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EFFECT OF TUNGSTEN ON THE TEMPER BRITTLENESS IN STEELS WITH 9% Cr

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The impact toughness and the structure of high-chromium martensitic steels with different tungsten contents are studied after tempering at 300 – 800°C. It is shown that when the tungsten content is increased from 2 to 3%, the temperature range of the irreversible temper embrittlement is widened and the impact toughness is decreased by a factor of 4.

Key words: martensitic steel, impact toughness, $M_{23}C_6$ carbides, segregations over boundaries.

INTRODUCTION

Temper brittleness in low-alloy heat-hardenable steels with less than 0.5% carbon [1] has been studied well enough [2]. The effect of temperature on the temper brittleness of these steels may be represented in the form of a classical scheme (Table 1) [3]. The austenite retained between laths of quenched martensite is preserved to about 300°C, which provides a relatively high impact toughness, because intragrain fracture does not develop in the steels with ≤ 0.5% C in contrast to those with ≥ 0.5% C [2 – 4]. Under tempering at $t \geq 350$°C the retained austenite decomposes yielding cementite films over the boundaries of original austenite grains (OAG) [3, 4]. This results in irreversible temper brittleness connected with intragrain fracture over these boundaries [3, 4]. The formation of grain-boundary cementite films promotes nucleation of cracks on them and subsequent propagation of the cracks over the cementite/ferrite phase boundaries coinciding with the boundaries of the OAG, because the energy required for formation of two new surfaces becomes much lower while the toughness of the martensite matrix is high enough [5]. This kind of fracture by the intragrain brittle mechanism is very dangerous and reduces the impact toughness of the metal by a factor of 10 or more [5]. When the tempering temperature is raised to = 450°C, the cementite films coagulate, and this removes the irreversible temper brittleness completely. Firstly, this is connected with the considerable increase of the stresses and strains required for crack nucleation on spherical cementite particles [2]. Secondly, the energy of crack propagation over the intergrain boundaries of the OAG is quite high, which causes crack propagation inside the grains.

At a tempering temperature ≥ 500°C, segregations of P, Sn, Sb, and As atoms form over the boundaries of the OAG and martensite packs, which results in reversible temper brittleness [2, 5]. Cracks propagate over grain boundaries, because the segregations of these elements lower strongly the energy of the boundaries and thus the force of cohesion between the atoms of neighbor crystals [5]. When the steel is alloyed with Cr, the segregation of phosphorus and of the other three mentioned elements, which play the role of harmful impurities, intensifies, because their solubility in the ferrite decreases [5]. Accordingly, the reversible temper brittleness in chromium-alloyed steels may lower their impact toughness by a factor of 10 or more. It should be noted that segregations of P, Sn, Sb, and As may form on grain-boundary carbides of type $M_{23}C_6$ [5]. Alloying with Mo, which has a very high energy of interaction with phosphorus in the ferrite matrix, eliminates formation of grain-boundary segregations and suppresses the embrittlement [5].

New-generation chromium steels with 9 – 12% Cr and 0.5 – 1% Mo developed for parts of coal-fired power units keep the operating capacity at a high temperature up to 630°C [6, 7]. Despite the fact that the impact toughness is one of the most important characteristics of such steels, especially those designed for turbine and rotor blades [6], their temper brittleness has been studied in a limited number of works [8]. Accordingly, we do not have an exhaustive picture of the embrittlement of steels with 9 – 12% Cr under tempering and of the influence of the main alloying elements on it. We only know that like in the high-chromium steels of the preceding generations [9, 10], tempering of advanced steels with 9 – 12% Cr [8, 11] is accompanied by embrittlement at

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TABLE 1. Effect of Carbon Content and Tempering Temperature on Fracture Mechanisms of Carbon and Low-Alloy Steels [2]

t, °C	Fracture mechanism as a function of carbon content C, wt.%									
	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0
600 500	Reversible temper brittleness. Intragrain fracture									
400 300	Irreversible temper brittleness. Ductile (brittle) intragrain fracture									
200	Tempered martensite. Ductile fracture					Quench brittleness. Intergrain fracture				
100	Quenched martensite									

$t \geq 525$°C due to formation of films of $M_{23}C_6$ carbides over the boundaries of OAG [12].

The aim of the present work[2] was to determine the laws of embrittlement in steels 10Kh9K3B2MFBR and 10Kh9K3B3MFBR that differ in the content of vanadium (2 and 3% W respectively). The choice of these steels for the study makes it possible to detect the effect of W on the temper brittleness of martensitic steels with 9% Cr [6, 7].

METHODS OF STUDY

We melted two heat-resistant martensitic steels with composition (in wt.%) 0.1 C, 0.06 Si, 0.2 Mn, 9.4 Cr, 2.0 or 3.0 W, 3.0 Co, 0.04 Ni, 0.45 Mo, 0.06 Nb, 0.2 V, 0.05 N, 0.005 B, 0.08 Cu, 0.01 Al, 0.008 S, 0.008 P, the remainder Fe in a laboratory induction furnace. The blend was composed of pure materials, which allowed us to obtain a low level of sulfur, phosphorus and no trace of Sn, Sb and As by the data of the chemical analysis. After the roughing, the ingots were forged for billets shaped as bars with square section 20×20 mm in size by the method of free forging at from 1150 to 900°C. The hot-forged bars were subjected to normalizing from 1050°C and tempering at 300, 450, 525, 650 or 750°C for 3 h with subsequent air cooling. After the normalizing, we conducted double annealing with the temperature of the first stage 750°C and of the second stage 525°C. Air cooling was conducted after each stage; the time of the hold at each stage was 3 h. The impact toughness *KCV* was determined for standard specimens with cross section 10×10 mm and length 55 mm. A 2-mm V-notch was imposed by an "InstronIMP460" pendulum hammer at room temperature.

The critical points Ac_1 and Ac_3 for both steels were determined by differential scanning calorimetry using a Simultaneous DSC-TGA Q Series TM device. For both steels Ac_1 turned out to be 840°C; Ac_3 was 907°C and 936°C for the metals with 2 and 3% tungsten, respectively. The dilatometric analysis with the help of a DIL 402C dilatometer showed that when the content of tungsten was increased from 2 to 3%, the temperatures of the start and finish of the martensitic transformation decreased from 400 to 385°C and from 337 to 330°C, respectively.

The fractures of specimens after testing for impact toughness were studied using a Quanta 200 3D scanning electron microscope. The fine structure was studied and the elements were mapped for thin foils using a JEOL-2100 transmission electron microscope (TEM) with an attachment for energy dispersive microanalysis. The foils for the TEM were prepared by the method of jet electropolishing using a 10% solution of perchloric acid in acetic acid in a Struers Tenupol-5 device.

RESULTS AND DISCUSSION

It can be seen from Fig. 1 that the content of tungsten affects considerably the dependence of the impact toughness on the tempering temperature. For example, in the steel with

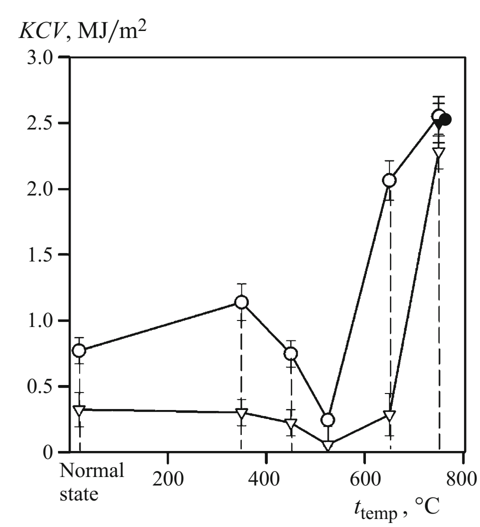

Fig. 1. Impact toughness of the steels as a function of the tempering temperature: ○, ●) 2% W; ▽, ▼) 3% W; ●, ▼) double tempering at 750°C + 525°C.

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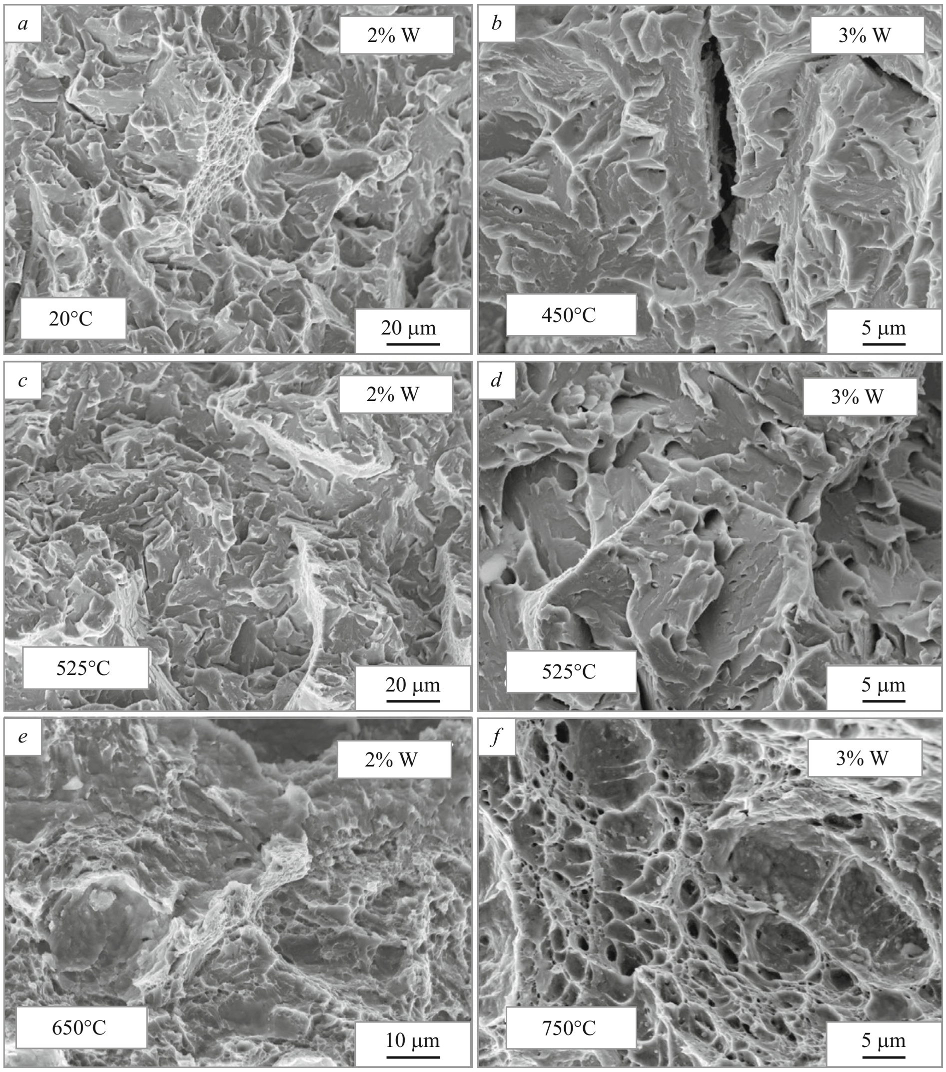

Fig. 2. Fracture surfaces after tempering the steels at different temperatures.

2% W tempered at up to 400°C the impact toughness increases with the temperature, whereas in the steel with 3% W it decreases. The steel with 2% W is embrittled only at 525°C, and its impact toughness remains quite high ($KCV = 0.24$ MJ/m^2). After the tempering at 650°C, the KCV exceeds 2.0 MJ/m^2. In the steel with 3% W the impact toughness falls to 0.06 MJ/m^2 and increases to only 0.28 MJ/m^2 with increase of the tempering temperature to 650°C. Such embrittlement may be classified as irreversible temper brittleness, because in the case of two-stage tempering conducted successively at 750 and 525°C the low-temperature tempering stage does not embrittle the steel and even promotes some increase in the impact toughness (Fig. 1).

TABLE 2. Effect of Tungsten Content and Tempering Temperature on Fracture Mechanisms of High-Chromium Martensitic Steels

t_{temp}, °C	Fracture mechanisms of steels containing W (in wt.%)	
	≤ 2	~ 3
700	Fine dispersed ferrite-carbide mixture. Ductile intragrain fracture	Fine dispersed ferrite-carbide mixture. Ductile intragrain fracture
600		Irreversible temper brittleness. Brittle (intragrain) intergrain fracture
500	Irreversible temper brittleness. Brittle (intragrain) intergrain fracture	
400	Tempered martensite. Brittle intragrain fracture	
300		
200		
100	Quenched martensite	

The studies of the fracture surfaces of specimens tested for impact toughness have shown that the range of low-temperature tempered martensite in the high-chromium martensitic steels (Table 2) widens to 400°C as compared to the low-alloy steels (Table 1), and the fracture mechanism is a brittle intragrain one (Fig. 2*a*). In the high-chromium steels with a structure of low-tempered martensite the impact toughness is higher than in the low-alloy ones with the same

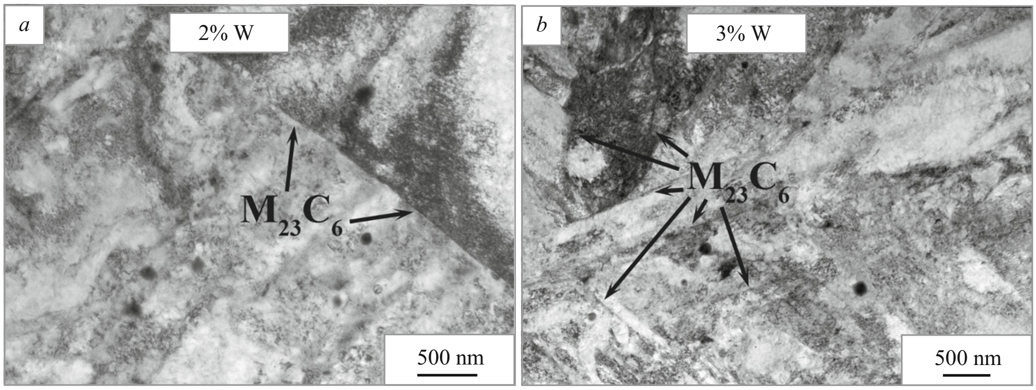

Fig. 3. Carbide films and laths in the structure of the steels with 2% W (*a*) and 3% W (*b*) after tempering at 525°C.

structure despite the fact that the low-alloy steels fracture by the ductile intragrain mechanism [2 – 5, 13]. In steel 10Kh9K3V2MFBR (with 2% W) the fracture surfaces exhibit quasi-cleavage (Fig. 2*a*), whereas in steel 10Kh9K3V3MFBR (with 3% W) we observe cleavage facets (Fig. 2*b*). At 52°C both steels undergo intergrain brittle fracture over the OAG boundaries. However, in the steel with 2% W it initiates crack propagation inside grains of the martensite matrix (Fig. 2*c*) like in low-alloy steels [2, 3, 13], while in the steel with 3% W it is the main mechanism of fracture (Fig. 2*d*). This is responsible for the fourfold difference in the impact toughness of the two steels. Dimple fracture takes a major part of the fracture surface in the steel with 2% W after the tempering at 650°C (Fig. 2*e*); in the steel with 3% W this occurs after the tempering at 750°C (Fig. 2*f*).

The studies of the microstructure have shown formation of $M_{23}C_6$ carbide films over OAG boundaries of both steels tempered at 525°C (Fig. 3) like in steel 10Kh9K3V1M1FBR with 1% W [8]. However, in the steel with 2% W individual films are arranged on individual OAG boundaries (Fig. 3*a*), whereas in the steel with 3% W they form chains over almost all the OAG boundaries (Fig. 3*b*). It should be noted that the mapping showed total absence of segregations including phosphorus ones over these boundaries. When the tempering temperature was increased to 650°C, the films in the steel with 2% W coagulated into round grain-boundary particles like in steels with a lower tungsten content [5]. In the steel with 3% W this process did not finish at 650°C; most of the films arranged over the OAG boundaries were preserved. This is connected with the fact that the tempering at 650°C yields segregations of W over OAG boundaries (Fig. 4).

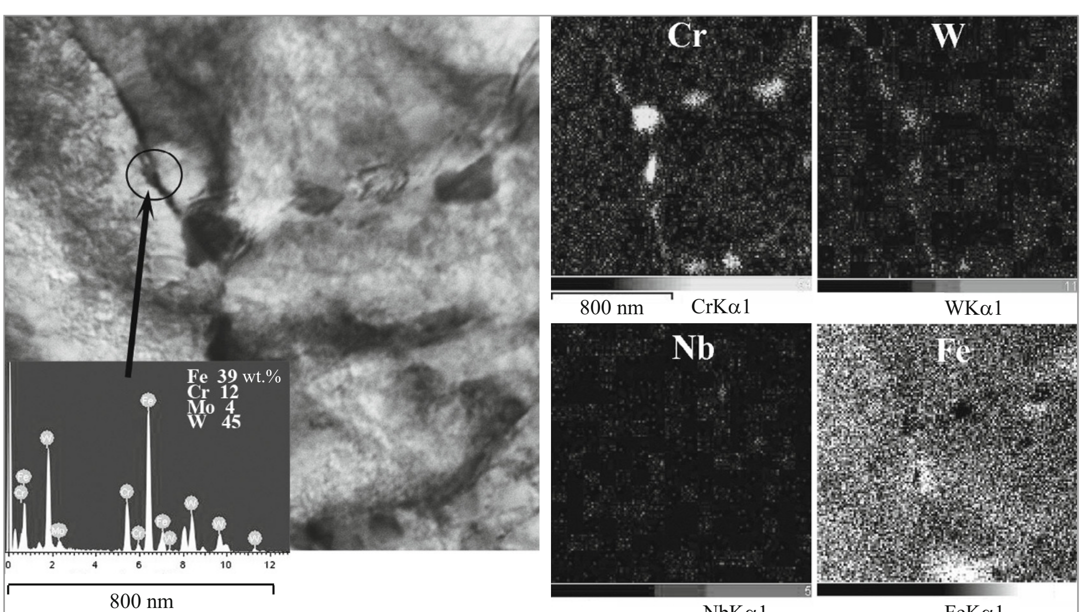

Fig. 4. Maps of elements (Cr, W, Nb, Fe) in the region adjoining OAG and lath boundaries in the steel with 3% W after tempering at 650°C.

Tungsten is an element strongly decelerating the diffusion in iron [5, 6]. Accordingly, the formation of segregations reduces considerably the rate of the coagulation of grain-boundary carbide films, which widens the temperature range of the irreversible temper brittleness. Though the rate of the diffusion of molybdenum over the boundaries is higher than that of tungsten, we detected no molybdenum segregation over the boundaries. This is explainable by the fact that the content of molybdenum in the steel is 6 times lower than that of tungsten. Combination of chains of $M_{23}C_6$ grain-boundary carbides with tungsten segregations is the cause of the low impact toughness of steel 10Kh9K3V3MFBR in the temperature range of 600 – 700°C.

It can be assumed that by analogy with the heat engineering steels of bainitic class [14], W segregations form over OAG boundaries due to the appearance of flows of W atoms between particles of $M_{23}C_6$ carbides over OAG boundaries. When the tempering temperature is raised to 750°C, W segregations cause formation of tungsten-containing M6C carbides and particles of a Laves phase over OAG boundaries in the steel with 3% W, which is not observed in the steel with 2% W. This is accompanied by disappearance of grain boundary segregations of W, which promotes a 10-times increase in the impact toughness. Since the final heat treatment of steels 10Kh9K3V2MFBR and 10Kh9K3V3MFBR involves tempering at 750°C [6, 7], the impact toughness of both steels before the start of their service is almost 6 times higher than the minimum specified values of *KCV*. Accordingly, the optimum content of W in the heat engineering high-chromium steels of martensitic class may be chosen in accordance with the requirements on the long-term strength.

CONCLUSIONS

1. The laws of temper brittleness in high-chromium steels differ considerably from similar processes in low-alloy steels, and the growth in the tungsten content from 2 to 3% affects them much.

2. When the content of tungsten is increased from 2 to 3%, the temperature range of the irreversible temper brittleness widens, and the impact toughness decreases by a factor of 4, which is connected with formation of semi-continuous chains of $M_{23}C_6$ carbides and segregations of W over the boundaries of original austenite grains.

3. In the steels with a lower content of W, the density of grain-boundary carbide films is substantially lower; tungsten segregations do not form, and the value of *KCV* is preserved at a quite high level even under embrittlement.

4. The final heat treatment for steels 10Kh9K3V2MFBR and 10Kh9K3V3MFBR should involve normalizing from 1050°C and tempering at 750°C, which provides a high impact toughness.

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