TOOL AND TUBE STEELS

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EFFECT OF SILICON AND GERMANIUM ON THE STRUCTURE AND PROPERTIES OF CAST HIGH-SPEED STEEL

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The effect of silicon and germanium additives on the structure and properties of cast cobalt tungsten-molybdenum high-speed steel of type R6M5K5 is studied. Results of metallographic and x-ray diffraction analyses of experimental steels after casting, annealing, quenching, and tempering are discussed. The interrelation of the structural parameters, the degree of contamination of the metal with nonmetallic inclusions, and mechanical parameters is determined with respect to the amount of additives of both elements.

INTRODUCTION

The interest in alloying of both conventional deformed steels and cast high-speed steels with elements less expensive and nontraditional for the given class of material has grown in the last decade. Specifically, this refers to the readily available and cheap silicon. Numerous publications have been devoted to investigation of the effect of this element in high-speed steels with various basic chemical compositions [1 – 20]. Analysis of the published data shows that the interest in silicon is primarily connected with introducing it into what are known as sparingly alloyed or low-alloy high-speed steels often bearing no tungsten [5, 7, 8, 10 – 15]. The use of silicon for modifying the structure and properties of widely used tungsten-molybdenum steels of type R6M5 [1 – 4, 6] and of high-speed steels containing 9 – 11% tungsten [9, 16, 18] has been reported. However, no information can be found in the literature on the mechanism of the effect of silicon in cobalt tungsten-molybdenum high-speed steels of type R6M5K5, despite the fact that cobalt-bearing steels form a quite representative group of tool materials [21]. In addition, no data can be found on the effect of a chemical counterpart of silicon, i.e., germanium, in high-speed steels [22].

In accordance with the estimation of the surface activity of various elements in molten iron performed with allowance for such criteria as the difference in the melting temperature, the surface energy, the specific heat of sublimation, the entropy in standard state, the statistical generalized moment, and the total potential barrier of the electrons of iron and of the additive, silicon[2] and germanium belong to surface-active elements [23, 24]. The activity series plotted using the results of analytical estimation of the additives in terms of the criteria mentioned [23] show that both elements possess a relatively low modifying potential as compared to other surface-active or inactive modifiers more promising as additives to cast high-speed steels than silicon and germanium [23 – 37]. However, the preliminary experiments performed in [23] have shown that the introduction of 0.2% silicon into cast tungsten-molybdenum steel is accompanied by growth in the wear resistance (steels R6M5 and R6M5K5) and in the temperature of the $\alpha \leftrightarrow \gamma$ transformation (steel R6M5). The latter circumstance is known [38] to be of principal importance from the standpoint of formation of heat resistance of tool steels.

The aim of the present work[3] consisted in studying the effect of silicon and germanium additives on the structure and properties of cast high-speed steel R6M5K5.

METHODS OF STUDY

The steels were melted in Alundum crucibles in an electric resistance furnace with graphite heaters. Deoxidation was performed by ferromanganese of grade FMn70 (GOST 4755–91) in an amount of 0.2% of the mass of the charge, by

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[2] In accordance with the entropy in the standard state, silicon belongs to inactive elements.

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ferrosilicon of grade FS75 (GOST 1415–93) in an amount of 0.2%, and by metallic aluminum of grade A7 in an amount of 0.1%. The metal was modified with silicon in the form of ferroalloy of grade FS75 and metallic germanium of grade GÉ (GOST 16153–80). The designed amounts of additives introduced into the melt of steel R6M5K5 were 0.4, 0.8, and 1.2% for silicon and 0.1, 0.3, and 0.6% for germanium. The additives were introduced into the melt after deoxidation with ferromanganese and ferrosilicon with a hold for full assimilation, after which the liquid metal was finally deoxidized with aluminum and then cast.

The temperature of the melt before casting was kept within 1480 – 1510°C and controlled by a W – Mo thermocouple. Liquid metal was poured into graphite molds heated to 300°C. The castings with a mass of 0.7 kg were used to prepare specimens for mechanical tests and metallographic and x-ray diffraction analysis.

The castings and the test specimens were subjected to isothermal annealing at 850°C with a hold of no less than 2 h, after which they were cooled to 720°C and held for 4 h. The cooling was performed in the furnace until 700°C and then in air. In order to prevent decarburization the castings were covered by iron chips. The final heat treatment included quenching from 1230°C and triple tempering at 560°C for 1 h. The heating for the quenching was performed in two stages, i.e., after heating in molten salt to 850°C the temperature of the specimens was raised to 1230°C in a bath of 95% $BaCl_2$ + 5% MgF_2 with a hold of 10 sec per 1 mm cross section. The quenching cooling was performed at 550°C in a mixture of 50% $CaCl_2$ + 50% NaCl and then in air.

The mechanical properties and the heat resistance were determined by methods standard for high-speed steel. We also used the generally accepted method of statistical processing of experimental results [39], which consisted in computing the estimates of the mean $\overline{Y}$ and the variance S^2 of the values of hardness and impact toughness. The mean $\overline{Y}$ of a sample of experimental data was estimated by the formula

$$\overline{Y} = \frac{\sum Y_i}{n}, \qquad (1)$$

where Y_i are the test (measurement) results and n is the number of tests (measurements).

The number of measurements n in the determination of the Rockwell and Brinell hardness was 40 and 10, respectively; the number of measurements in the determination of the impact toughness was 5. The obtained value of the Rockwell hardness was rounded to 0.5 *HRC*, that of the Brinell hardness was rounded to 5 *HB*, and that of the impact toughness was rounded to 0.01 MJ/m^2.

The variances for the 1st and 2nd samples were estimated by the formulas

$$S_1^2 = \frac{1}{n-1}\sum_{i=1}^{n}(Y_i - \overline{Y}_1)^2 \qquad (2)$$

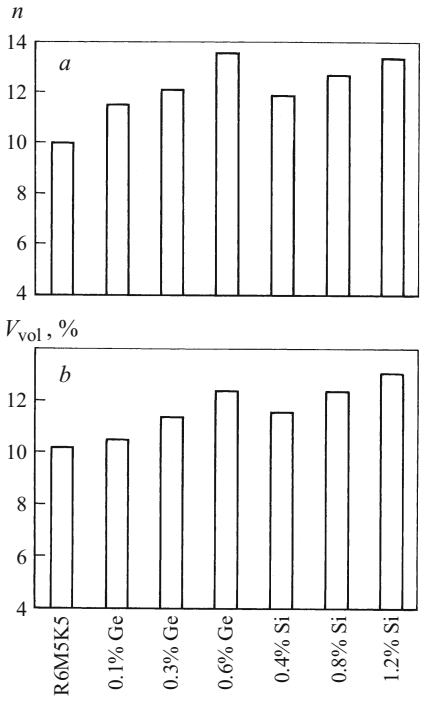

Fig. 1. Effect of silicon and germanium content on the size n of primary grains of metallic matrix (*a*) and on the volume fraction V_{vol} (*b*) of carbides in steel R6M5K5 (n is the number of grains in 1 mm of the chord).

for the first specimen (alloy) and

$$S_2^2 = \frac{1}{n-1}\sum_{i=1}^{n}(Y_i - \overline{Y}_2)^2 \qquad (3)$$

for the second specimen (alloy).

The significance or insignificance of changes in the properties was decided after checking the uniformity of the variances for the compared specimens of materials (S_1^2 and S_2^2) using Fisher's test (F-test) [39]. The F-criterion was determined in terms of the ratio of the higher variance to the lower variance, i.e., $F = S_1^2/S_2^2$ (where S_1^2 is the higher of the estimates of the variances in two samples) and compared with the tabulated (critical) value. The critical values of the F-criterion were determined for significance level $\alpha = 0.05$ and the number of degrees of freedom $f_1 = f_2 = n - 1$ (symmetric samples with the number of tests (measurements) n) [39].

The confidence intervals were computed using the formula

$$P\left\{\overline{Y} - t\frac{S}{\sqrt{n}} \le \eta \le \overline{Y} + t\frac{S}{\sqrt{n}}\right\} = 1 - \alpha. \qquad (4)$$

with probability P for significance level α.

The computation was performed at bilateral significance level $\alpha = 0.05$; the t-criterion was determined from a table [39] for the number of degrees of freedom $f = n - 1$.

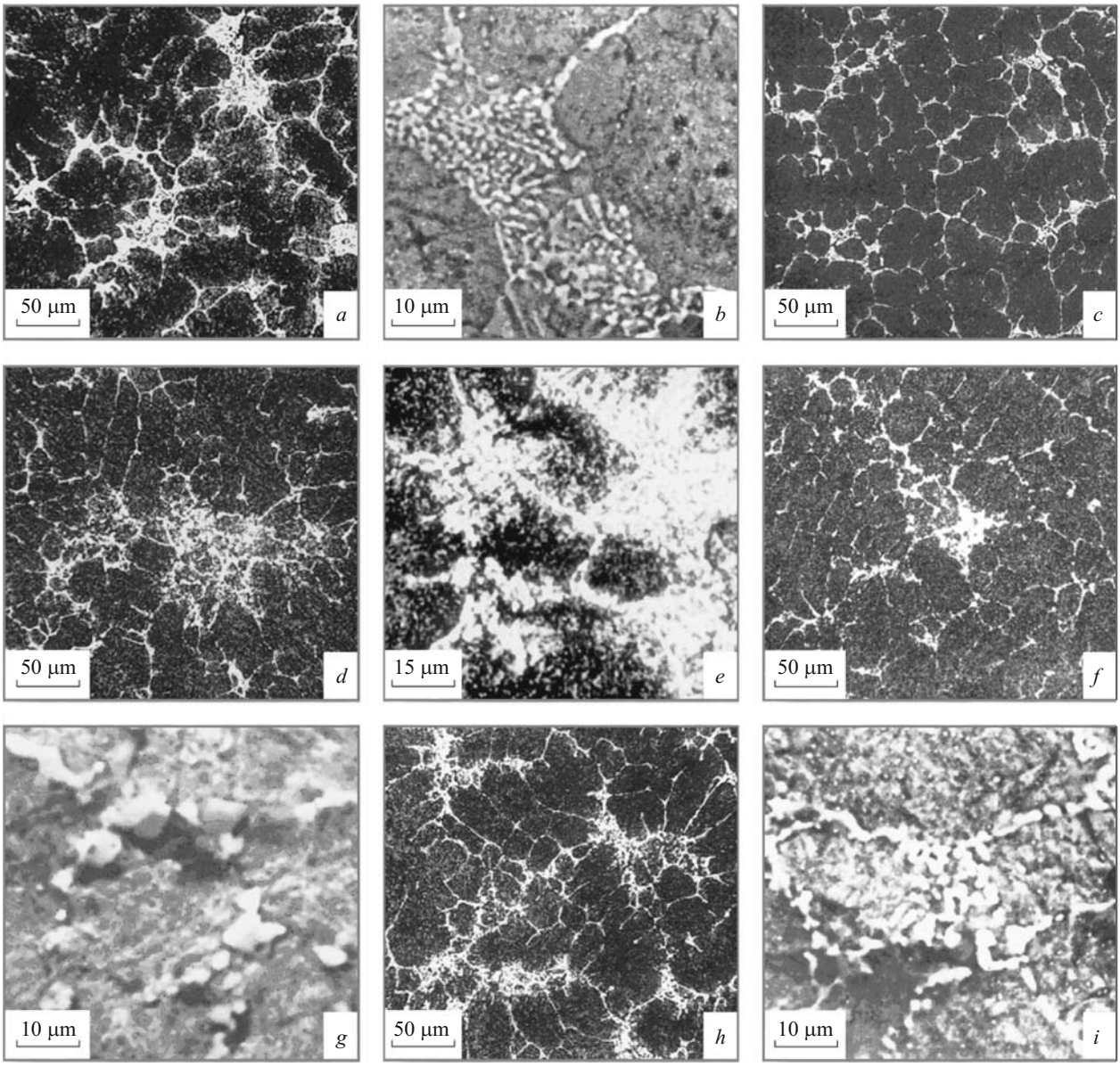

Fig. 2. Structure of steel R6M5K5 with additives of silicon and germanium after quenching and tempering: *a*, *b*) base steel (without additive); *c*) 0.4% Si; *d*, *e*) 1.2% Si; *f*, *g*) 0.1% Ge; *h*, *i*) 0.6% Ge; *a*, *c* – *f*, *h*) light microscope; *b*, *g*, *i*) scanning electron microscope.

The wear resistance was estimated in terms of the loss in the mass of the specimens per unit time as a result of attrition against a hard-alloy disc ($\varnothing = 55$ mm, $b = 2.5$ mm) under sliding friction without lubricant at load $P = 200$ N in a Skoda-Savin-type machine.

The microstructure was studied with the help of a "Neophot-2" light microscope and an EMAX-8000 scanning electron microscope ("Horiba"); the topography of the worn surfaces of special specimens 10 × 10 × 30 mm in size was studied using a light microscope at magnification × 60. The grain size of the metallic matrix and the volume fraction of carbides were determined by the method of random secants [40]. The x-ray diffraction analysis was performed using a DRON-3 diffractometer in cobalt K_α radiation at $U = 30$ kV and $I = 20$ mA. The content of retained austenite was determined by comparing the integral intensities of lines (110) of martensite and (111) of austenite.

RESULTS AND DISCUSSION

Upon the introduction of silicon and germanium the size of the primary grains of the metallic matrix formed due to primary crystallization of the melt decreased (Fig. 1*a*) and the volume fraction of the eutectic component increased (Fig. 1*b*) in accordance with the growth in the content of the additive. The structure of the steel with silicon and germanium additives after heat treatment is presented in Fig. 2. In the steels with silicon, just as in the base steel (Fig. 2*a*), the

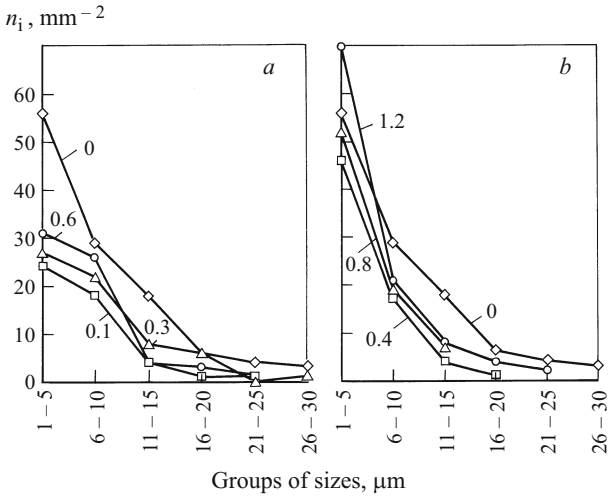

Fig. 3. Effect of additives of germanium (*a*) and silicon (*b*) on contamination of steel R6M5K5 with nonmetallic inclusions (n_i is the number of inclusions per 1 mm^2; the figures at the curves are the contents of modifiers in %).

formed primary grains are primarily of an equiaxial shape (Fig. 2*c* and *d*), whereas in the steel with germanium they are of a nonequiaxial shape (Fig. 2*d* and *h*). The length of the net of eutectic and secondary carbides increases upon growth in the degree of alloying of all the steels (see Fig. 2). After the introduction of 1.2% silicon (Fig. 2*d*) and of germanium in the whole of the studied range, i.e., starting with 0.1% (Fig. 2*f*) and ending with 0.6% (Fig. 2*h*), the structure of the metal bears regions of segregation accumulation of ledeburite. It should be noted that despite the general growth in the volume fraction of the carbide component (see Fig. 1*b*), the eutectic carbides in the structure of the steel with germanium become finer when the amount of this element increases (Fig. 2*g* and *i*).

Analysis of the effect of the added elements on the contamination of the metal shows (Fig. 3) that both silicon and germanium lower the amount of nonmetallic inclusions and their sizes; low additives of both elements are the most effective.

As the amount of the introduced additives is increased, the hardness of the steel in the cast and annealed states increases continuously. However, the nominal value of the hardness in the steels with silicon is higher and that in the steel with germanium is lower than in the metal of the base composition (Table 1). After quenching, a well manifested dependence of the hardness behavior on the content of retained austenite is absent. On the whole, the hardness is higher and the amount of retained austenite is lower in all the experimental steels as compared to the steel of the base composition (Table 1).

The mechanical properties of the studied steels after quenching and tempering are presented in Table 2. It can be seen that the steels with 0.4 and 0.8% silicon are superior and the steels with 1.2% silicon and any tested content of germanium are inferior to the base steel R6M5K5 with respect to the impact toughness. The most effective additive is 0.4% germanium; it promotes formation of a relatively thin and broken carbide net over grain boundaries of the metallic matrix without regions of segregation accumulation of ledeburite (see Fig. 2*c*). At the same time, the presence of regions with ledeburite accumulations in the structure of the steel with 1.2% silicon (see Fig. 2*d*) and in all the steels with germanium (see Fig. 2*f* and *h*) seems to be the main cause of their lower impact toughness as compared with the steel of the basic composition (Table 2). This assumption is confirmed first of all by the fact that reduced impact toughness is observed in the metal with 1.2 silicon, which possesses the

TABLE 1. Amount of Retained Austenite and Hardness of the Studied Steels

Additive, wt.%	A_{ret}, %	Hardness after		
		casting, *HRC*	annealing, *HB*	quenching, *HRC*
–	18	62.0	255	63.5
Silicon:				
0.4	8	60.0	250	64.5
0.8	13	62.0	265	64.0
1.2	15	63.0	270	64.0
Germanium:				
0.1	7	51.5	250	64.5
0.3	10	54.0	255	65.0
0.6	15	55.0	260	65.0

TABLE 2. Properties of the Steels after Complete Heat Treatment

Additive, wt.%	Impact toughness, MJ/m^2	Hardness, *HRC*	Heat resistance, *HRC*	Wear resistance (loss in the mass), mg/h
–	0.10 ± 0.009	65.5 / 65.0	61.0 / 59.5	67
Silicon:				
0.4	0.13 ± 0.010	65.0 / 65.5	58.5 / 59.5	59
0.8	0.11 ± 0.008	64.0 / 64.5	57.5 / 58.0	62
1.2	0.08 ± 0.009	63.0 / 64.0	56.0 / 56.5	70
Germanium:				
0.1	0.08 ± 0.010	66.5	59.0	64
0.3	0.08 ± 0.009	66.0	58.0	73
0.6	0.07 ± 0.008	66.0	58.0	80

Notes. 1. The numerators present the hardness after triple tempering (1 h) at 560°C; the denominators present the same at 540°C.
2. The heat resistance was determined from the results of hardness measurement after additional 4-h annealing at 620°C.

lowest hardness after complete heat treatment (Table 2) that could have been expected to promote growth in the ductility and hence in the impact toughness. However, the negative embrittling action of the ledeburite accumulations prevails in this steel too.

The metal with 0.4% silicon has the best wear resistance, but as the silicon content is increased, the hardness of the steel decreases (Table 2) and, as a consequence, so does the resistance to attrition. At 1.2% silicon in the composition the steel becomes inferior to the base variant with respect to this parameter. However, it should be noted that in contrast to the base steel R6M5K5, in which wear develops by two mechanisms (abrasive and adhesive) [this is confirmed by the characteristic microtexture of the worn surface (Fig. 4*a*)], the presence of silicon virtually prevents fracture wear during friction due to formation of strong passivating films on the rubbing surfaces [41] that do not break even under the most intense (within the conditions of the test) forms of abrasive wear thus preventing formation of large sources of seizure (Fig. 4*b*). With allowance for the fact that silicon, in accordance with the data of [42], increases the scale resistance of high-speed steels by 30% due to formation of scale of a Fe_2SiO_4 fayalite phase, the two circumstances can be decisive for choosing such an inexpensive alloying element as silicon for improving the structure and properties of cobalt high-speed steels.

In contrast to silicon, germanium does not affect substantially the wear resistance of the metal in the whole of the studied concentration range, though in the presence of 0.1% germanium the abrasion resistance somewhat increases. It is possible that this occurs primarily due to the presence of coarser eutectic carbides in the structure of this metal (see Fig. 2*f*). Upon growth in the germanium content the eutectic carbides formed in the structure become finer, which seems to be the cause of some worsening of the wear resistance (see Table 2). It is important that the wear of specimens with germanium, just as in the case of the base steel, occurs primarily by two mechanisms (abrasive and adhesive), which is reflected in the characteristic morphology of the surface of the worn specimens (Fig. 4*c*).

The hardness of the steels with germanium additives in the whole of the studied concentration range is somewhat higher than the hardness of steel R6M5K5 of the base composition. The picture differs upon the addition of silicon, which causes rectilinear decline of the hardness (see Table 2); the maximum decrease in the hardness (by 2.5 *HRC*) is observed in the steel with 1.2% silicon.

The effect of both elements on the heat resistance is even more substantial. In the presence of germanium, and especially of silicon, the heat resistance of steel R6M5K5 decreases markedly upon growth in the content of the introduced additives (see Table 2). Hypothetically, this is explainable to a certain measure by depletion of the tested solid solutions of carbon and alloying elements due to formation of a high amount of carbide phase in their structure as compared

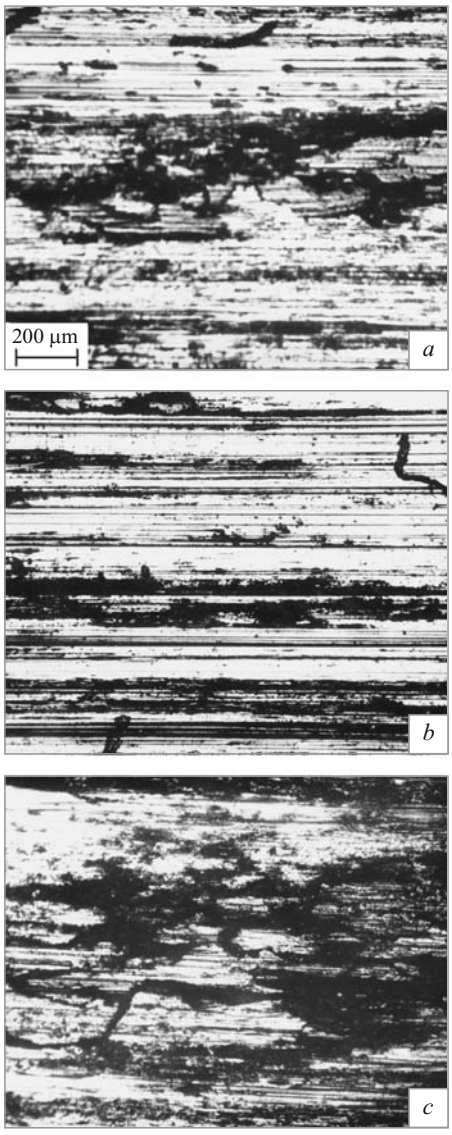

Fig. 4. Worn surfaces of specimens of the base steel R6M5K5 (*a*) and of the base steel with silicon (*b*) and germanium (*c*) additives.

to the base variant (see Fig. 1*b*). However, with allowance for the difference in the hardness behavior of the steels after complete heat treatment and for the mentioned growth in the temperature of the $\alpha \leftrightarrow \gamma$ transformation under the effect of silicon [23], it is more probable that the reason behind the decrease in the heat resistance is connected primarily with the change in the degree of stability of martensite and of the phases segregating in the stage of tempering in the process of secondary hardening under the action of both silicon and germanium. This assumption is confirmed by the results of [16] that show that high-speed steels with silicon have a critical tempering temperature below which this element causes, in particular, growth in the bending strength of the steel and above which the bending strength decreases. With allowance for this we varied the tempering temperature of the silicon-

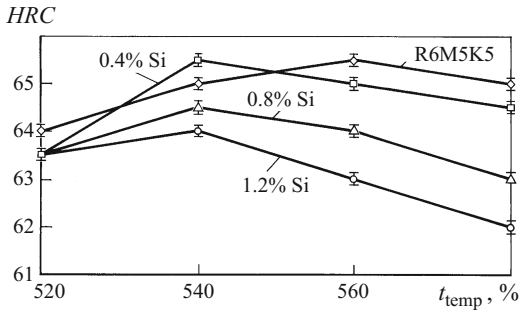

Fig. 5. Dependence of the hardness of the base steel R6M5K5 and of the base steel with silicon additives on the tempering temperature after hardening from 1230°C.

bearing steels quenched from 1230°C within 520 – 540 – 560 – 580°C.

The results obtained (Fig. 5) show that silicon in the high-speed steel with cobalt does shift the maximum of secondary hardening toward lower temperatures. However, even after tempering at 540°C the hardness and the heat resistance of the silicon-bearing steels remain lower than in the base steel R6M5K5 (see Table 2). Thus, the assumption that silicon and germanium weaken the stability of martensite and of the carbides segregated from it in the stage of tempering and responsible for secondary hardening and for the heat resistance of the metal finds confirmation.

CONCLUSIONS

1. An interrelation has been established between the variation of the parameters of structure and the mechanical properties in cobalt tungsten-molybdenum high-speed steel R6M5K5 under the effect of silicon and germanium introduced into the melt of the base steel in an amount of 0.4 – 0.8 – 1.2 and 0.1 – 0.3 – 0.6 wt.%, respectively. Growth in the content of these elements is accompanied by refinement of the structure of the metallic matrix and by growth in the volume fraction of excess phases, which intensifies the structural heterogeneity of the steels. The best combination of the modifying and refining actions with well manifested effect of refinement of the carbide component is ensured by silicon additive in an amount of 0.4%. As a consequence, the impact toughness increases to 0.13 MJ/m^2 against 0.10 MJ/m^2 in the base steel R6M5K5.

2. Silicon promotes formation of strong passivating films on rubbing surfaces, which do not fracture under abrasion and thus prevent formation of seizure sources and limit the development of adhesive wear. From the standpoint of growth in the wear resistance of the steel, an optimum additive is also 0.4% silicon.

3. Germanium additives do not affect substantially the hardness of the steel after quenching and tempering, whereas the addition of silicon causes its substantial decrease due to the shift of the maximum of secondary hardening toward lower temperatures. The main reason behind the worsening of the heat resistance of the tested steels seems to be the low resistance to softening of both martensite and the carbide phases segregated from supersaturated solid solution in the process of tempering of the steel.

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