

Influence of the Zr and Ce on the structure of experimental hot-work tool steel

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Materials

ABSTRACT

Purpose: of this paper was to examine of the influence of the Zr i Ce on the structure of the newly developed complex hot-work tool steel 47CrMoWVTiCeZr16-26-8 in relation to standard hot-work tool steel X40CrMoV5-1.

Design/methodology/approach: The investigations steels were made using the specimens made from the experimental steel, for which the working 47CrMoWVTiCeZr16-26-8 denotation was adopted, similar to the ones used in the ISO Standard on using the standard alloy hot-work tool steel X40CrMoV5-1. Both investigated steels were melted in a vacuum electric furnace. Specimens made from the investigated steels were heat treated with austenitizing in salt bath furnaces for 30 minutes in the temperature range of 970-1180°C with gradation of 30°C. Next, the specimens were tempered twice in the temperature range of 450-660°C for 2 hours.

Findings: The 47CrMoWVTiCeZr16-26-8 steel quenched from the temperature of 1120°C has the martensitic structure with the small portion of the retained austenite and alloy carbides partially dissolved during austenitizing (about 3.5%), including the MC type carbides (based on ZrC, TiC, (Ti,V)C and VC, with differing chemical compositions and crystallographic lattice parameter) and of the M₂C₃ type (based on Ce₂C₃).

Research limitations/implications: Basing on the investigations of the newly developed 47CrMoWVTiCeZr16-26-8 steel and the standard X40CrMoV5-1 steel, the most advantageous heat treatment conditions were determined to obtain thesis most advantageous structure and mechanical properties: for the 47CrMoWVTiCeZr16-26-8 steel quenching at the temperature of 1120°C and tempering at the temperature of 540°C, and for the X40CrMoV5-1 one quenching at the temperature of 1060°C and tempering at the temperature of 510°C.

Originality/value: The newly developed hot-work tool steel include Zr and Ce characterizations good structure and can be used to hot work small-size tools which requires higher strength properties at elevated temperature.

Keywords: Tool materials; Structure; Secondary hardness effect; Thermal fatigue

1. Introduction

The complex hot-work tool steel, in which, due to suitable selection of alloying elements and their concentration as well as due to suitably performed thermal treatment, one can modify the structure and properties, is a group of steel that requires the effective utilisation of alloying elements contained in a considerable portion of carbides [1-4]. One of the factors that decides on operation life and reliability of tool materials is structure and chemical composition of carbides undissolved during austenitizing,

whose fraction and type determines saturation of matrix with alloying elements and with carbon, thus obtaining good steel properties as a result of separation of dispersion carbides during tempering. Entering rarely met elements in this group of steel such as Zr, Ce and Ti to the steel under examination allows the analysis of their influence on structure and properties of newly developed steels. Alloy carbides, in steel enriched with such elements, differ considerably both in structure and in chemical composition from carbides in Cr-Mo-V steels, which fact has influence on temperature of phase transformation, structure as well as steel properties.

The purpose of this paper is to examine of the influence of the Zr i Ce on the structure of the newly developed complex hot-work tool steel 47CrMoWVTiCeZr16-26-8 in relation to standard hot-work tool steel X40CrMoV5-1.

2. Experimental procedure

The investigations were made using the specimens made from the experimental steel, for which the working 47CrMoWVTiCe-Zr16-26-8 denotation was adopted, similar to the ones used in the ISO Standard [5] on using the standard alloy hot-work tool steel X40CrMoV5-1. Chemical compositions of these steels are given in Table 1. Heat treatment of the specimens was carried out following the procedure described in [1].

Metallographic examinations were carried out using MEF4A metallographic microscope made by Leica Company utilising Leica-Qwin computer image analysis system. Carbides surface fraction as plastic state as well as quenched state after austenitizing within the temperature scope under examination were measured using computer image analysis techniques at enlargement 1000x. Qualitative and quantitative X-ray microanalysis as well as analysis of surface distribution of alloying elements in samples of steel as quenched under examination was carried out using DSM-940 scanning microscope made by Opton provided with the EDS LINK ISIS spectrometer of X-ray scattered radiation made by Oxford Co. at accelerating voltage 20 kV as well as JEOL JCSA 733 X-ray microanalyser. Crystalline dispersion-wave spectrometers of X-ray radiation (WDS) were used using the accelerating voltage 20 kV, whereas at analysis of carbon – 10 kV. The X-ray analysis of carbides isolates was carried out using Philips PW 1140 diffractometer provided with cobalt anode supplied with voltage 40 kV at filament current intensity 30 mA, using graphite monochromator on diffracted beam side. Diffraction and chemical composition examinations in microareas as well as structures of thin foils were carried out using JEOL 2000X transmission electron microscope, at accelerating voltage 200 kV, equipped with EDS LINK ISIS spectrometer of X-ray scattered radiation made by Oxford Co.

3. Results and discussion

The investigated steels in the soft annealed state have the ferrite structure with the alloy carbides. The volume fraction of these carbides in the 47CrMoWVTiCeZr16-26-8 steel is about 8.2%.

It was found out, using the qualitative X-ray phase analysis method, that among the carbides secluded from the annealed 47CrMoWVTiCeZr16-26-8 steel, the M_6C carbides with the complex cubic crystallographic lattice (Fd3m space group) and lattice parameter of about 1.106 nm have the maximum fraction. Several types of the MC type carbides with the cubic crystallographic lattice (Fm3m space group) occur in the steel also. These include, in the decreasing order of their fraction in the steel: carbides close to VC with the lattice parameter of about 0.418 nm, intermediate carbides between VC and TiC - denoted in short form as (Ti,V)C - with the lattice parameter of about 0.424-0.427 nm, carbides close to TiC with the lattice parameters of about 0.433 nm, and also carbides close to ZrC with the lattice parameters of about 0.461 nm. The M_2C_3 type carbides, close to the Ce_2C_3 ones with the cubic crystallographic lattice ($\bar{I}43d$ space group) with the crystallographic lattice parameter of about 0.845 nm, have the smallest fraction. All these carbides have dissolved inside all other carbide forming element occurring in the steel, and their proposed simplified denotations are aimed at shortening their symbols only. It turns out from the chemical composition investigations made using the X-ray microanalysis with the WDS spectrometer for the small carbides located in ferrite, that they have an average carbon atomic concentration of about 12.4%, that is close to the one occurring in the M_6C type carbides (about 14.3% at). The average composition of these carbides is given by the approximate formula $(Fe_{0.76}Mo_{0.12}W_{0.06}Cr_{0.04}V_{0.02})_6C_{1-x}$. Due to the small size of the carbides and the possible influence of the iron-rich matrix, activated by the electron beam, iron concentration in these carbides is likely to be overestimated.

In the soft annealed X40CrMoV5-1 steel, the matrix is ferrite with the alloy carbides (table 3) whose volume fraction in the structure is about 5%. The interstitial phases include the M_6C carbides with the crystallographic lattice parameter of about 1.103 nm, the MC type carbides, close to the VC ones with the crystallographic lattice parameter of about 0.416 nm, the $M_{23}C_6$ type carbides with the complex cubic crystallographic lattice (Fm3m space group) and lattice parameter of about 1.065 nm, and the M_7C_3 type carbides with the orthorhombic crystallographic lattice (Pmcm space group) and the approximate lattice parameters $a=0.702$ nm, $b=1.215$ nm and $c=0.453$ nm (lattice of this phase can also be described by the complex hexagonal one - P31c space group).

As a result of the investigation of the surface distribution of elements in the matrix and carbides undissolved during austenitizing supplemented by the quantitative analysis of the chemical composition of the matrix and particular types of carbides in solid specimens, it was found out that in the quenched 47CrMoWVTiCeZr16-26-8 steel the undissolved carbides can be

Table 1
Chemical composition of the investigated steels

Steel denotation	Mass concentration of elements, %											
	C	Mn	Si	Cr	W	Mo	V	Ti	Ce	Zr	P	S
47CrMoWVTiCeZr16-26-8	0.47	0.13	0.27	4.04	1.97	2.60	1.10	0.26	0.1	0.06	0.012	0.008
X40CrMoV5-1	0.41	0.44	1.09	5.40	0.01	1.41	0.95	–	–	–	0.015	0.010

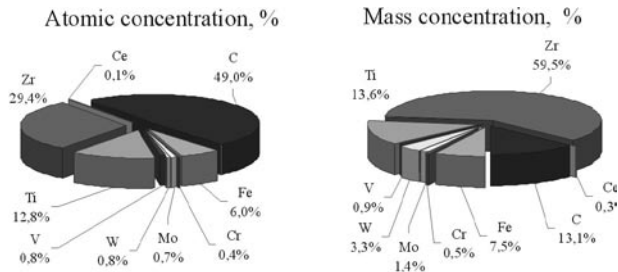


Fig. 1. The average chemical composition of ZrC carbides in the 47CrMoWVTiCeZr16-26-8 steel.

divided into three groups differing clearly with their chemical composition (table 2). These carbides are of the MC type - denoted in short as (Ti,V)C and ZrC - as well as of the M_2C_3 type (fig.1 and fig.2). The average chemical composition of the (Ti,V)C carbides may be used for the following denotation: $(Ti_{0.56}V_{0.14}Mo_{0.10}W_{0.09}Fe_{0.06}Zr_{0.03}Cr_{0.01})C_{1-x}$, where $x < 1$. These carbides are characterised by significant differences of their chemical composition. The maximum concentration of Ti was found, for instance, in the carbide denoted as: $(Ti_{0.70}V_{0.09}W_{0.08}Mo_{0.05}Zr_{0.04}Fe_{0.03}Cr_{0.01})C_{1-x}$, whereas the predomination of V over Ti was found out in the $(V_{0.34}Ti_{0.31}Mo_{0.17}W_{0.09}Fe_{0.06}W_{0.02}Zr_{0.02})C_{1-x}$ carbide. This last carbide may feature the representative of the VC type carbides that mostly get dissolved in the solid solution during austenitizing. From among the MC type carbides are also those few containing, except Ti, as the second main component not V but Zr instead, e.g., $(Ti_{0.44}Zr_{0.37}V_{0.06}Fe_{0.05}W_{0.04}Mo_{0.04}Cr_{0.01})C_{1-x}$. Carbides from the ZrC group with the prevailing fraction of Zr may be denoted as $(Zr_{0.58}Ti_{0.25}Fe_{0.12}W_{0.02}V_{0.02}Mo_{0.01}Cr_{0.01})C_{1-x}$, some carbides from this group with greater fraction of Fe than Ti were found also, e.g., $(Zr_{0.61}Fe_{0.22}Ti_{0.11}W_{0.03}V_{0.01}Cr_{0.01})C_{1-x}$. Carbides from the third group, whose main metallic component is Ce, may be denoted - basing on their average composition - as $(Ce_{0.49}Fe_{0.33}V_{0.07}Mo_{0.06}Cr_{0.04}W_{0.01})_2C_{3-x}$.

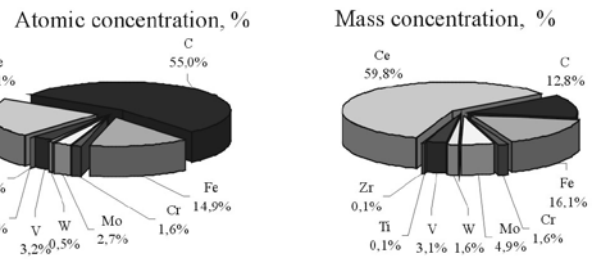


Fig. 2. The average chemical composition of M_2C_3 carbides in the 47CrMoWVTiCeZr16-26-8 steel.

In small carbides of the M_2C_3 type Fe predominates over Ce sometimes, e.g., $(Fe_{0.43}Ce_{0.39}V_{0.07}Mo_{0.05}Cr_{0.05}W_{0.01})_2C_{3-x}$, however, this may be connected with the iron-rich matrix influence on the microanalysis results. In the 47CrMoWVTiCeZr16-26-8 steel the MC type carbides undissolved during austenitizing have the average chemical composition, that may be described with the $(V_{0.76}Cr_{0.09}Fe_{0.08}Mo_{0.07})C_{1-x}$ formula (table 2). The C concentration in carbides of both investigated steels determined with the X-ray microanalysis using the WDS spectrometer is miscounted due to, e.g., contamination of the specimens' surfaces and is overestimated usually. The measurements carried out indicate that the average concentration of C in the MC type carbides is about 49% (from 41 to 60% at.), whereas, in the, M_2C_3 type carbides - it is about 55% (from 46 to 62% at.). Accounting for the possibility of overestimating the measurement results, and bearing in mind that the theoretical atomic concentration of C in the MC type carbides is equal to 50% at., and in the M_2C_3 type carbides it is 60% at., one may claim that these carbides in the investigated steels have the deficiency of carbon atoms in their positions in the crystalline lattice. Basing on the results of the X-ray qualitative phase analysis of carbides secluded from the matrix, and also basing on the investigations of the chemical composition of the solid specimens carried out in the X-ray micro-analyzer and also on the investigation of chemical composition of the selected micro-regions of thin foils from the investigated steels, one may assume that the M_6C , $M_{23}C_6$, and M_7C_3 type carbides, as the interstitial

Table 2 Results of the quantitative X-ray microanalysis of the carbides undissolved during austenitizing

Steel	Carbide type	Atomic concentration ^{*)} , %					minimum average maximum			
		Fe	Cr	Mo	W	V	Ti	Zr	Ce	
47CrMoWVTiCeZr16-26-8	(Ti,V)C	2.8	0.6	5.1	7.3	10.0	36.5	0.5	0.0	
		6.1	1.0	9.7	9.2	14.4	56.2	3.3	0.1	
		9.1	2.3	13.2	12.6	24.8	65.6	6.2	0.4	
	ZrC	4.1	0.3	0.0	0.5	0.4	11.6	37.9	0.1	
		11.8	0.8	1.3	1.6	1.6	25.0	57.6	0.2	
		35.1	2.4	4.0	3.7	4.9	34.2	74.3	0.4	
M_2C_3	25.3	1.0	4.4	0.6	1.0	0.0	0.0	40.6		
	33.1	3.6	5.9	1.0	7.0	0.2	0.1	49.1		
	39.8	5.7	7.7	2.1	10.1	1.4	1.0	61.0		
X40CrMoV5-1	VC	2.8	8.2	3.9	0.0	67.2	-	-	-	
		7.6	9.3	6.9	0.1	76.1	-	-	-	
		19.5	11.7	12.4	0.3	83.2	-	-	-	

^{*)} Atomic concentration of elements occupying metal atoms' positions in the carbide lattice. Remaining elements < 0.1 % at.

phases with the complex structures, demonstrate a stronger tendency to dissolving in the solid solution during austenitizing, than the MC type carbides with the simple structures having better stability. Multiple microanalyses of the chemical composition of the matrix turned out to be rather unreliable, mostly of the carbon concentration, whose result is overestimated. However, the average concentration of the metallic elements in the matrix is close to their concentration in the steel. This is caused most probably by the presence of carbides that, being close the microsection surface, have their input into the analysis result, raising the carbide-forming elements' concentration in the matrix. Taking this into account, it was decided to assume the minimum concentration values of these elements as the most reliable ones and close to the real chemical composition of the matrix. Concentrations of the alloying elements in the 47CrMoWVTiCeZr16-26-8 steel's matrix determined in this way are: 3.2% Cr, 2.3% Mo, 1.4% W, 0.9% V, and 0.01% Ti. These elements occur mostly in the M_6C and VC type carbides that mostly dissolve in the solid solution during austenitizing of the 47CrMoWVTiCeZr16-26-8 steel. In the X40CrMoV5-1 steel, the decreased concentration, compared to the average composition of the steel, have V and Mo only, bonded in the partially undissolved carbides of the MC type. Other alloying elements, forming mostly carbides of the $M_{23}C_6$, M_7C_3 , and M_6C types, pass into matrix during austenitizing.

On the basis of examination of thin foils in transmission electron microscope it was found that structure of examined the 47CrMoWVTiCeZr16-26-8 alloy hot-work tool steel and X40CrMoV5-1 as quenched are martensite, retained austenite as well as alloy carbides undissolved in solid solution during austenitizing. In 47CrMoWVTiCeZr16-26-8 steel the MC type carbides were identified by means of diffraction methods and M_6C , whereas in the X40CrMoV5-1 steel – only MC type carbides, which were isomorphous with VC. The carbides undissolved during austenitizing were also identified in structure of steel after tempering. The strip martensite is characterised by large density of dislocation as well as is partially twinned. In X40CrMoV5-1 steel, martensite is twinned in higher fraction than in 47CrMoWVTiCeZr16-26-8 steel. The structure examinations accomplished by means of electron microscopy methods show that in steel under examination as quenched and tempered at the temperature 450°C – separation of alloy cementite from martensite occurs, which fact contributes to reduction of steel hardness as compared with quenched condition. Starting from tempering temperature 480°C the coalescence occurs and dissolving the alloy cementite in solid solution as well as independent separation of M_7C_3 carbides starts in X40CrMoV5-1 steel as well as – above the temperature 510°C – also the M_4C_3 carbides in 47CrMoWVTiCeZr16-26-8 steel, causing the secondary hardness effect after tempering the 47CrMoWVTiCeZr16-26-8 steel in temperature 540°C, and X40CrMoV5-1 steel – at 510°C. The M_4C_3 type carbides are isomorphous with VC, and their determination proves also the presence of other carbide-creative elements as well as insufficiency of carbon atoms in crystal lattice.

The presence of MC (M_4C_3) type carbides in steels under discussion, thermally treated under conditions providing the maximum effect of secondary hardness, were also confirmed by examination of carbon extraction replica. In thin foils of the 47CrMoWVTiCeZr16-26-8 steel the retained austenite has been

identified after tempering at the temperature up to 510°C. In the X40CrMoV5-1 steel, during tempering at the temperature 540°C the M_4C_3 type dispersion carbides are separated, and their presence contributes to limitation of decrease of hardness of steel connected with decrease of carbon concentration as well as martensite matrix recovery.

4. Conclusions

The investigated steels after soft annealing the examined steels indicate the alloy-ferrite structure with the great number of the carbides of the type of M_6C and MC (nearing VC, (Ti,V)C and ZrC) as well as M_2C_3 (nearing Ce_2C_3) in the 47CrMoWVTiCeZr16-26-8 steel and with the carbides of the type of M_6C , MC, $M_{23}C_6$ as well as M_7C_3 in the X40CrMoV5-1 steel. The volume fraction of carbides in the 47CrMoWVTiCeZr16-26-8 steel amounts to 8.2% and is higher than in the X40CrMoV5-1 steel. After hardening from temperature of 970-1180°C the 47CrMoWVTiCeZr16-26-8 and X40CrMoV5-1 steels obtain the lath martensitic structure, partially twinned with a small fraction of retained austenite and the carbides partially undissolved in solid solution of the type of MC (TiC and ZrC) as well as M_2C_3 in the 47CrMoWVTiCeZr16-26-8 steel and of the type of MC (VC) in the X40CrMoV5-1 steel. The 47CrMoWVTiCeZr16-26-8 steel characterises itself by the greater fraction of carbides partially undissolved in solid solution during austenitizing as well as by the greater resistance to the grain growth of primary austenite than the X40CrMoV5-1 steel. Tempering the examined steels within the range of temperatures between 450-540°C results in starting the precipitation processes in martensite and the secondary hardness effect after tempering from temperature of 540°C in the 47CrMoWVTiCeZr16-26-8 steel and from temperature of 510°C for the X40CrMoV5-1 steel, which is caused by the carbides M_4C_3 and M_7C_3 in the 47CrMoWVTiCeZr16-26-8 steel and M_7C_3 in the X40CrMoV5-1 steel.

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