Enhanced creep resistance of Y-bearing 9Cr ferritic/martensitic steel via vacuum casting technique

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ABSTRACT

9Cr ferritic/martensitic (F/M) steels with 0 and 0.3 wt.% yttrium (Y) addition were fabricated via vacuum casting technique and were creep tested at 650 °C and 120 MPa. The creep property of 9Cr F/M steel was improved by the addition of yttrium. Even though the initial creep rates of 9Cr-0Y and 9Cr-0.3Y were almost the same, the creep rupture life of 9Cr-0.3Y specimen was extended about 23 times with the longer steady state creep stage and the lower minimum creep rate than 9Cr-0Y specimen. The coarsening of grains and martensitic laths occurred during creep, and M_{23}C_{6} carbides, MX/M_{2}X-type carbonitrides and Fe_{2}W/Mo Laves phase were identified along the boundary in both specimens. For 9Cr-0.3Y, the nano-sized oxide clusters were formed during creep, because of the diffusion and local segregation of the dissolved yttrium and oxygen atoms at high temperature and with the promotion of creep stress. The softening of microstructure recovery is compensated by the dispersion strengthening of nano-particles and the balance of them was the reason of longer steady state creep stage of the creep curves.

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1. Introduction

Oxide dispersion strengthened (ODS) F/M steels containing nano-sized Y-O particles have been considered as candidate materials for fuel cladding in fission reactors and blanket in fusion reactors, due to the low thermal expansion, high thermal conductivity, superior high-temperature strength and excellent radiation resistance [1-4]. Especially the thermal creep properties of ODS steels have been improved significantly due to dispersion strengthening of the high density of nano-scale oxide particles and other microstructural features...
in the martensitic/ferritic matrix [5–7]. The previous studies demonstrated that the loss of creep strength was closely related to the microstructural instability of 9Cr steels, which consisted of recovery of dislocations and growth of martensite lath were occurred with the aid of stress [8,9]. The critical consideration of improving the creep property is to maintain the stable microstructures of steels during the creep. Based on the creep testing data of ODS steels, the creep rupture strengths of the best ODS steels are nearly triple that of the equivalent non-ODS steels, and the corresponding creep rupture lifetime at a given stress is about 1000 times higher for the ODS steels [10–12]. Up to now, almost all the ODS steels are fabricated by powder metallurgy (PM) route, which consists of mechanical alloying (MA), degassing and capping, hot consolidation and heat treatment [13]. But the MA process is expensive and energy-intensive. The variable quality of experimental heats, the anisotropic properties of materials and the lack of suitable joining technologies are still the challenges for the MA-ODS steels. Aiming to solve the problems in industrial fabrication and cost reduction, an alternative fabrication method for 9Cr-ODS steel has been explored, that is, the vacuum casting technique with the addition of yttrium.

Taneike et al. reported a creep-resistant 9Cr martensitic steel with nano-sized carbonitride dispersions produced by conventional steel-making techniques. The creep rupture time of the steel was increased by two orders of magnitude, with the strengthening mechanism of boundary pinning [14]. Verhie et al. used a rapid solidification production (RSP) technique to prepare T91-YM, T91-Y2O3 and T91-YM-Y2O3 alloy, via adding a 0.3 wt% colloidal Y2O3 dispersion to a T91 steel melt in combination with metallic yttrium [15]. Being inspired by those, we explored the possibilities to fabricate ODS steels

### Table 1 – The nominal composition of 9Cr-0Y and 9Cr-0.3Y steels.

<table>
<thead>
<tr>
<th></th>
<th>Fe</th>
<th>C</th>
<th>Cr</th>
<th>Mo</th>
<th>W</th>
<th>Mn</th>
<th>V</th>
<th>Ta</th>
<th>Ti</th>
<th>Si</th>
<th>N</th>
<th>Y</th>
</tr>
</thead>
<tbody>
<tr>
<td>9Cr-0Y</td>
<td>Bal.</td>
<td>0.06</td>
<td>9.0</td>
<td>0.5</td>
<td>1.2</td>
<td>0.5</td>
<td>0.2</td>
<td>0.18</td>
<td>0.02</td>
<td>0.15</td>
<td>0.06</td>
<td>0</td>
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<tr>
<td>9Cr-0.3Y</td>
<td>Bal.</td>
<td>0.06</td>
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Fig. 1 – The creep behaviour of 9Cr-0Y and 9Cr-0.3Y specimens tested at 650 °C/120 MPa. (a) strain-time curves, tested in USTB; (b) rate-time curves, tested in USTB; (c) strain-time curves, tested in CISRI; (d) rate-time curves, tested in CISRI.
by adding element yttrium to molten steel and casting. Two specimens of steels with/without yttrium addition, termed by 9Cr-0Y and 9Cr-0.3Y, were creep tested at 650 °C and 120 MPa. The creep rupture life was extended about 23 times compared to non-yttrium steel. Under the SEM observation, large sulfide inclusions with size of 3 μm was found in the steel without yttrium addition but not in the yttrium-added steel. In addition, for the yttrium-added steel, Y-containing complex particles with size of 1 μm was found in the matrix, and the Y-O clusters were observed after 3800 h creep. In this paper, we described the testing results and discussed the probable cause.

2. Materials and experiments

2.1. Material preparation and heat treatment

The nominal chemical compositions of 9Cr-0Y and 9Cr-0.3Y steels are listed in Table 1. The ingots were prepared by vacuum induction melting & casting method. 200 kg pure irons and alloying elements with at least 99.9% purity were firstly induction melted and stirred continuously using an electro-magnetic stirrer under the protective argon atmosphere. For the 9Cr-0.3Y steel, 300 g metallic Y powders with 99.9% purity were subsequently placed at the bottom of mould before pouring. Then the melt steel was poured into two moulds and solidified rapidly from 1600 °C to room temperature under the protective argon atmosphere. Because of the massive loss of Y while casting, the actual contents of Y according to the ICP-AES measurement were 0.026 wt.% for the 9Cr-0.3Y. The measured Y content reflected the Y dissolved into the steel matrix excluding in Y-bearing particles. The yield of Y of 8.67% was acceptable according to the ref [16]. Both of the 100 kg ingots were hot-forged into sticks with 240 × 240 mm² section as the deformation temperature changed from the initial 1100 °C to the target 900 °C, then hot-rolled into plates with 30 mm thickness followed by water cooling. The rolled steels were subjected to the heat treatment as following: austenitizing at 1050 °C for 30 min followed by oil quenching, then tempering at 750 °C for 2 h followed by air cooling.

2.2. Creep tests

According to Chinese Standard of GB/T 2039-2012, creep rods with a gauge length of 50 mm and a diameter of 10 mm were cut from the as-heated-treatment plate by electron discharged machine. The axial direction of the rods was along the rolling direction of the plates. The creep tests were conducted at the temperature of 650 °C and the constant stress of 120 MPa until the rods were ruptured. After creep test, the as-received and crept specimens were both prepared for the following microstructure characterization.

Considering the reliability of the experiment, the creep tests were conducted twice under the same creep condition of 650 °C/120 MPa, in different equipment at State Key Laboratory for Advanced Metals and Materials (SKL-AMM) in University of Science and Technology Beijing (USTB) and at NCS Testing Technology Co., Ltd (NCS) in Central Iron & Steel

![Fig. 2 – The SEM images of fracture surface and dimples of the crept specimens of 9Cr-0Y and 9Cr-0.3Y steels.](image-url)
Research Institute (CISRI). The recorded experimental data of two creep tests were both analysed in section 3.1. But the creep test in CISRI is interrupted by the unexpected factor so the microstructure characterizations were carried out only for the crept specimens tested in USTB.

2.3. **Microstructure characterization**

The as-received specimens of 9Cr-0Y and 9Cr-0.3Y steels were cut from the middle of plates after heat-treatment, and the crept specimens were cut from gauge portion of the rods after creep tests. All the specimens were grounded to 2000# by silicon carbide abrasive papers and then mirror polished. After grounding and polishing, specimens were etched by a solution of 5 vol.% HF +95 vol.% HNO₃. Microstructure was examined by a confocal laser scanning microscope (CLSM, OLYMPUS), a scanning electron microscope (SEM, LEO 1450) and a transmission electron microscopy (TEM, F20).

Chemical compositions of the second particles were confirmed by an energy dispersive spectrometer (EDS) equipped in the SEM and TEM system. Phase fraction, grainsize and precipitate size were calculated statistically by ImageJ software.

3. **Results**

3.1. **Creep curves and rupture surface**

The creep behaviour of 9Cr-0Y and 9Cr-0.3Y steels were evaluated by the relationship of strain, time and creep rate. Fig. 1 showed the creep strain-time curves and corresponding creep rate-time curves of 9Cr-0Y and 9Cr-0.3Y specimens tested at 650 °C/120 MPa. For the specimens tested in USTB (Fig. 1a & 1b), the creep strain of 9Cr-0Y specimen was maintained <1% before ~1000 h and then quickly increased until the specimen ruptured with an elongation of ~8%. The strain curve of 9Cr-
0.3Y specimen showed a relative longer steady state creep stage before \( \sim 2000 \) h with the creep strain less than 2%. At the end of accelerated creep stage, the 9Cr-0.3Y specimen ruptured with an elongation of \( \sim 5\% \). The creep rate-time curves of 9Cr-0Y and 9Cr-0.3Y specimens at 650 °C/120 MPa. The initial creep rate of both specimens were at the same magnitude order of \( \sim 10^{-3}\%/h \) at the primary creep stage. The creep rate of 9Cr-0Y specimen decreased from the initial to the minimum of \( 4 \times 10^{-4}\%/h \) at \( \sim 300 \) h and then gradually increased to \( 10^{-2}\%/h \) at the end of accelerated creep stage. But for 9Cr-0.3Y specimen, the creep rate decreased to minimum creep rate of \( 3 \times 10^{-4}\%/h \) at \( \sim 1000 \) h, and it kept stable at low level for a long time until \( \sim 3000 \) h, indicating the obvious steady state creep stage. The increase of creep rate at accelerated creep stage was similar with the 9Cr-0Y specimen, from \( 10^{-3}\%/h \) to \( 10^{-2}\%/h \) during the last 800 h.

For the specimens tested in CISRI (Fig. 1c & 1d), the creep curves and creep rate-time curves showed the similar tendency with the specimens tested in USTB. The creep strain of 9Cr-0Y specimen was maintained \(<1\% \) before \( \sim 1000 \) h. The strain curve of 9Cr-0.3Y specimen also showed the same (even longer than USTB specimen) steady state creep stage before \( \sim 4000 \) h with the creep strain less than 2%. The initial creep rates of both specimens were also at the same magnitude order of \( \sim 10^{-3}\%/h \) at the primary creep stage. The creep rate of 9Cr-0Y specimen decreased from the initial to the minimum at \( \sim 300 \) h and then gradually increased at accelerated creep stage. For 9Cr-0.3Y specimen, the creep rate showed the stable minimum value of \( \sim 2 \times 10^{-4}\%/h \) at the range of 500~2000 h then increased at the accelerate creep stage.

Fig. 2 showed the fracture surface of the crept specimen. The density of dimples in 9Cr-0.3Y were higher and their size were smaller than 9Cr-0Y. In addition, the trend of brittle fracture was found in the 9Cr-0.3Y specimen, with the lower of reduction of area of 69.7% than 88.4% for the 9Cr-0Y.

### 3.2. Microstructure characteristics

The microstructures evolution of 9Cr-0Y and 9Cr-0.3Y steels were characterized by different scales. Fig. 3 illustrated the CLSM photographs of the non-creep and crept specimens. Before the creep, the microstructure of 9Cr-0Y steel was fully tempered martensite with pockets and blocks. But for 9Cr-0.3Y steel, the microstructure was dual phase structure consisting of tempered martensite and a few of ferrite with the area fraction of 0.37%. The prior austenitic grain size for 9Cr-0Y and 9Cr-0.3Y were 13.41 µm and 11.53 µm, respectively. After creep, more ferrite appeared in both creep specimens and the area fraction increased to 0.31% for 9Cr-0Y and 3.31% for 9Cr-0.3Y. The mean size of grain was also increased to 54.51 µm for 9Cr-0Y and 30.35 µm for 9Cr-0.3Y. Moreover, the most of ferrite showed a triangular morphology and located at the triple junction of grain boundaries. Fig. 4 showed the SEM photographs of the non-creep and crept specimens of 9Cr-0Y and 9Cr-0.3Y steels. For the non-creep specimens, compared to 9Cr-0Y with fully tempered martensitic structure, ferrite was found in the 9Cr-0.3Y, which was consistent with the CLSM images. Plenty of precipitates were located along the grain boundaries and in the grain. For the non-creep specimens of 9Cr-0Y and 9Cr-0.3Y, precipitates are mostly identified to be Cr-rich carbides or...

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![Fig. 4 - SEM photographs of the non-creep and crept specimens. (a) 9Cr-0Y, non-creep; (b) 9Cr-0.3Y, non-creep; (c) 9Cr-0Y, crept; (d) 9Cr-0.3Y, crept.](image-url)
Ti, V, Ta-rich carbon-nitrides containing yttrium. For the creep specimens, extra type of precipitates with W, Mo were found at the grain boundaries and in the grain. It is as same as the reported results in other 9–12%Cr steels [17–20].

Fig. 5 showed the TEM photographs of the non-creep and creep specimens. For the non-creep specimens, martensitic laths were obvious in both 9Cr-0Y and 9Cr-0.3Y, with the mean width of 0.30µm and 0.23µm, respectively. After creep, the coarsen of martensitic laths occurred and a part of parallel laths changed into subgrain structure, especially in the 9Cr-0.3Y specimen. The mean width of martensitic lath increased to 0.42µm for 9Cr-0Y specimen after 1800 h creep. For 9Cr-0.3Y specimen, the laths width of 0.62µm were estimated by the short axial diameter of subgrains after 3800h.

The details of precipitates were confirmed by selected area electron diffraction (SEAD). The Cr-rich carbides in SEM images were identified to be Cr23C6 carbides, and V, Ti, Ta-rich MX/M2X-type precipitates were also found in the matrix of the steels. These results were in accordance with other 9Cr-F/M steels [17–20]. For the precipitates containing W and Mo elements in the creep specimen, it was identified as Fe2W/Mo Laves phase, which were only appeared after the long-time creep.

4. Discussions

4.1. The existing state of yttrium

The superior creep resistance of 9Cr-0.3Y was attributed to the addition of yttrium. The state of yttrium was illustrated in the schematic diagram of Fig. 6. Firstly, yttrium was considered as the purification element for the steel-making. When the yttrium was contacted with the melts, it was easy to com-
Fig. 6 – The schematic diagram of the existing states of yttrium in the steels.

Fig. 7 – The HAADF and corresponding FFT images of non-creep and crept 9Cr-0.3Y specimens.
bine with the impurities such as oxygen and sulphur. Most of large oxides/sulfides float over with the steel slags, so the yield of yttrium was relatively as low as 8.67% compared to the theoretical content. Secondly, a few of yttrium formed small oxide/sulfide particles during the rapid solidification and stay in the steels, which are found in the SEM with size of 1~2 µm (Fig. 4b). Thirdly, the yttrium dissolved in the matrix of the steel according the Fe-Y phase diagram. When the steels were exposed under the elevated temperature and stress during the creep, it might precipitate under a proper condition and form the nano-particles or nano-clusters, which provided the dispersion strengthen for the steel.

Therefore, the improved creep property of 9Cr-0.3Y was related to the solid dissolved yttrium and the yttrium-containing particles. The effects of yttrium on the microstructure of non-creep specimens were the formation of ferrite. With the addition of yttrium, the phase transformation point was changed and incomplete austenitizing occurred during the heat treatment. However, according to the creep curve, the initial creep rate of 9Cr-0Y and 9Cr-0.3Y were almost in the same order of magnitude. It could conclude that the original ferrite (~0.3%) in non-creep specimens have little effect on the creep behaviour at the primary creep stage. Even though the amount of ferrite increased during the creep and it could be regarded as the soft phase to relax the stress concentration, the relatively low amount of ferrite of 9Cr-0.3Y was only 3% after the long-term creep, which was considered not enough to determine the improvement of the creep property.

4.2. Influence of nano-particle on the creep behavior

As mentioned above, the critical influence of yttrium addition on the creep behavior should be the dispersion strengthening of nano-particles. Furthermore, precise characterization on nanoscale particles was performed on the non-creep and creep 9Cr-0.3Y specimens. Fig. 7 showed the HAADF and corresponding FFT images of non-creep and creep 9Cr-0.3Y specimens. As seen, the nano-particles were not obvious in the non-creep specimen (Fig. 7a) but were clearly found in the creep specimen (Fig. 7d). According to the comparison of FFT image, there is only one set of diffraction spots for the non-creep specimens, but the second sets of diffraction spots appeared for the creep specimens, which could be the sign of new-formed Y-O particles. The mechanism of the nucleation and growth of the nano-particles is still unclear and the investigation is undergoing. It is deduced that the particles of yttrium oxides might be formed during the creep. Zhang et al. reported that the nucleation of nanoclusters started from the O-enriched solute clustering and proceed to grow during annealing [21]. Therefore, the attractive interaction between dissolved oxygen and yttrium atoms under the creep condition may be an effective way for the formation of nano-particles. In the non-creep specimens, the most of yttrium existed with the solid dissolved state. When the specimens were exposed under the high temperature and stress loading, the diffusion and local segregation of yttrium and oxygen atoms was promoted, and then the oxide particles were gradually formed during the long-term creep [22]. Thereafter, the dispersed nanoscale particles played and significant role on the creep-resistance, for the pinning effect of the dislocation, martensitic lath and subgrain boundaries. The sub-structure of the steel kept stable during the longer steady-state-creep stage with lower creep strain and rate.

It is known that the creep behavior is controlled by the competition between the hardening effect due to the deformation under the stress, as well as the softening effect due to the microstructure recovery at high temperature. The balance of softening and hardening effect results in steady-state-creep

![Fig. 8 - Different microstructure evolution between 9Cr-0Y and 9Cr-0.3Y steels during the creep.](image-url)
stage, and the creep rupture life of the materials was determined by the steady-state-creep stage. For the 9Cr-0Y and 9Cr-0.3Y specimens, the similar behavior at the initial creep stage comes from the strengthening of tempered martensite structures. However, the different of microstructure evolution appears in the steady-state-creep stage, as shown in Fig. 8. For 9Cr-0Y steel, the microstructure recovery occurs all the time. The stress concentration needs to be relaxed through the sliding of dislocations and the movement of grain boundaries. So, the growth of grain and the broadening of the martensitic laths are promoted with the increasing of creep strain. The instable of microstructure and sub-structure results in a shorter steady-state-creep stage. In contrast, for the 9Cr-0.3Y steel, the sliding of dislocations and the movement of grain boundaries are hindered by the new-formed nano-particles, so that the microstructure can be stable in a relatively long period. Even though the microstructure recovery at high temperature also exist, the loss of strength is compensated by the dispersion strengthening of nano-particles. Therefore, the steady-state-creep stage of 9Cr-0.3Y specimen are extended, leading to a longer creep rupture life. As for the accelerated creep stage, the creep rupture of the specimens is attributed to the gathering and growth of micro-cracks, which is usually formed at the triple junction of grain boundaries. Compared to 9Cr-0Y specimen, the soft ferrite in 9Cr-0.3Y specimens acts as the buffer phase and relaxes the local stress concentration. It is also helpful to delay the creep rupture of the steel.

4) The 9Cr-0.3Y specimens showed the trend of brittle fracture with the lower of reduction of area, which is related to the higher creep strength with the strengthening of oxide dispersions.

Conflicts of interest

The authors declare no conflicts of interest

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References


