EVOLUTION OF LAVES PHASE PARTICLES IN A 9 %CR-3 %CO-3 %W MARTENSITIC STEEL DURING CREEP AT 650 °C

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Abstract

9 % Cr martensitic steels are perspective candidates for elements of boilers, steam pipes and tubes for novel fossil fuel power plants which are able to work at ultra-supercritical parameters of steam (T = 600 - 620 °C, P = 25 - 30 MPa). Crept structure and creep properties of 0.1C-9Cr-3Co-3W-VNbBN steel after creep tests at 650 °C under a stress of 100 - 220 MPa with a step of 20 MPa were studied. During first 5.000 h, Laves phase particles are essentially stable their sizes remain unchanged, while after 5.000 h the extensive coarsening of these precipitates starts to occur. The coarsening of the Laves phase particles was also calculated using the Prisma software. The results of the calculations are corroborated by experimental observations. There are three features of microstructural evolution of the Laves phase particles during creep in the steel studied. First, volume fraction of Laves phase increases with time. Second, there is well-defined peak in the size distribution of Laves phase. Third, interfacial energy of Laves phase changes with transition from short-term creep to long-term creep.

Keywords: Creep-resistant steel, tempered lath martensite, Ostwald ripening, Laves phase particles

1. INTRODUCTION

Creep-resistant 9 % Cr martensitic steels are widely used as materials for fossil power plants working at temperatures up to 620 °C [1-2]. The improvement of the creep strength of 9 % Cr martensitic steels is achieved by formation of tempered martensite lath structure, which is stabilized at the expense of the precipitation hardening during creep [1]. $M_{23}C_6$ carbides precipitate along boundaries of prior austenite grains (PAGs) and laths during tempering and pin migration of boundaries under creep condition, MX carbonitrides precipitate inside martensitic laths and serve as obstacles for movement of dislocations, Laves phase precipitate, mainly, at PAG boundaries during creep or ageing at 550 - 650 °C [1,3,4].The coarsening of $M_{23}C_6$ carbides, MX carbonitrides and the Laves phase particles deteriorates the creep strength. An effective way to slow down the particle coarsening is to optimize the content of the elements, which suppress diffusion-controlled processes, such as cobalt or/and tungsten. The addition of 3 % Co in P92-type steel positively affects the long-term creep strength because of decreasing diffusion of alloying elements [5]. Efficiency of W as alloying element in hindering the diffusion is much higher than that of Co. As a result, W is known as effective alloying additive to enhance creep resistance of the high-chromium martensitic steels. However, in contrast with cobalt, the tungsten has limited solubility within the ferrite, and their excessive content leads to the precipitation of such W-rich particles as Laves phase (Fe_2W) or M_6C carbides [1,5-8].

There are a lot of studies focused on the development and investigation of creep-resistant steels with improved long-term creep strength [1-4]. Now, special attention is given to the stability of MX carbonitrides and $M_{23}C_6$ carbides during high-temperature creep [9-11], but the stability of the Laves phase particles is an open question. Moreover, the evolution and stabilization of the Laves phase particles in creep-resistant martensitic steels have not been studied in detail. The aim of the present paper is to clarify the coarsening behavior of Laves phase particles in high-Cr steel with 3 % Co and 3 % W during creep at 650 °C.

2. EXPERIMENTAL PROCEDURE

Here denoted steel as 9Cr3W, with the chemical composition (in wt. %) Fe (bal.), 0.12C, 9.5Cr, 3.2Co, 3.1W, 0.45Mo, 0.06Si, 0.2Mn, 0.2V, 0.06Nb, 0.05N, 0.005B, was prepared by air melting as 20 kg ingots. Square bars with a 13 x 13 mm^2 cross-section were cast and hot forged by the Central Research Institute for Machine-Building Technology, Moscow, Russia. This steel was solution treated at 1050 °C for 0.5 h, cooled in air, and subsequently tempered at 750 °C for 3 h. Flat specimens with a gauge length of 25 mm and a cross section of 7 × 3 mm^2 and cylindrical specimens with gauge length of 100 mm and a 10 mm diameter were crept until rupture at 650 °C under an applied stress ranging from 100 to 220 MPa with a step of 20 MPa. The structural characterization was carried out using a transmission electron microscope JEOL-2100 (TEM) with an INCA energy dispersive X-ray spectrometer (EDS) and a Quanta 600FEG scanning electron microscope (SEM) on ruptured creep specimens. Identification of the precipitates was performed based of combination of EDS composition measurements of the metallic elements using the manufacturer's library of internal reference standards and indexing of the electron diffraction patterns using TEM. M_6C carbides and Laves phase particles were separated from each other using TEM EDS composition measurements and using the particle size distribution. The TEM specimens were prepared by electro polishing at room temperature using a solution of 10 % perchloric acid in glacial acetic acid with Struers «Tenupol-5» machine. The precipitates were identified from both the chemical analysis and the selected-area diffraction method on at least 200 particles on the each portion by using extraction carbon replicas. The carbon replicas were prepared by using Q 150REQuorum vacuum deposition machine. The volume fractions of the precipitated phases were calculated using the Thermo-Calc software with the TCFE7 database. The following phases were selected independently for calculation: BCC, FCC, $M_{23}C_6$ carbide, Laves phase (Fe_2(W,Mo) (C14). The particle coarsening kinetic was calculated using Prisma-software on the base Calphad Database Calculation with the kinetic MOBFE1 and the thermodynamic TCFE6 databases. The model compositions consisting of Fe, Cr, Mo, W and Co in accordance with the chemical composition of the steels studied were used for estimating the coarsening of the Laves phase particles assuming that a grain boundary is a nucleation site. The interfacial energy was estimated by the comparison of calculated kinetic of the particle growth using the Prisma-software and the experimental data [5].

3. RESULTS AND DISCUSSION

The effect of tempering on the structural changes in the present steel was detailed elsewhere [12]. The mean PAG size is approximately 20 μm, the mean transverse lath size is ~400 nm and the dislocation density is about 2×10^{14} m^{-2} that is in a good agreement with other investigations of 9 % Cr martensitic steels after tempering [3,6,7,9,10]. The mean size of $M_{23}C_6$ carbides is about 90 nm after tempering at T = 750 °C. Boundary W-rich M_6C carbides and Laves phase particles were observed [12]. Some Laves phase particles with a mean size of 90 nm were surrounded by $M_{23}C_6$ carbides, whereas large M_6C particles with a mean size more than 300 nm were located separately from other particles. V-rich MX carbonitrides have a mean longitudinal size of 20 nm. Nb-rich MX carbonitrides with round shape have an average size of ~40 nm. The solubility of (3W+0.5Mo - in wt. %) excesses the thermodynamically equilibrium solubility limit at the tempering temperature of 750 °C.

The results of the structural investigations after creep tests at 650 °C are summarized in **Table 1**. The plastic deformation during creep test strongly affected the sub-structural changes. The lath size in the gauge section increased almost 1.5 times after 500 h of creep. A further increase in the test time was accompanied by the continuous increase of lath size and decrease of dislocation density (**Table 1**). Laves phase precipitates at elevated temperatures during long-term tests. **Figure 1** shows the Laves phase particles, which were formed after 50 h (a), 454 h (b), 3,489 h (c) and 15,998 h (d) in the gauge section of crept specimens along with the EDS data for the indicated particles.

Table 1 Some structural parameters of the 9 %Cr martensitic steel with after tempering and creep at 650 °C in the gauge section

Parameters	Lath size, nm	Dislocation density, $\times 10^{14}$ / m^2	Laves Precipitate size, nm	W content in the solid solution, wt. %
Tempered at 750 °C	400 ± 55	2.0 ± 0.9	90 ± 20	3.56 ± 0.5
Crept at 220 MPa, 50 h	410 ± 85	1.3 ± 0.7	93 ± 20	2.72 ± 0.3
Crept at 180 MPa, 454 h	590 ± 90	1.1 ± 0.5	108 ± 30	1.43 ± 0.2
Crept at 140 MPa, 3.489 h	610 ± 70	1.0 ± 0.5	130 ± 40	1.24 ± 0.2
Crept at 100 MPa, 15.998 h	770 ± 115	0.5 ± 0.04	550 ± 160	1.03 ± 0.1

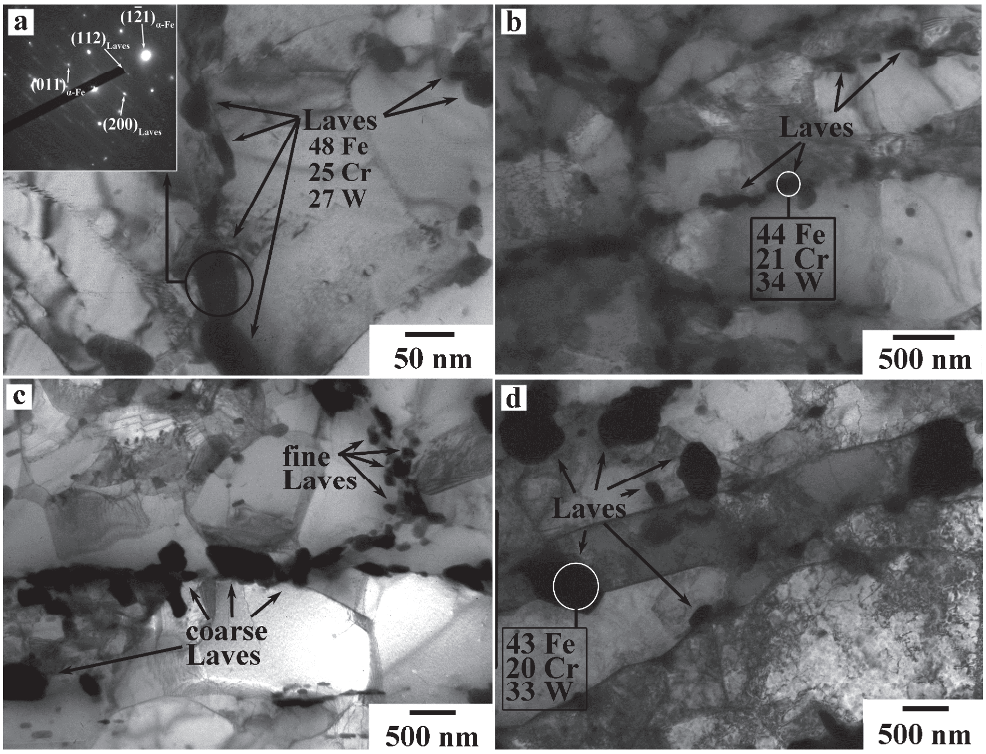

Figure 1 Precipitation of Laves phase in the gauge section of the specimen crept at 650 °C for 50 h (a), 454 h (b), 3,489 h (c), 15.998 h (d). The amount of main elements in the particles is indicated in atomic% measured from extraction carbon replicas by EDS with TEM

The precipitation of the Laves phase particles is accompanied by the depletion of excess W from the solid solution (**Table 1**). The precipitation of the Laves phase particles in the present steel after 50 h of creep is observed mainly at the boundaries of PAGs and martensitic laths (**Figure 1a**). The Laves phase particles precipitated under tempering remain their size of ~100 nm up to 3.489 h. Then, the rapid coarsening of Laves phase starts to occur, and their average size attains ~550 nm after creep time of 15.998 h (**Figure 1d**).

The calculation of the particle growth kinetic using the Prisma-software was carried out (**Figure 2**) for the model alloy consisting of Fe, Cr, Mo, W and Co in accordance with the chemical composition of the steel studied for the exposure time of 20.000 h. On the base of comparison of these theoretically predicted curves with experimental data (particle sizes measured using TEM in the gauge sections of the crept specimens after creep tests at 650 °C under the different applied stresses), the value of the interfacial energy γ of the Laves phase particles was estimated (**Figure 2**).

The interfacial energy *γ* between the precipitates and the ferritic matrix affects the particle coarsening and their final size under creep conditions. A good agreement with the experimental data was obtained with the interfacial energy of 0.53 J / m^2 (**Figure 2**). However, the point at 15,998 h cannot be described by the interfacial energy of 0.53 J / m^2. So, the value of the interfacial energy increases from 0.53 to 0.78 J / m^2 after ~5.000 h of exposure at 650 °C. The interfacial energy of 0.5 - 0.8 J / m^2 indicates the incoherent boundary between the Laves phase particle and the ferritic matrix that is in accordance with the microstructure observations.

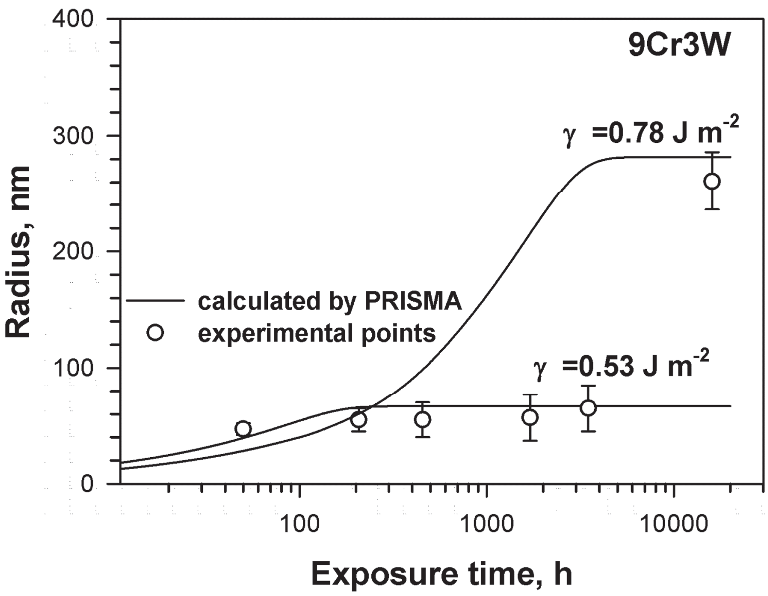

Figure 2 Time dependence of the radius of Laves phase particle in the steel studied during creep. Circle points are the experimental data for the steel studied; solid lines are the calculated curves obtained by Prisma-software for the model steel

Therefore, the Laves phase size is determined by two concurrent processes, i.e., particle precipitation and particle coarsening, during the short-term creep [13]. The low value of growth rate of the Laves phase particles in the short-term creep can be associated with continuous precipitation of new fine Laves phase particles from solid solution. On the other hand, the Laves phase precipitation is fully complete for 1.703 h of creep test. Thus, the coarsening behavior during creep is associated with coarsening of the precipitated particles resulting in an increase in the coarsening rate [13].

The mean size of Laves phase particles is unchangeable for about 3.489 h in the 9Cr3W steel. The high W content in the solid solution leads to the initial narrow size distribution of the Laves phase particles in the 9Cr3W steel (**Figure 3a**).

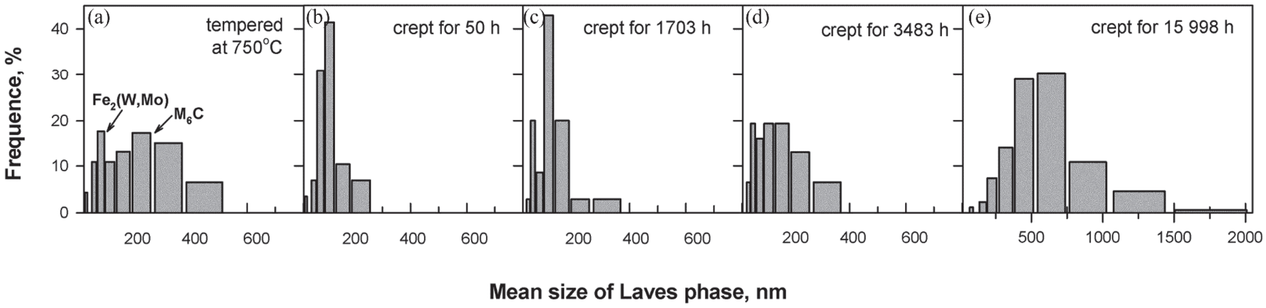

Figure 3 The size distribution of the Laves phase particle in the steel studied during creep

Despite the rapid decrease in W content in the solid solution of the 9Cr3W steel (**Table 1**) for first 500 h of creep tests, no significant changes in the size distribution of the Laves phase particles ranging 50 - 500 h of creep tests have been found (**Figure 3b**). However, after 1,703 h of creep tests, the large fraction of the fine Laves phase particles precipitates that leads to appearance of bimodal size distribution (**Figure 3c**). At the same time, W content in the solid solution almost reaches an equal value (**Table 1**). The bimodal distribution is kept for 3,489 h, until the fraction of coarse particles is less 10 % (**Figure 3d**). With increasing creep time the peak of the size distribution is shifted to the side of larger sizes, and the standard unimodal distribution with the very large particles (up to 2 μm) takes place after creep test for 15,998 h (**Figure 3e**).

The precipitation of the Laves phase particles at boundaries of PAGs and laths [5,8,10,13] indicates that their coarsening rate is controlled by the grain boundary diffusion. In this case, the continuous growth of the Laves phase particles (**Figure 2**) should obey the following relationship [10,14,15]:

$$d^n - d_0^n = K_p \tau , \tag{1}$$

where d is the particle size at the time, d_0 is the initial particle size, K_p is the constant of growth rate, τ is the time, the coefficient n depends on the coarsening mechanism: $n = 4$ corresponds to the mechanism of the grain boundary diffusion. The interfacial energy γ between the matrix and the particles is a very important characteristic of particle coarsening because it is included in the value of the rate constant K_p [13,15-17]. The value of theoretical rate constant $K_{theory} = 5 \times 10^{-34}$ m^4 / s^1 for the 9 % Cr martensitic steels was reported in [13] suggesting $\gamma = 1$ J / m^2.

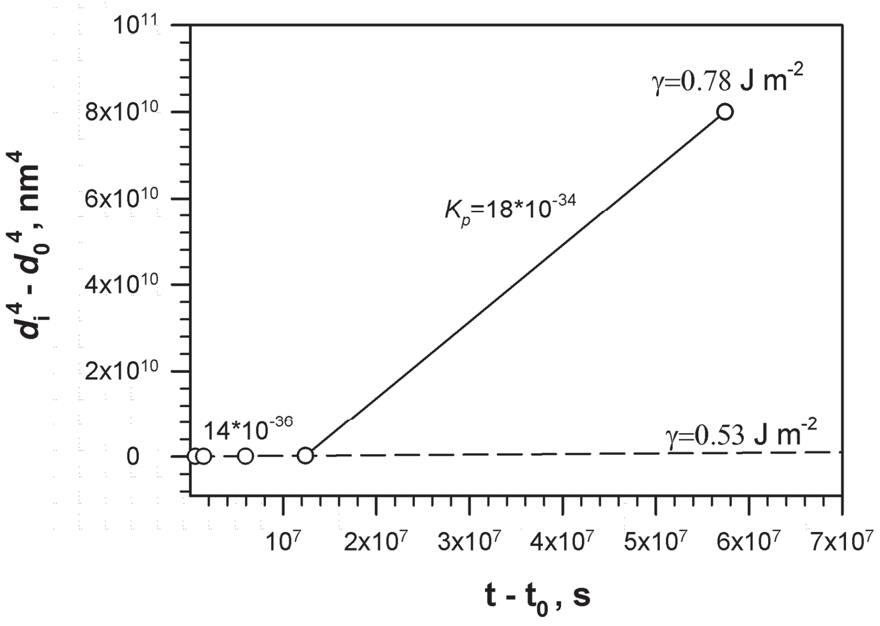

Figure 4 The dependence of the Laves phase particle size on the creep time at 650 °C in the gauge section of the 9Cr3W steel. The coarsening rate constant is also provided.

Creep deformation induces an increase in the interfacial energy between the Laves phase particles and matrix that affects the coarsening rate constant. The growth behavior of precipitation in the gauge sections of the specimen during creep test for $\gamma = 0.53$ J / m^2 (the tempered point and crept points at 220, 200, 180, 160 and 140 MPa) and for $\gamma = 0.78$ J / m^2 (crept points at 140 and 100 MPa) is illustrated in **Figure 4**. The theoretical rate constant is in a good agreement with the experimental one at $\gamma = 0.78$ J m^{-2}, which is 18×10^{-34} m^4 / s. However, for $\gamma = 0.53$ J / m^2, the coarsening rate constant K_p is a two orders of magnitude less than theoretical rate constant K_{theory} and coarsening rate constant for 3.489 - 15.998 h. At $\gamma = 0.78$ J / m^2, the coarsening of the Laves phase particles during creep for 3,489-15,998 h is controlled by the grain boundary diffusion. Actually, at γ = 0.53 J / m^2, the size stabilization of the Laves phase particles is observed in the 9Cr3W steel for first 3,500 h of creep, and particle coarsening cannot be described in terms of grain boundary diffusion.

4. CONCLUSION

The evolution of the Laves phase particles in 3 % Co-modified P92-type steel with 3 % W under creep test at 650 °C was investigated. The Laves phase particles were observed after creep for 50 h. The average size of the Laves phase particles retained less than 150 nm during creep for 3.500 h. Then, the average size of the particles increases with an increase in the creep time. The creep deformation induces an increase in the interfacial energy of the Laves phase particles from 0.53 to 0.78 J / m^2 that correspond to an increase in the coarsening rate constant from 10^{-36} to 10^{-34} m^4 s^{-1}. The coarsening of the Laves phase particles during creep for ~3,500 - 16,000 h is controlled by grain boundary diffusion and can be described by $R^4 - R_0^4 = K_p\tau$ relation, where $K_p = 18 \times 10^{-34}$ m^4 s^{-1}.

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