dependencies of the mean radius were determined for TaN nitrides and Z-phase particles assuming their simultaneous growth; dislocations acted as a nucleation site.

RESULTS AND DISCUSSION

Modeling of Normalizing Temperature

A1 and A3 temperatures corresponding to start and finish of the ferrite → austenite transformation, respectively, were calculated using Thermo-Calc software. A1 and A3 temperatures comprised 840 and 878°C, respectively.

TABLE 1. Effect of normalizing temperature on the mass fraction of phases predicted by Thermo-Calc

Predicted phase	1050°C	1070°C	1100°C	1150°C	1200°C
Austenite	99.86	99.87	99.88	99.90	99.92
δ-ferrite	0	0	0	0	0
Ta(C, N)	0.14	0.13	0.12	0.10	0.08

The first step of modeling of TMT regimens was the determination of normalizing temperature ranging from 1050 to 1200°C. For this goal, the following temperatures of 1050, 1070, 1100 and 1150°C were chosen for prediction of the phase composition using Thermo-Calc software. The effect of normalizing temperature on the phase compositions (in wt %) predicted by Thermo-Calc software is represented in Table 1.

For all normalizing temperatures, austenite was dominant phase (Table 1). Small amount of TaN nitride with the chemical composition (in wt %) of 86% Ta–1% Cr–12% N was observed at all normalizing temperatures (Table 1). When normalizing temperature increased from 1050 to 1200°C, the mass fraction of TaN nitride decreased from 0.14 to 0.08%, respectively (Table 1).

The Cr equivalent (Creq) value was also used for the estimation of the susceptibility of a low-carbon 9% Cr steel to form δ-ferrite as follows [12]:

$$Creq = Cr + 0.8Si + 2Mo + 1W + 4V + 2Ta + 1.7Al + 60B - 20C - 20N - 2Ni - 0.4Mn - 0.6Co - 0.6Cu \text{ (in wt \%)}. \quad (1)$$

Creq for the low-carbon 9% Cr steel comprised 7.9 wt %. δ-ferrite is not present at $Creq \leq 10$; therefore, this low-carbon 9% Cr steel is not susceptible to the formation of δ-ferrite. Thermo-Calc calculations confirm this conclusion (Table 1). No evidence for δ-ferrite presence was revealed for all normalizing temperatures (Table 1).

Temperature of 1200°C was chosen as the normalizing temperature, because it provides the minimum amounts of the secondary phase particles and maximum content of Ta and N in the solid solution.

Modeling of Temperature of Forging and Annealing

The second step of modeling of TMT regimens was the determination of temperature for forging and annealing. It ranged from 600 to 680°C. For this goal, the following temperatures of 600, 620, 650, 680 and 750°C (as the temperature of conventional tempering) were chosen for prediction of the phase composition using Thermo-Calc software. The effect of temperature on the phase compositions (in wt %) at the forging and annealing predicted by Thermo-Calc software is summarized in Table 2.

Analysis of phase compositions predicted by Thermo-Calc software showed the presence of secondary phase such as Z-phase, Laves phase and "Cu"-rich phase at all forging/annealing temperatures, excepting 750°C (Table 2). The chemical composition of Z-phase was 55 wt % Ta–26% Cr–7% Fe–8% N at all temperatures. When forging/annealing temperature increased, the mass fraction of Laves phase and "Cu"-rich phase significantly decreased, whereas the mass fraction of Z-phase comprised 0.24% regardless of the forging/annealing temperatures (Table 2). It was found [8] that an increase in creep temperature to 675°C facilitates the nucleation of Z-phase particles in a 9% Cr–3% Co steel. On the other hand, the precipitation of Laves phase and "Cu"-rich phase occurs at the exposures with durations of more than 500 hrs [13]. This indicates that these phases will not be observed during forging and annealing at all temperatures. At temperature of conventional tempering of 750°C, Ta(C, N) was stable phase instead of Z-phase (Table 2). The mass fraction of Ta(C, N) at temperature of 750°C was 0.25% that was close to mass fraction of Z-phase at lower temperatures (Table 2).

So, temperature of 680°C was chosen as the temperature for forging and annealing, because it provides high mass fraction of Z-phase together with low fractions of other secondary phases.

Modeling of Annealing Time

The third step of modeling of TMT regimens was the determination of annealing duration. For this goal, the simultaneous growth of TaN nitrides and Z-phase particles was modeled for estimation of the time dependence of the mean radius using Prisma software (Fig. 2). The temperature of modeling was 680°C as it was suggested in the above part.

TABLE 2. Effect of forging/annealing temperature on the mass fraction of phases predicted by Thermo-Calc

Predicted phase	600°C	620°C	650°C	680°C	750
Ferrite	94.81	94.99	95.32	95.75	97.35
Z-phase	0.24	0.24	0.24	0.24	–
Laves phase	3.04	2.90	2.63	2.29	1.04
"Cu"-rich phase	1.90	1.87	1.81	1.72	1.36
Ta(C, N)	–	–	–	–	0.25

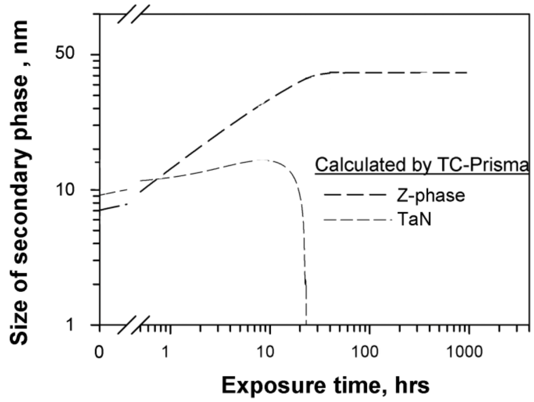

FIGURE 2. The time dependence of the growth of Z-phase particles at a temperature of 680°C predicted by Prisma software.

For calculation of particle growth in Prisma software, the chemical composition of the low-carbon 9% Cr steel was used as follows (in wt%): Fe (balance)–9% Cr–3% Co–0.3% Ta–0.02% N. The dislocations were chosen as nucleation sites. Nucleation sites were 8.83×10^{23} m^{-3} at dislocation density 2×10^{14} m^{-2}.

The interfacial energies of TaN/ferrite and Z-phase/ferrite were 0.85 and 0.4 J m^{-2}, respectively. The full dissolution of TaN together with the growth of Z-phase occurred after 25 hrs of exposure at a temperature of 680°C. After 50 hrs of exposure at a temperature of 680°C, the size of Z-phase reached 40 nm. The size of Z-phase particles even after 1000 hrs of exposure at a temperature of 680°C retained less than 50 nm.

SUMMARY

Modeling of phase compositions of a low-carbon 9% Cr steel with Co, Cu and Ta doping and growth kinetic of Z-phase particles using Thermo-Calc and Prisma software showed that TMT regime described as follows:

(I) normalizing at temperature of 1200°C, air cooling;

(II) forging at temperature of 680°C with various strains (10 to 60%), air cooling;

(III) annealing at temperature of 680°C with duration of 50 hrs, air cooling;

(IV) final tempering at temperature of 750°C for 3 hrs, air cooling

can provide the precipitation of the stable Z-phase particles with a mean size less than 50 nm in the initial state. Future research will be aimed at the experimental verification of these conditions.

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REFERENCES

1. F. Abe, T. U. Kern, and R. Viswanathan, *Creep Resistant Steels* (Woodhead Publishing in Materials, Cambridge, 2008).
2. K. Sawada, H. Kushima, and K. Kimura, ISIJ Int. **46**, 769–775 (2006).
3. H. Danielsen, Mater. Sci. Tech. **32**, 126–137 (2016).
4. A. Strang and V. Vodarek, Mater. Sci. Technol. **12**, 552–556 (1996).
5. A. Fedoseeva, I. Nikitin, N. Dudova, and R. Kaibyshev, Russ. Metall. **2019**, 932–938 (2019).
6. A. Fedoseeva, I. Nikitin, N. Dudova, and R. Kaibyshev, Phys. Met. Metall. **121**, 561–567 (2020).
7. A. Fedoseeva, I. Nikitin, N. Dudova, and R. Kaibyshev, Mater. Sci. Eng. A **724**, 29–36 (2018).
8. A. Fedoseeva, I. Nikitin, N. Dudova, and R. Kaibyshev, Mater. Sci. Eng. A **799**, 140–271 (2021).
9. J. Hald, Trans. Indian Inst. Met. **69**, 183–188 (2016).
10. M. Rashidi, A. Golpayegani, S. Sheikh, S. Guo, H.-O. Andrén, and F. Liu, Mater. Des. **158**, 237–247 (2018).
11. F. Liu, M. Rashidi, L. Johansson, J. Hald, and H.-O. Andrén, Scripta Mater. **113**, 93–96 (2016).
12. Ch. Cui, X. Gao, G. Su, C. Gao, Zh. Liu, and R. D. K. Misra, Mater. Sci. Technol. **34**, 2087–2096 (2018).
13. R. L. Klueh, Int. Mater. Rev. **50**, 287–310 (2005).