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Long-term stability of TaC particles during tempering of 8%Cr–2%W steel

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Abstract

Precipitation behavior of 8%Cr–2%W martensitic steel during tempering at 740 °C was studied. Both $M_{23}C_6$ and TaC were observed at an early stage of tempering by TEM and XRD. $M_{23}C_6$ is coarse, about several 10's nm. On the other hand, TaC is very fine, about 10 nm, when tempering up to 10 h. Particle size of TaC is gradually increases, however the size remains below 30 nm even after tempering for 1000 h. This suggests that TaC particles grow very slowly under the actual service conditions. After the saturation of precipitation of TaC, the time exponent for coarsening of TaC particles is about 0.1, the value of which is much smaller than the theoretical value, 1/3 or 1/5. This is re-confirmed by the X-ray integral breadth for (1 1 1) TaC peak. The reason for the small time exponent is discussed in terms of the interaction between TaC and dislocations during tempering.

1. Introduction

A fine dispersion of nano-scale particles is an effective strengthening mechanism for the reduced activation martensitic steel (hereinafter RAM) [1,2]. Several researchers have confirmed that RAM precipitates fine particles of an NaCl type (hereinafter MX), the major constituent elements of which are Ta and C [3–5]. Therefore, the coarsening kinetics of TaC should be known in order to estimate the long-term stability of the particle size, which is closely correlated with the long-term strength. Tamura et al. reported that TaC is difficult to precipitate and the growth rate is very low in bcc iron compared to TaN [2]. The sizes of MX particles are reported as 17–23 nm in F-82H thermally aged at 600–650 °C for 30000 h [3], 18 nm in Eurofer'97 thermally aged at 600 °C for 1000 h [4] and 100 nm in JFL-1 irradiated to 5 dpa at 300 °C [5]. MX particles in JFL-1 are rather large compared to the others, which may be caused by the small addition of nitrogen. It is well accepted that TaC particles are thermally stable and in bcc iron at high temperatures can form much finer dispersions than $M_{23}C_6$ and Laves phase. However, the precipitation and coarsening behavior of TaC in more severe conditions has not been studied. In this paper, precipitation behavior of TaC during long-time tempering of 8%Cr–2%W steel at 740 °C is reported.

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2. Experimental procedure

A 50 kg ingot of the experimental steel (TAC1) was vacuum induction cast and hot-rolled to a 13-mm thickness. The chemical composition is 0.11%C–0.17%Si–0.50%Mn–0.007%P–0.001%S–7.9%Cr–1.8%W–0.089%Ta–0.02%Al–0.001%N and the balance is Fe. The hot-rolled plate was austenitized at 1250 °C for 2 h and air cooled. Optical and scanning electron microscopy confirmed that neither Ta-rich compounds nor delta ferrite was present in a normalized specimen. Small coupons of the normalized plate were rapidly heated in a furnace pre-heated at 740 °C and held a maximum of 1000 h.

Vickers hardness was determined under 10 kg load. An extracted carbon replica was studied using a field emission transmission electron microscope (FE-TEM) operating at 200 kV. The chemical compositions of some particles were analyzed using energy dispersive spectroscopy (EDS).

A tempered specimen was electrolyzed using 10% acetyl acetone–1% tetramethyl ammonium chloride–methanol solution (10% AA solution) and the residue was separated using a filter with 0.2 μm pores and analyzed using Cu Kα X-ray diffraction (XRD).

A tempered specimen was dissolved in 6 N HCl solution, Ta content in the filtered solution was directly measured using an inductively coupled plasma atomic emission spectroscope. TaC is not decomposed by HCl and, therefore, the dissolved Ta in the matrix was determined from the Ta content in the filtered solution. This method is simple compared to the usual method, decomposing the extracted residue, and the precision of this method is comparable to the usual method [6].

3. Results and discussion

3.1. Microstructure and hardness

The microstructure was 100% martensite and no delta ferrite was observed. Fig. 1 shows the change in hardness as a function of tempering time. A hardness of 399 in the normalized condition was measured, and hardness decreases rapidly to 260 on tempering for 30 min. After 30 min, hardness decreases gradually following the 0.05th power of tempering time in hours.

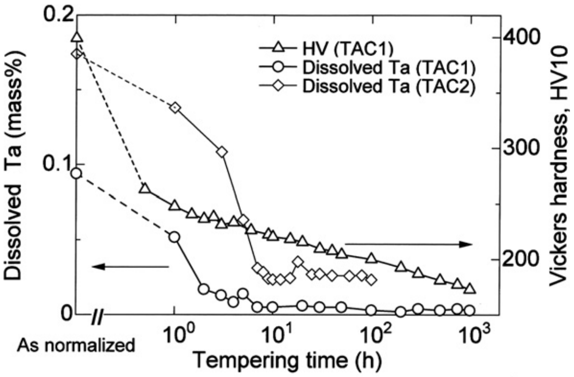

Fig. 1. Hardness (TAC1) and dissolved Ta in the matrix (TAC1 and TAC2) as a function of tempering time at 740 °C.

3.2. Dissolved Ta

Dissolved Ta in the matrix is also plotted in Fig. 1. Dissolved Ta decreases rapidly with time up to 4 h followed by a small increase at 5 h. This suggests that part of precipitated TaC particles re-dissolved at this time and subsequently the re-precipitation of TaC occurred. TaC is a thermally stable phase in this alloy system. Therefore, this phenomenon is judged to be unusual. In order to reconfirm this unusual phenomenon, dissolved Ta in the matrix was measured by using the same method as described in the experimental procedure for the similar experimental steel without W (TAC2). The chemical composition is 0.08% C–0.10%Si–0.48%Mn–0.007%P–0.004%S–8.0%Cr–0.17%Ta–0.018%Al–0.009%N and the balance is Fe. The results are also plotted in Fig. 1. Dissolved Ta in TAC2 behaves similar to that of TAC1 and it is reconfirmed that the re-dissolution of the precipitated TaC particles takes place. Furthermore, similar phenomena have been reported in martensitic steel precipitating NbC [6] and VN [7], so the phenomenon observed in this study is believed to be real. Dissolved Ta decreases further with increasing tempering time, and after 7 h the amount of dissolved Ta is roughly constant and the precipitation of TaC is complete.

3.3. TEM–EDS

Fig. 2 shows the microstructure of an extracted replica from a specimen tempered for 10 h at 740 °C. Precipitate particles of $M_{23}C_6$ and TaC are

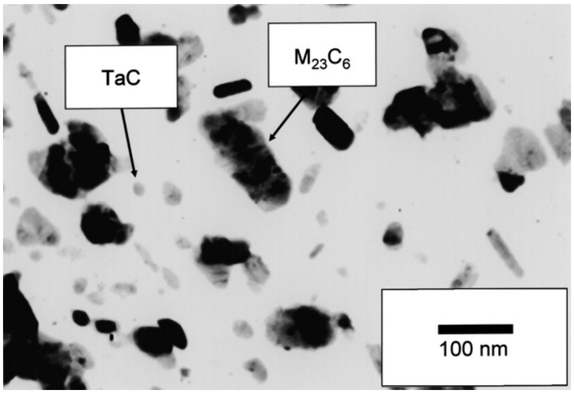

Fig. 2. Transmission electron microstructure of an extraction replica from TAC1 tempered at 740 °C for 10 h.

found. Average compositions of the metallic constituents of $M_{23}C_6$ particles are 66Cr–29Fe–4W–1Ta in at% and the average size is 110 nm with an aspect ratio of 1.6. Chemical composition of the metals in the finer TaC particles is 70Ta–13Cr–9Fe–8W in at%, and the average size is 17.8 nm with an aspect ratio of 1.5. These observations roughly coincide with the literature data for nitrogen-free RAM [4].

The time dependence of the chemical composition of TaC is plotted in Fig. 3. The chemical composition of TaC remains almost constant during tempering at 740 °C up to 1000 h, though Ta decreases slightly with increasing tempering time and Cr increases. EDS data may be affected by the co-existing compound near the observed MX particles [7]. That is, a large particle of $M_{23}C_6$ near the TaC particles observed may affect the apparent Cr content of TaC. However, since the precipitation of $M_{23}C_6$ was complete after 10 h, the slight decrease in Ta content of TaC at a longer time may be an intrinsic trend.

3.4. Coarsening of TaC particles

Fig. 4 shows an accumulated size distribution plot for the precipitates on the extracted replicas from the specimens tempered up to 100 h. The figure illustrates a bimodal distribution of a lognormal type. The data were temporally divided into two groups at $d = 30$ nm, where d is the average particle size. Each data group is fitted with a normal distribution curve. The number of particles at the cross point ($d = 24$ nm) of the two regression curves is very small compared to each peak height. Therefore, we regarded the particles smaller and larger than 24 nm as TaC and $M_{23}C_6$, respectively. Then, the average size and the aspect ratio of TaC are plotted as a function of tempering time in Fig. 5. Though the aspect ratio stays constant at 1.5, and the average

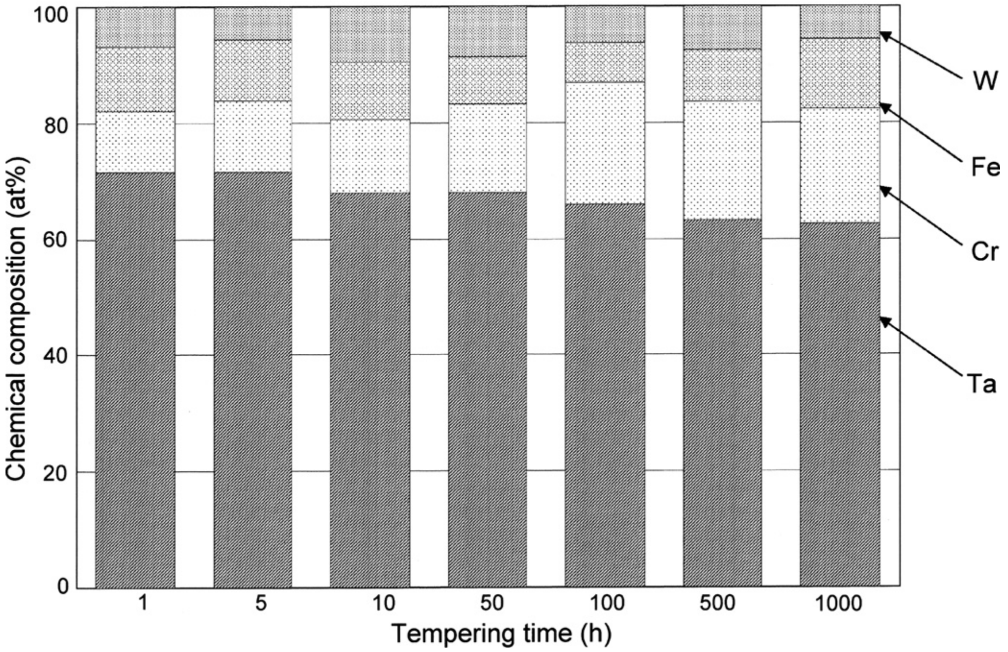

Fig. 3. Chemical composition of the metallic constituents of TaC precipitates (TAC1) as a function of tempering time.

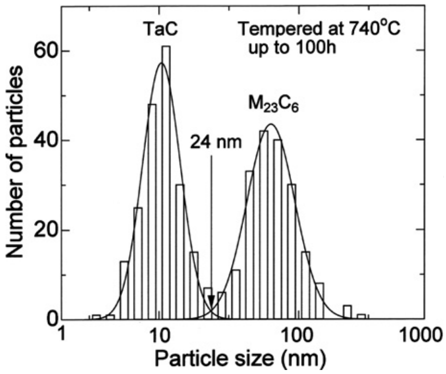

Fig. 4. Size distribution curve of extracted particles. TAC1 was tempered at 740 °C for 1 to 100 h.

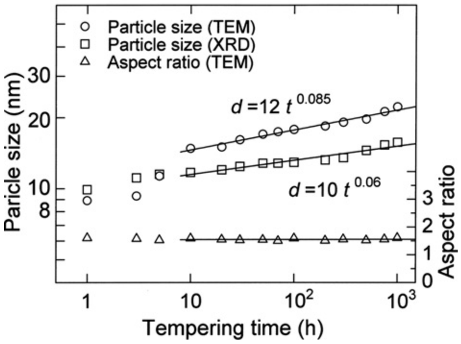

Fig. 5. Particle size and aspect ratio of TaC (TAC1) as a function of tempering time. Particle size was measured by TEM and by XRD.

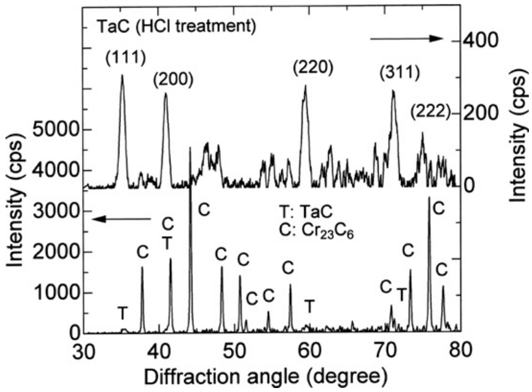

Fig. 6. XRD analysis of extracted residue. TAC1 was tempered at 740 °C for 20 h and both $M_{23}C_6$ and TaC were observed. (Bottom) The residue was further treated in HCl so that $M_{23}C_6$ was preferentially removed. (Top)

particle size increases gradually, the particle size is very small through the whole test duration. As shown in Fig. 3, the precipitation of TaC is nearly complete at 10 h. The growth rate was estimated for the data for tempering times over 10 h tempering. The average particle size after 10 h was fitted by a power law of time, and the relation $d = 12 \cdot t^{0.083}$ was obtained, where d and the tempering time, t, are in nm and hour, respectively.

In order to re-confirm the d–t relation obtained using FE-TEM, the particle size of TaC was measured using XRD. The diffraction peaks for the extracted residue from a specimen tempered for 20 h are shown in Fig. 6. As shown in the figure, the peak height for TaC is very low and comparable with the background. Therefore, the residue was re-treated in 6 N HCl solution at 90 °C and $M_{23}C_6$ carbide was dissolved. An XRD chart for the re-filtered residue is also shown in Fig. 6. Among the diffraction peaks, the TaC(1 1 1) peak is isolated and can be distinguished clearly from the background. The integral breadth of the (1 1 1) peak was corrected using Si powder prepared by NIST as reference material. The true integral breadth for TaC is converted to the particle size using the Scherrer's equation [8]. The results are shown in Fig. 5. The particle size by XRD is comparable to that measured by FE-TEM, though the particle size by XRD is a little smaller than by FE-TEM. The coarsening kinetics after the saturation of the precipitation of TaC is expressed by the relation, $d = 10 \cdot t^{0.06}$. After 200 h the coarsening rate seems to be higher than at the beginning. It was re-calculated, and a time exponent of 0.13 was obtained for both cases. Temperature dependence of the coarsening kinetics of TaC has not been investigated yet. However, the extrapolated particle size for 100 000 h at 740 °C is only 39 nm, even if the TEM data after 200 h are used. Therefore, the particle size of TaC under service conditions at lower temperatures should remain smaller.

Theoretical values for the time exponent for coarsening of precipitates after the saturation of precipitation are 1/3 or 1/5 for lattice diffusion [9,10] and dislocation pipe diffusion [11], respectively. Kadoya et al. [12] reported the coarsening behavior of MX carbonitride in 12Cr steel at 500–650 °C, and a time exponent of 1/5 was found. On the other hand, Sawada et al. [13] reported that the time exponent for MX particles precipitated in P92 steel (Fe–9Cr–0.5Mo–1.8W–VNb) aged or creep tested at 650–750 °C for up to 10 000 h is ranging from 1/15 to 1/8. They claimed that their 650 °C data could be fitted by the 1/3 law if the re-calculation for the Ostwald ripening was made using the value $r_0 = 15$ nm as the initial precipitate radius. However, their data at 700 and 750 °C did not follow the 1/3 law, even if the data were compensated for the initial particle size. Though the average size of MX particles in P92 is considerably larger, about 70 nm, the time exponent of 0.066–0.13 coincides closely to the values of the present data shown in Fig. 5.

The data for tempering time longer than the saturation of the precipitation of TaC, i.e. 10 h, were plotted in a linear scale, and the data were fitted by the equation $d = (a * (t - 10) + b)^c$, where d, a and b are particle size and constants in nm, t is time in hour and c is a time exponent. As a result, time exponents of 0.091 and 0.14 were obtained for FE-TEM and XRD data, respectively. These values are much smaller than the theoretical values. Therefore, it can be concluded that the small time exponent for the coarsening TaC particles as compared with the theoretical values is intrinsic to this precipitate in martensite.

In order to explain the coarsening of MX particles it is important to recognize that nano-scale TaC particles precipitate on dislocations and/or other defects and also the dislocations should annihilate during tempering. When dislocations annihilate or move from the precipitates due to the changes in internal stress, the precipitate particles become unstable, because the precipitate particles lose their precipitation sites and, thus, in a moment the total energy increases by the interaction energy between the dislocations and the particles. Tamura et al. [6,7] reported that nano-scale particles of VN and NbC precipitated in martensite dissolved temporally during tempering. They also claimed that the dissolution was accompanied by the discontinuous changes in integral breadth of a (1 1 0) matrix diffraction peak, which was caused by the rotation of the preferred orientation or the generation of subgrains, and this induced the local changes in internal stress. This process may take place continuously during tempering. In this alloy system, dissolution of TaC particles was confirmed as shown in Fig. 1. If this happens and the dissolved atoms are consumed in precipitating new particles and not in coarsening the pre-existing particles, the coarsening rate of MX particles slows down. This may be one of the possible reasons for the small time exponent of coarsening of TaC particles observed in this alloy system.

4. Conclusions

The stability of TaC particles precipitated during tempering of 8%Cr–2%W–VTa steel at 740 °C has been studied, and the following conclusions were obtained:

1. The particle size of TaC precipitated in the ferritic matrix remains fine, near 30 nm, even after tempering at 740 °C for 1000 h.
2. The reason the size of TaC particles remains fine under severe tempering conditions is correlated with the phenomenon of TaC particles precipitated on dislocations and it is postulated that it is possible for the TaC to re-dissolve due to the annihilation or movement of dislocation during tempering.

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