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SECONDARY HARDNESS AND HEAT RESISTANCE OF HIGH-SPEED STEELS

This paper presents the research results concerning factors affecting the secondary hardness and heat resistance of high-speed steels. Processing parameters making possible to achieve the necessary levels of heat resistance and hardness are considered. The phase and structural transformations accompanying this process are studied. The role of the different carbide-forming elements is described. The hardening phases, which contribute to an increase in hardness and heat resistance during the heat treatment, are identified. Morphology and type of crystal lattice of the hardening phases are considered. Different approaches to the process of precipitation of strengthening phases are studied. The dependences between the secondary hardening of heavily alloyed iron alloys and the magnitude of the stresses in the crystal lattice are considered.

Keywords: secondary hardness, heat resistance, high-speed steel, hardening phases, carbides.

1. Introduction

High-speed steels are used for cutting and cold forming operations. The requirements to high-speed steels are hardness, heat resistance, wear resistance and sufficient toughness. These properties are provided by alloying with high amounts of carbide forming elements such as tungsten, molybdenum, vanadium and chromium. High-speed steel tools are shaped in the annealed condition and subsequently heat treated by hardening from about 1500 K and tempering at 820–830 K, usually three times. The steels consist of about 6–15 vol.% of micron-size hard carbides of MC and M_6 C (where M is a metal) type that dispersed in a matrix of tempered martensite after this treatment [1].

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The specific feature of the cutting tool made of high-speed steel is the heating of cutting edge at the high cutting speeds. Hard cutting conditions lead to greater edge heating. Therefore, the cutting properties of high-speed steel depend on heat resistance [2]. All other characteristics, even such significant as wear resistance, have a subordinate (secondary) value.

The decrease of heat resistance at 450-750 K of high-speed steels is caused by heating softening. This is a reversible process.

The intensity of loss of strength significantly depends on changes in the composition of the solid solution and hardening phases during the heat treatment of high-speed steel. Heat resistance (but not to a large extent) also depends on the initial hardness, quantity, size, and distribution of carbides.

Heating above 750-900 K of tools made of high-speed steel is accompanied by decreasing in hardness to HRC 59-60. Thus, wear out of the cutting edge is raised abruptly and almost complete loss of cutting properties occurs [3]. Hardness reduction is caused by the development of irreversible processes that change the structure of steel: solid solution decay (martensite of high-speed steels) and coagulation of dispersed hardening phases precipitated during the previous tempering [4]. Particles enlarge during coagulation and heating, as a result, their number decreases. In addition, the hardness of a tool is reduced [5]. The metal base significantly loses strength closer to the phase transformation temperatures.

The goal of the present work is to review the factors affecting the secondary hardness and heat resistance of high-speed steels.

2. Features of Heat Resistance and Secondary Hardening of High-Speed Steels

Significant alloying of steel, the formation a sufficient number of hardening phases, and a quenching temperatures increase leads to an increase in heat resistance (the result is a more saturated solid solution). This reduces strength and toughness.

The quantity of hardening carbides increases with increasing solubility of carbon and alloying components in austenite. Therefore, the quantity of carbides increases in martensite of heat-resistant steels and alloys during quenching. The highest solubility is characteristic of chromium in austenite than (as it decreases) molybdenum, tungsten and vanadium [5].

Thus, the heat resistance of high-speed steels is being formed by the special alloying and quenching from high temperatures of 1470-1570 K.

The optimum exposure during the final heating for quenching of the high-speed steel is such an exposure, which leads to the most complete

dissolution of the carbide phase and obtain maximum microcrack resistance [6]. The heat resistance increase with an exposure time increase above the optimum is associated with a decrease in solubility and precipitation of carbide particles along grain boundaries. Heat resistance increases, microcrack and tool resistance decreases with increasing exposure above the optimal.

A sufficiently large proportion of carbide (or intermetallic) should be transferred into a solution (austenite, martensite) to provide heat resistance. This saturates it with tungsten (molybdenum) and vanadium.

The microstructure of hardened and tempered high-speed steels consists of a martensitic matrix with a dispersion of two sets of carbides (primary and secondary carbides).

Primary carbides forming during solidification and assuming a more spherical morphology during hot forming show an incoherent interface to the matrix. The primary carbides in different high-speed steels are type M_6 C and MC carbides [7].

W.E. Henderer and B.F. Turkovich [8] have described the full data about volume fraction, average particle size, particle size distribution, chemical composition and crystallography.

Primary carbides do not contribute to the strength of the steels [9]. The primary carbides and their distribution have a major influence on the wear resistance and the toughness of the material. During soft annealing in the high-speed steels, additionally annealing carbides 50-300 nm in size have precipitated in a ferritic matrix.

Secondary carbides are those carbides formed during secondary hardening in processing of heat treatment. Secondary hardening carbides of high-speed steels are plate-shaped, between 20 nm and 40 nm across and about 3 to 5 nm in thickness [10].

After hardening and during tempering, secondary carbides grow, revealing different morphologies. In some regions, they appear as regularly distributed dark spots 3-10 nm in diameter. In others, rods or plates occur with 2-3 nm in thickness [11].

The properties of carbides depend on their chemical composition. They are determined by the ratio of the concentrations of alloying components and carbon in martensite, from which they are evolved during tempering. The properties of hardening carbides are the higher, the more tungsten, molybdenum, vanadium and less carbon are dissolved in martensite.

As known [3], the maximum hardness of high-speed steel is achieved by secondary hardness treatment including several tempering, providing the most complete conversion of residual austenite.

Consequently, tempering of high-speed steels at a temperature of 820-850 K increases the hardness to maximum values (HRC 62-69) due to the release of a large amount (~ $10^{16}-10^{18}$ cm⁻³) of dispersed carbides



500 K $M_{23}C_{6}$ Forms $M_{23}C_6$ 700 K precipitation + lower allov γ M_6C M_6C 820 K precipitation + precipitation lower alloy γ To martensite Coagulation and No change growth of carbides on cooling

Fig. 1. The scheme of the phase transformations during tempering

from supersaturated martensite. The size of dispersed carbides is much smaller than they were in annealed steel.

An increase of hardness during tempering is associated both with the precipitation of finely dispersed carbides at tempering temperatures from the matrix, and the transformation of residual austenite into martensite upon cooling [12].

The scheme of the phase transformations occurring during tempering is shown in Fig. 1.

As shown schematically in the graph (Fig. 2), high-temperature hardness is possible only by a very important straightening mechanism: secondary hardening, promoted by the precipitation of fine alloy carbides. The stronger the secondary hardening (meaning more intense carbide precipitation), the higher the tempering resistance of hot-work tool steels. Such precipitation intensity depends on the amount of alloy



Fig. 2. The tempering-temperature-dependent hardness for high-speed steels [13]

elements in solid solution, which is related to the alloy composition and heat-treating practice obtained by molybdenum, vanadium, or tungsten alloying [13]. The graph shows a

schematic of hardness after tempering and the effect of secondary hardening in high-alloy steels. As observed, the high-temperature hardness is only possible through precipitation hardening caused by alloy carbides (secondary hardening). At low temperatures, hardness is less than martensite due to the presence of retained austenite, which is eliminated after high-temperature tempering.

The hardness and heat resistance of high-speed steels is the higher, the more hardening carbides are in them and they are more resistant to the coagulation. It is also obvious that the heat resistance of high-speed steels is greater, the higher the tempering temperature, which provides maximum secondary hardness.

In the case of high-speed steels, the finely dispersed hardening phases released during tempering have a great influence. These phases distort greatly the crystal lattice of the metal base according to x-ray analysis [14].

The strength of the martensite is a result of the degree of tetragonality of the martensitic lattice. Such tetragonality is a direct result of the dissolution of the interstitial atoms [15]. Carbon is the interstitial atom of high-speed steels. The strength of the martensitic matrix of highspeed steels is depended on the carbon content in the matrix.

The solid solution is depleted by about 1/3 chromium, 1/2 tungsten and 2/3 vanadium during triple tempering at 830 K. The proportion of the alloying element (transferred from solid solution to carbides upon tempering) does not depend on the initial concentration of this element in the solid solution and is directly proportional to its carbide-forming ability [16].

Low tempering temperature does not provide a sufficiently intensive development of carbide formation processes, austenite is insufficiently depleted in carbon and alloying elements, the process of destabilization of austenite is incomplete. As a result, when cooling not only to room temperature, but also to a negative temperature, the martensitic transformation is not sufficiently realized. Contrariwise, a significant increase in tempering temperature not only accelerates the coagulation of the carbide phase precipitated both from martensite and residual austenite, but can also lead to diffusion decomposition of austenite. In this case, the secondary hardening phenomenon may not be fully appeared in the case of a significant development of the diffusion decomposition of austenite [17].

3. Hardening Phases of High-Speed Steels

The hardening phases of high-speed steels (carbides) according to the level of properties (resistance to coagulation, hardness, shear modulus, specific weight, mismatch of crystal lattices and martensite lattices while maintaining a coherent or semi-coherent boundary between them, *etc.*) are arranged in the order of its increase: $M_{23}C_6$, M_2C and MC. Intermetallic compounds based on tungsten, molybdenum and cobalt possess particularly high properties [5].

Almost all alloying components and carbon are concentrated in carbides of high-speed steels. Some of these carbides dissolve in austenite while heating to a quenching temperature. In this case, austenite is saturated with carbon and alloying components. Another part of carbides (not soluble in austenite) inhibits the growth of its grains. Thus, soluble carbides serve to obtain high hardness and heat resistance in high-speed steels and insoluble carbides are used to obtain high tensile strength in bending and toughness [18].

The first group of properties provides a sufficiently high cutting speed and the second group of properties increases the feed and depth of cut, *i.e.*, parameters on which the productivity of the cutting process depends.

Hardening phases are carbides of the M_2C type (in particular, W_2C and Mo_2C [19]) and MC type (vanadium carbide VC), as well as iron and chromium carbides $M_{23}C_6$ and, in addition, $M_7^{\rm I}M_6^{\rm II}$ intermetallic compounds based on iron and cobalt ($M^{\rm I}$), tungsten and molybdenum ($M^{\rm II}$) in tool steels [20].

Hexagonal M_2C carbide [19], $M_{23}C_6$ carbide [21], MC carbide [22] have been claimed to be responsible for the secondary hardening of high-speed steels. These carbides are highly resistant to coagulation and give high heat resistance to high-speed steels. M_2C carbides turn into stable M_6C carbides of the composition (Fe, Cr)₄(W, Mo, Cr)₂C with an increase in tempering temperature and the steel structure approaches to the equilibrium thermodynamic state [19].

Two kinds of precipitate morphology were found: platelets and rods. The platelets are of the MC type, whereas the rod-shaped precipitates are of the M_2C structure. However, an increase in the vanadium content mainly leads to higher amounts of primary MC carbides without affecting the secondary carbide composition. The small size of the precipitates in the cobalt containing steels leads to a higher chromium and a slightly lower vanadium content [1].

Experimental researches [23, 24] have proved that secondary hardening carbides are not hexagonal Mo₂C, nor MC, nor M_6 C carbides. The secondary hardening carbide is the cubic M_2 C carbide rich in molybdenum and containing vanadium and chromium.

According to W. Rong and G.L. Dunlop [25], the secondary carbides are usually MC and/or M_2C . In some alloys, the M_3C may also precipitate during heat treatment.

A part of retained austenite transforms already during heating for tempering in quenched high-speed steels, but its significant part transforms only during cooling process after tempering. Change of heating rate during tempering has strong influence on the temperatures of beginnings and the ends of individual transitions as well as on the accompanying dilatation effects [26].

In the paper [10], authors have established the volume fraction of secondary hardening carbides in high-speed steels as 20%.

The high-resolution electron microscopy (HREM) investigations revealed a coherent transition to the matrix. Elemental maps on a nanometer scale were achieved by the energy-filtered transmission electron microscopy (EFTEM), showing an enrichment with vanadium and carbon and a depletion of iron in the namometer-size *MC*-type carbides [11].

The finely dispersed precipitates having only a very small misfit to the matrix contribute to the secondary hardening at elevated temperatures [27].

Dispersed precipitates block sliding planes that preventing plastic deformation.

A.M. El-Rakayby [23] has provided analytical studies of the strengthening of high-speed steels based on dislocation theory. He devoted his PhD thesis to this study.

Plastic deformation of steels develops due to cutting or bending around by particles of reinforcing phases during tool operation. The dimensions of the hardening phases are of $(2-6) \cdot 10^{-6}$ cm after the final heat treatment of the cutting tool. Therefore, the resistance to plastic deformation during heating (heat resistance) is determined by the volume fraction of the hardening particles and their properties [28].

4. Mechanism of Precipitation for Hardening Phase

The forming of the special carbides is considered as a process consisting of two stages: (i) formation of clusters — zones consisting of carbide forming elements and carbon; (ii) the reconstruction of these areas into special carbide. The first step is spinodal decomposition, and this mechanism underlies the observed structural phenomena [29].

According to Ref. [2], the precipitation of the excess phase from the supersaturated solid solution can be divided into three consecutive sta-

ges. The first stage consists in the atoms' migration of the solute to certain sections (or sites) of the lattice. At the second stage, the smallest crystalline particles of a new phase are precipitated in areas of accumulation of excess atoms. Finally, at the third stage, these dispersed precipitates grow. The small and thermodynamically least stable crystals dissolve. The dissolved atoms diffuse and attach to larger crystals.

All three processes are diffusion, occur in time and accelerate with increasing temperature. Therefore, it is necessary to complicate the passage of these processes and transfer them to the region of higher temperatures for increasing the heat resistance.

The work [30] revealed that a high value of the type II stress parameter is observed during tempering at a temperature of 670 K due to the preservation of a large quantity of defects in the crystal structure obtained during the previous hardening. The lattice tension decreases with an increase in tempering temperature to 770 K due to a structure defect decreasing. However, an increase in microstresses in the composite surface layer causes tempering at a temperature of 820 K. This effect is explained by the formation of the zones similar to the Guinier-Preston ones at tempering temperature of 820 K. That contributes to the distortion of the crystal lattice of the solid solution. An increase in the tempering temperature from 820 to 860 K and higher leads to a significant decrease (of $\cong 30\%$) in microstresses due to their relaxation during the precipitation of special carbides.

Analysis of electron diffraction patterns of carbide precipitates showed that the only carbide phase, which is determined electronically, is cementite M_3C [30]. Dispersion particles of cementite are formed in places of dislocations accumulation. Then, the dispersion particles stabilize the dislocation substructure; specifically they inhibit the movement and redistribution of dislocations. It is noteworthy that no traces of the release of special carbides were found in the analysis of microdiffraction images. It should be noted that the formation of cementite M_3C does not cause secondary hardening of high-speed steels, because the precipitation of M_3C carbide during tempering occurs in the temperature range 520–600 K.

5. Conclusions

The heat resistance of high-speed steels is being formed by special alloying and quenching from high temperatures 1470–1570 K.

The optimum exposure during the final heating for quenching of high-speed steel is such exposure, which leads to the most complete dissolution of the carbide phase and obtain maximum microcrack resistance. Heat resistance increases, microcrack and tool resistance decreases with increasing exposure above optimal.

An increase of hardness during tempering is associated both with the precipitation of finely dispersed carbides at tempering temperatures from the matrix, and the transformation of residual austenite into martensite upon cooling.

High-temperature hardness is only possible through precipitation hardening caused by alloy carbides (secondary hardening). At low temperatures, hardness is less than martensite due to the presence of retained austenite, which is eliminated after high-temperature tempering.

The hardness and heat resistance of high-speed steels is the higher, the more hardening carbides are in them and they are more resistant to coagulation.

Soluble carbides serve to obtain high hardness and heat resistance in high-speed steels and insoluble carbides are used to obtain high tensile strength in bending and toughness.

The properties of carbides depend on their chemical composition. The properties of hardening carbides are the higher, the more tungsten, molybdenum, vanadium and less carbon are dissolved in martensite.

Hardening phases are carbides of the M_2 C type (particularly, W_2 C and Mo_2 C) and MC type (vanadium carbide VC), as well as iron and chromium carbides $M_{23}C_6$ and, in addition, $M_7^{T}M_6^{T}$ intermetallic compounds based on iron and cobalt (M^{T}), tungsten and molybdenum (M^{T}) in tool steels.

The resistance to plastic deformation during heating (heat resistance) is determined by the volume fraction of the hardening particles and their properties.

The precipitation of the excess phase from the supersaturated solid solution can be divided into two or three consecutive stages.

The formation of the Guinier-Preston-type zones by tempering on secondary hardness, which promote distortion of solid-solution crystal lattice, was shown.

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ВТОРИННА ТВЕРДІСТЬ І ТЕПЛОСТІЙКІСТЬ ШВИДКОРІЗАЛЬНИХ СТАЛЕЙ

Наведено результати дослідження чинників, які впливають на вторинну твердість і теплостійкість швидкорізальних сталей. Розглянуто параметри оброблення, що уможливлює досягнення необхідних рівнів теплостійкости та твердости. Вивчено фазові та структурні перетворення, які супроводжують цей процес. Описано роль різних карбідоутворювальних елементів. Визначено зміцнювальні фази, що сприяють підвищенню твердости та теплостійкости в процесі термічного оброблення. Розглянуто морфологію та тип кристалічної ґратниці зміцнювальних фаз. Вивчено різні підходи до процесу виділення зміцнювальних фаз. Розглянуто залежності між вторинним твердінням високолеґованих залізних стопів і величиною напружень у кристалічній ґратниці.

Ключові слова: вторинна твердість, теплостійкість, швидкорізальна сталь, зміцнювальні фази, карбіди.

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ВТОРИЧНАЯ ТВЁРДОСТЬ И ТЕПЛОСТОЙКОСТЬ БЫСТРОРЕЖУЩИХ СТАЛЕЙ

Изложены результаты исследования факторов, которые оказывают влияние на вторичную твёрдость и теплостойкость быстрорежущих сталей. Рассмотрены параметры обработки, позволяющей достичь необходимых уровней теплостойкости и твёрдости. Изучены фазовые и структурные превращения, сопровождающие этот процесс. Описана роль различных карбидообразующих элементов. Определены упрочняющие фазы, способствующие повышению твёрдости и теплостойкости в процессе термической обработки. Рассмотрена морфология и тип кристаллической решётки упрочняющих фаз. Изучены различные подходы к процессу выделения упрочняющих фаз. Рассмотрены зависимости между вторичным твердением высоколегированных железных сплавов и величиной напряжений в кристаллической решётке.

Ключевые слова: вторичная твёрдость, теплостойкость, быстрорежущая сталь, упрочняющие фазы, карбиды.