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Carbide transformation behaviors of a Cr–Mo–V secondary hardening steel during over-ageing

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Abstract

The transformation of carbides in a 1.9Cr–1.4Mo–0.3 V secondary hardening steel that was subjected to over-ageing at 600 °C–700 °C has been investigated. The carbides were characterized using scanning electron microscope (SEM), x-ray diffraction (XRD), inductively coupled plasma-atomic emission spectrometry (ICP-AES), and transmission electron microscopy (TEM) preformed on carbon replicas. The results indicate that MC, M2C, and M3C were formed during over-ageing from 600 to 700 °C, whereas M23C6 and M23C6 started to be formed at 650 and 700 °C, respectively. In addition, the co-existence of hexagonal and orthorhombic M7C3 structures in a carbide particle was firstly observed. M3C was transformed to other carbides, and the formation of both M2C and M23C6 may follow the ‘separate nucleation’ mechanism, whereas M23C6 was transformed from M3C via the ‘in situ’ nucleation mechanism. The crystallographic orientation relationships between the in situ transformed M7C3 and M2C are \((112)_{\text{MC}} // (330)_{\text{M}_{2}\text{C}}, \text{and} (312)_{\text{MC}} // [1013]_{\text{M}_{2}\text{C}}.

1. Introduction

Cr–Mo–V steels are widely used in the hot mold industry, due to their excellent room temperature and high temperature strength [1–3], which is strongly correlated with the precipitation of carbides in martensite [4–7].

The behavior of alloy steels following carbide transformation during tempering has been widely studied, and has been reported for transformations such as M7C to MC [8], M2C to M2C [9, 10], M2C to M2C [11–13], M7C to M23C6 [14–16], M2C to M2C [16–18], M2C to M2C [19], M2C to M2C [20] and M23C6 to M2C [21]. Tsai and Yang [11] observed the transformation of M2C to M2C in the martensitic region, resulting from the ‘in situ nucleation’ mechanism. Sung et al [17] concluded that M7C carbides are directly formed from the supersaturated matrix of solutes, or through the dissolution of pre-formed M7C carbides, into a matrix and the subsequent nucleation reaction. For these reasons, it has been suggested that some carbides may be transformed to produce different carbides, via two basic mechanisms [22, 23]: (1) ‘separation nucleation’, in which the pre-existing carbides dissolve firstly into the matrix, and the new carbide then nucleates and grows. In general, the new alloy carbides nucleate separately at new sites, primarily on dislocations, grain boundaries and sub-boundaries; (2) ‘in situ nucleation’, during which the new carbide nucleates directly from the pre-existing carbide, and grows at the expense of the mother carbide.

In order to gain an in-depth understanding of the carbide transformation mechanism, it is essential to characterize the crystallographic orientation relationships (CORs) between the carbides. However, relatively few studies have been published concerning the CORs between in situ transformed carbides. This may be due to the difficulties encountered in (1) capturing the in situ transformed complex carbides among the tens of thousands of carbides in the specimen, and (2) precisely indexing the complex selected area diffraction patterns produced by the in situ transformed carbides. The CORs between some in situ transformed carbides has been characterized and documented, such as \((415)_{\text{MC}} // (422)_{\text{M}_{2}\text{C}}\), \((1213)_{\text{MC}} // (001)_{\text{M}_{2}\text{C}}, \text{in a low-alloy Cr–Mo–V steel after long-term ageing treatment at 650 °C} \), and \((001)_{\text{M}_{2}\text{C}} // (001)_{\text{M}_{2}\text{C}}, \text{in a low-alloy 1Cr–1.25Mo–0.25 V steel, tempered at 700 °C} \). However, the CORs between M7C and its subsequent in situ transformed carbides are rarely reported, especially in Cr–Ni–Mo–V secondary hardening steels during an over-ageing stage.
The aim of this study is to reveal the carbide transformation mechanism occurring in a 1.9Cr-1.4Mo-0.3 V secondary hardening steel during an over-ageing stage, and in particular, to characterize the CORs between the in situ transformation of carbides from M₃C to M₇C₃.

2. Experimental procedure

In the present study, a 1.9Cr-1.4Mo-0.3 V secondary hardening steel was used. The composition of the steel is listed in table 1. The blank samples (Φ36 mm × L70 mm) were cut from an annealed steel bar along the rolling direction. All samples were initially heat-treated at 950 °C for 1 h (austenitizing), followed by an oil cooling process, and were then tempered at 600, 625, 650, 675 and 700 °C for 2 h, respectively (the over-ageing stage).

To know the distribution of carbides, the sample was cut into 10 × 10 × 10 mm, and its cross section was polished and then was etched with 4% nitric acid alcohol. And then, the microstructure was observed by JEOL-7800 field emission scanning electron microscope.

For qualitative and quantitative analysis of carbides, the over-ageing samples were machined to produce cylindrical specimens with a diameter of 8 mm and a length of 70 mm. They were subsequently dissolved in a 1% tetramethylammonium chloride + 10% acetylacetone methanol solution, to achieve precipitation using an electrolytic extraction technique. After washing in a 10 g l⁻¹ citric acid ethanol solution, the extracted precipitation was filtered using a microporous filter film, thoroughly dried at 70 °C, and weighed with an electronic balance accurate to ±0.1 mg. To identify the precipitation, the extracted powders was analyzed with a Panacow X’pert MPD x-ray diffractometer using Cu Kα radiation. In order to separate the different carbides present in the precipitation, the latter was immersed in a 6% (V/V) H₂SO₄ + 20% (V/V) H₂O₂ aqueous solution in a bath heated with boiling water, for 1 ~ 1.5 h. During this process, hydrogen peroxide was added to dissolve the M₇C₃, MC and M₃C; and then to separate the M₇C₃. Another step, the precipitation was placed in a 10 g l⁻¹ citric acid ethanol solution, and then with a 10 g l⁻¹ citric acid solution. Finally, it was washed with distilled water. The filter film and precipitation were transferred to a Teflon beaker with 10 ml HCl, 1 ml HNO₃ and 1 ml HF, which were added to dissolve the sample, and then diluted with water in a 100 ml Teflon volumetric flask at constant volume. The content of each element was determined using an inductively coupled plasma-atomic emission spectrometer (ICP-AES).

To further characterize the precipitation (morphology, size, etc), the precipitation extracted by carbon replicas was used to prepare the TEM sample. Firstly, a thin carbon film was evaporated onto the surface of the etched steel metallographic sample, using SBC-2 multi-functional sample surface treatment instrument. The carbon film was then stripped from the surface and the precipitation was extracted from the surface region of the martensite matrix by means of deep etching with a 10% nitrate acid alcohol. Finally, it was placed on a 300-mesh Cu grid, and was examined in a JEM-2100F TEM operating at 200 kV. JMAtPro 7.0 was used to calculate the kinetics of the carbide transformation, which is based on the classical Johnson-Mehl-Avrami theory with an adaptation that allows the morphology of the precipitate to be considered as well as specific associated with potential nucleant sites [27]. The carbide evolution holding at 600, 650 and 700 °C, respectively, after austenitizing at 950 °C, was computed by JMAtPro 7.0.

3. Results and discussion

3.1. Carbide identification and morphologies

Figure 1 shows the SEM images of the samples at different over-aging temperatures. The microstructures consist of tempered martensite matrix and carbides in globular, needle-like and rod-like shapes. The globular and rod-like carbides are mainly distributed at the martensite lath and the grain boundaries, while the needle-like carbides are distributed between the lath and the grain boundaries. Figure 1(f) demonstrates the EDS energy spectra of the red-marked carbide in figure 1(a). This result indicates that the globular carbide is a V-rich phase, which is likely to be MC carbide.

Figure 2 shows the XRD patterns of the powders extracted from the samples during the over-ageing stage, between 600 and 700 °C. Orthorhombic M₇C₃, hexagonal M₃C, and face-centered cubic MC were detected.
throughout the full duration of the over-ageing stage tests, whereas hexagonal $M_7C_3$ was detected only at temperatures higher than 625 °C.

Figure 3 illustrates typical TEM images and SAED patterns of carbides at 600, 675 and 700 °C, respectively. The results indicate that the MC has a globular shape, the $M_2C$ is rod-like, the $M_3C$ is needle-like, and the $M_7C_3$ is polygonal with well-defined edges. Figure 4 shows the TEM and SAED pattern for the rod-like $M_23C_6$ at 700 °C.
Figure 3. TEM images and SAED patterns: (1a∼d) at 600 °C; (2a∼d) at 675 °C; and (3a∼d) at 700 °C.

Figure 4. TEM image and SAED pattern for rod-shaped M23C6 carbide at 700 °C.

Table 2. Crystallographic characterization of carbides.

| Temperature (°C) | Type    | Crystal system | Lattice constant (nm) |
|------------------|---------|----------------|-----------------------|
| 600~700          | M7C3    | Hexagonal      | $a_0 = 0.4510, b_0 = 0.5040, c_0 = 0.46730$ |
|                  | M7C     | Cubic          | $a_0 = b_0 = c_0 = 0.416$ |
| 650~700          | M7C3    | Hexagonal      | $a_0 = b_0 = 1.3982, c_0 = 0.4506$ |
|                  | M7C     | Orthorhombic   | $a_0 = 0.4526, b_0 = 0.7010, c_0 = 1.2142$ |
| 700              | M23C6   | Cubic          | $a_0 = b_0 = c_0 = 1.0610$ |
The M23C6 carbide was not detected by XRD analysis, which may have been due to its low content. It is interesting to note that orthorhombic M7C3 was also observed by TEM and SAED, and this is further discussed in the following section.

The crystallographic characteristics of these carbides, derived from XRD, TEM and ICP-AES, are summarized in table 2.
3.2. Carbide precipitation sequence
Figure 5 plots the ICP-AES characterized content variations of three different types of carbide, as a function of tempering temperature. The weight percentage $f$ of the carbides extracted from the specimens was calculated using the following formula:

$$f = \frac{m_c - m_e}{m_o - m_e} \times 100\%$$

where $m_c$ is the weight of each specific carbide, and $m_o$ and $m_e$ are the weights of the specimen before and after electrolytic extraction, respectively. As it is difficult to distinguish MC from M$_2$C using the electrolytic extraction technique, the sum of the weight percentages of MC plus M$_2$C is shown (red curve). These results show that at temperatures ranging between 600 and 700 °C, M$_3$C decreases from 2.42 wt% to 0.56 wt%, whereas the sum of MC plus M$_2$C increases from 0.76 wt% to 1.18 wt%. M$_7$C$_3$ is initially detected at 650 °C, and its weight content then increases with increasing temperature.

Figures 6(a)–(c) plots the weight content variations of various metals detected in the M$_3$C, M$_2$C and MC, and M$_7$C$_3$ carbides, respectively, following ICP-AES characterization. These results show that as the temperature increases, the weight content of all detected metals (i.e. Fe, Cr, Mo, V, Mn) and C decreases in M$_3$C, implying that this carbide is progressively dissolved. Under the same conditions, the weight content of Fe, Cr and Mo in M$_2$C and MC increases, whereas the weight content of V in these carbides remains constant. This implies that the precipitation of M$_2$C increases, whereas MC remains insensitive to tempering temperature. M$_7$C$_3$ is rich in Cr and Fe, and contains only small relative amounts of Mo, V and Mn. The weight content of all elements in M$_7$C$_3$ also increases with increasing temperature. Figure 6(d) plots the combined weight content variation of these carbides as a function of tempering temperature. It can be seen that the total carbide content varies only slightly over the range 600 °C–675 °C, and declines somewhat when the temperature increases to 700 °C. This reveals that at 700 °C, a small amount of these carbides has been dissolved into the martensite matrix, leading to an increased alloy content in the matrix.

The results obtained using TEM and ICP-AES thus lead to the conclusion that, as the tempering temperature increases during the over-ageing stage, M$_3$C is gradually converted to M$_2$C, M$_7$C$_3$ and trace quantities of M$_{23}$C$_6$. 

![Figure 7. Volume percentage of carbides as a function of holding time at different tempering temperatures, computed by JMatPro 7.0.](image-url)
The carbide evolution holding at 600, 650 and 700 °C, respectively, after austenitizing at 950 °C, was computed by JMatPro 7.0, as shown in Figure 7. In the temperature range, the M₃C dissolves gradually with increased precipitation of M₂C and no precipitation of MC as the holding time progresses, which is slightly different from the experimental result. The precipitation of M₇C₃ begins at approximately 650 °C, and becomes clearly visible at 700 °C, which is consistent with the experimental measurements (figures 5 and 6). A small quantity of M₂₃C₆ was detected at 700 °C, thus further confirming the existence of M₂₃C₆ at high temperatures.

Following the results of theoretical calculations and experiments on the carbide precipitation, our proposed carbide transformation sequence during the 600 °C–700 °C over-ageing stage is: M₃C + M₇C₃ + MC → M₇C₃ + M₂C + MC + M₃C₃ → M₃C + M₂C + MC + M₇C₃ + M₂₃C₆. Many studies [3, 7] have revealed that carbide transformation in Cr–Mo steels during the over-ageing stage is predominantly correlated with the Cr/Mo ratio, with the preferential formation of M₃C₇, M₇C₃, and M₂₃C₆ corresponding to low, moderate and high Cr/Mo ratios, respectively.

3.3. Carbide transformation mechanism
It is well-known that carbide transformation takes place either through separate nucleation or by way of in situ nucleation.

Figure 8. TEM characterization of the in situ transformation of M₃C to M₇C₃ in the tested steel, tempered at 650 °C for 2 h: (a) BF image, (b) DF image produced by the orthorhombic M₃C (112) and the hexagonal M₇C₃ (3 3 0 1) reflections; (c) DF image produced by the orthorhombic M₃C (1 3 3) reflection; (d) corresponding SAED pattern for orthorhombic M₃C and M₇C₃; (e) DF image produced by the hexagonal M₇C₃ (3 2 5 1) reflections; (f) DF image produced by the orthorhombic M₅C₃ (1 1 2) reflection and corresponding SAED pattern for orthorhombic M₅C₃.
The TEM images shown in figure 8 reveal the transformation from existing M3C to M7C3 in the sample that was over-aged at 650 °C for 2 h. Figures 8(a) and (b) show the BF (Bright-Field) and DF (Dark-Field) TEM images of the M3C and M7C3, which ultimately come into direct contact with each other. The spot used for the DF image in figure 8(c) was (133)_{M3C}. The indexing SAED patterns shown in figure 8(d) reveal that the diffraction spots generated by different phases are entangled, which is completely different to the ordered pattern to be expected with a single phase. This shows that the transformation of M3C and M7C3 took place according to an in situ nucleation mechanism. The observation of this in situ nucleation was also found in other carbide particles, as shown in figure 9. The crystallographic orientation relationships between the M3C and M7C3 obtained from the SAED diffraction pattern were identified as follows:

\[
\begin{align*}
(112)_{M3C} & / / (3301)_{M7C3} \\
[312]_{M3C} & / / [1013]_{M7C3}
\end{align*}
\]

In addition, the co-existence of hexagonal and orthorhombic M7C3 structures was observed in a carbide particle. Although hexagonal and orthorhombic M7C3 structures have been reported in the literature [28], this is the first time that both structures have been detected in a single carbide particle transformed by in situ nucleation. The nucleation of carbides at various types of boundary is to be expected since these are energetically

![Figure 9. TEM characterization of the in situ transformation of M3C to M7C3 in the tested steel, tempered at 650 °C for 2 h: (a) BF image, (b) DF image produced by the orthorhombic M3C (112) and the hexagonal M7C3 (3 3 0 1) reflections; (c) DF image produced by the orthorhombic M3C (133) reflection; (d) corresponding SAED pattern for orthorhombic M3C; (e) DF image produced by the hexagonal M7C3 (3 2 5 1) reflections; (f) corresponding SAED pattern for hexagonal M7C3.](image-url)
favorable sites, which also provide paths for the relatively rapid diffusion of solute, especially at the interface between the carbide and the matrix. Indirect proof of this observation is given by the nature of the in situ nucleation sites that lead carbide particles to grow more rapidly than those nucleated on dislocations [29]. In two different studies [10, 22] the transformation of M3C to M2C has been reported to follow either the mechanism of ‘separate nucleation’ or that of ‘in situ nucleation’, depending on the nature of the studied systems. In the present study, the transformation of M3C to M2C is implied by the ‘separate nucleation’ mechanism, because all of the observed M2C particles are isolated from the M3C particles. The formation of M23C6 is inferred by the ‘separate nucleation’ mechanism, because no other carbides are found in the vicinity of the M23C6. As the separate nucleation transformation of M3C to M23C6 [11] and M2C to M23C6 [17] are both plausible scenarios, it is difficult to identify the alloy element leading to the growth of M23C6.

4. Conclusion

The transformation of carbides in a 1.9Cr-1.4Mo-0.3 V secondary hardening steel during an over-ageing stage has been investigated using SEM, XRD, ICP-AES and TEM preformed on carbon replicas. The main results of this research are summarized as follows:

1. Globular MC, rod-like M2C, and needle-like M3C were observed during the over-ageing stage at temperatures between 600 and 700 °C, whereas polygonal M3C and rod-shaped M23C6 started to be formed at 650 and 700 °C, respectively. The co-existence of hexagonal and orthorhombic M3C3 structures in a carbide particle was observed.

2. The carbide transformation sequence in the over-ageing stage is as follow: M3C + M2C + MC → M3C + M2C + MC + M3C3 → M3C + M2C + MC + M3C3 → M23C6.

3. The formation of both M2C and M3C6 can follow the ‘separate nucleation’ mechanism, whereas M7C3 was transformed from M3C via the ‘in situ nucleation’ mechanism. The crystallographic orientation relationships between the in situ transformed M2C and M3C are (112)hM2C // (330)hM7C3 and [312]hM2C // [1013]hM7C3.

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References

[1] Wen T, Hu X, Song Y, Yan D and Rong L 2013 Carbides and mechanical properties in a Fe–Cr–Ni–Mo high-strength steel with different V contents Mater. Sci. Eng. A 588 201–7
[2] Wang M, Li W, Wu Y, Li S, Cai C, Wen S F, Wei Q S, Shi Y S, Ye F Y and Chen Z P 2019 High-temperature properties and microstructural stability of the AISI H13 hot-work tool steel processed by selective laser melting Metall. Mater. Trans. B 50 531–42
[3] Mebarki N, Delanges D, Lamele P, Delmas F and Levaillant C 2004 Relationship between microstructure and mechanical properties of a 5% Cr tempered martensitic tool steel Mater. Sci. Eng. A 387 171–5
[4] Mondière A, Dénieux V, Binot N and Delanges D 2018 Controlling the MC and M7C3 carbide precipitation in Ferrium® M54® steel to achieve optimum ultimate tensile strength/ fracture toughness balance Mater. Charact. 140 103–12
[5] Gao Y H, Liu S Z, Hu X B, Ren Q Q, Li Y, Dravid V P and Wang C X 2019 A novel low cost 2000 MPa grade ultra-high strength steel with balanced strength and toughness Mater. Sci. Eng. A 759 298–302
[6] Viswanathan U K, Dey G K and Sethumadhavan V 2005 Effects of austenite reversion during overaging on the mechanical properties of 18Ni (350) maraging steel Mater. Sci. Eng. A 398 567–72
[7] Michaud P, Delanges D, Lamele P, Mathon M H and Levaillant C 2007 The effect of the addition of alloying elements on carbide precipitation and mechanical properties in 5% chromium martensitic steels Acta Mater. 55 4877–89
[8] Janovec J, Vyrostkova A and Svozoba M 1994 Influence of tempering temperature on stability of carbide phases in 2.6Cr–0.7Mo–0.3V steel with various carbon content Metall. Mater. Trans. A 25 267–75
[9] Kwon H 1991 Comparison of secondary hardening embrittlement in tungsten and molybdenum steels Metall. Trans. A 22 1119–22
[10] Cho K S, Choi J H, Kang H S, Kim S H, Lee K B, Yang H R and Kwon H 2010 Influence of rolling temperature on the microstructure and mechanical properties of secondary hardening high Co–Ni steel bearing 0.28 wt% C Mater. Sci. Eng. A 527 7286–93
[11] Tsai M C and Yang J F 2003 Microstructural degeneration of simulated heat-affected zone in 2.25Cr–1Mo steel during high-temperature exposure Mater. Sci. Eng. A 340 15–32
[12] Jiang Z, Wang P, Li D and Li Y 2017 The evolutions of microstructure and mechanical properties of 2.25Cr-1Mo-0.25V steel with different initial microstructures during tempering Mater. Sci. Eng. A 699 165–75
[13] Tao P, Zhang C, Yang Z and Takeda H 2010 Evolution and coarsening of carbides in 2.25Cr-1Mo steel weld metal during high temperature tempering J. Iron. Steel Res. Int. 17 74–8

[14] Chen J, Liu H, Pan Z, Shi K, Zhang H and Li J 2015 Carbide evolution and service life of simulated post weld heat treated 2.25Cr–1Mo steel Mater. Sci. Eng. A 622 153–9

[15] Lee T H, Oh C S, Ryu S H and Kim J T 2011 Crystallography and morphology of carbides in a low-cycle fatigued 1Cr–1Mo–0.25V steel Metall. Mater. Trans. A 42 147–57

[16] Shen Y, Matsuura H and Wang C 2018 Evolution of carbide precipitates in 1.25Cr–0.5Mo steel during simulated postweld heat treatment Metall. Mater. Trans. A 49 4413–8

[17] Sung H J et al 2014 Anomalous segregation kinetics of phosphorus and carbon governed by carbide reactions in 2.25 Cr–1.5 W heat-resistant steel ISIJ Int. 54 2643–8

[18] Liu Z, Liu C, Miao L, Guo X, Ding J and Zhang H 2019 The evolution of complex carbide precipitates in a low alloy Cr–Mo–V steel after long-term aging treatment Materials. 12 1724

[19] Collons M J 1989 Carbide stabilities in a Cr–Mo–V bolting steel Mater. Sci. Technol. 5 323–7

[20] Luo Y W, Guo H J, Sun X L, Guo J and Wang F 2020 Effects of nitrogen on the morphology and evolution of M2C eutectic carbides in Fe–Mo–W–Co–Cr–VC alloy JOM 72 326–32

[21] Kuo K H and Jia C L 1985 Crystallography of M23C6 and M6C precipitated in a low alloy steel Acta Metall. 33 991–6

[22] Bhadeshia H and Honeycombe R 2017 Steels: microstructure and properties (Butterworth-Heinemann) pp 196–220

[23] Shhtansky D V, Nakai K and Ohmori Y 2000 Decomposition of martensite by discontinuous-like precipitation reaction in an Fe–17Cr–0.5C alloy Acta Mater. 48 969–83

[24] Hu C D, He X, Lu H C, Dong H and Li J S 2019 Effect of matrix microstructure of gun barrel on its lifetime Acta Arma. 40 728–36

[25] Jin X K, Xu L, Yu W C, Yao K F, Shi J and Wang M Q 2019 The effect of undissolved and temper-induced (Ti, Mo) C precipitates on hydrogen embrittlement of quenched and tempered Cr–Mo steel Corr. Sci. 166 108421

[26] Ma X and Lou S J 1995 Etching and quantitative analysis of carbides in high-speed steel Prok. Metal. 32 518–26

[27] Miodownik A P and Saunders N 2002 Modelling of materials properties in duplex stainless steels Matz. Sci. Tech. 8 861–8

[28] Liu C J, Chen X D, Chen T, Nie D F and Wang J L 2016 Carbide transformation in carburised zone of 25Cr35NiNb+MA alloy after high-temperature service Mater. High Temp. 33 98–104

[29] Won Y J, Kwon Y J, Moon H K, Park S K, Kwon H and Cho K S 2018 Secondary hardening behavior in ausformed martensitic alloys with different Co content Phys. B 551 16–20