STRENGTH AND PLASTICITY

Effect of Alloying Elements on the Composition of Carbide Phases and Mechanical Properties of the Matrix of High-Carbon Chromium–Vanadium Steel

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Abstract—Based on the results of phase physicochemical analysis of high-carbon chromium–vanadium steel, the predominant type of carbide that provides high wear resistance has been established, and its amount and amount of carbon in martensite have been determined. Data on the composition and the amount of carbide phase and on the chemical composition of the martensite of high-carbon steel have been obtained, which allows determination of the alloying-element concentration limits. The mechanical testing of heats of a chosen chemical composition has been carried out after quenching and low-temperature tempering. The tests have demonstrated benefits of new steel in wear resistance and bending strength with the fatigue strength being retained, compared to steels subjected to cementation. The mechanism of secondary strengthening of the steel upon high-temperature tempering has been revealed. High-temperature tempering can be applied to articles that are required to possess both high wear resistance and heat resistance.

Keywords: phase physicochemical analysis, chemical composition, high-carbon steel, wear resistance, martensite, strengthening, heat resistance

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INTRODUCTION

The systematic investigation of materials for aircraft began in the late 1930s as a new step of aviation development brought about by the invention of jet engines. The strategic mission of modern progressive engineering and technological thought is to create revolutionary new materials for aircraft. These materials should be superlight to provide weight efficiency of constructions and highly heat-resistant to enhance the operational life of an engine under severe thermal operating conditions [1-7].

High requirements are also imposed on special steels that are used as materials for aircraft devices and modules, in particular for gearwheels. The gearwheels for units of an aircraft are produced from medium-alloyed steels that can be subjected to cementation and nitrogen cementation. The necessary properties of these steels, i.e., wear resistance, fatigue strength, and contact strength, are provided by combining an extremely hard surface layer ($\geq 60 \ HRC$), in which compression stresses are created in the course of chemical and heat treatment, and a soft core (30–40 $\ HRC$). It is

worth noting that the process of chemical and heat treatment is laborious and multistage [8].

Steels containing nitrogen are not employed in production of gearwheels [9, 10]. The development of modules of a new aircraft apparatuses requires the creation of a new steel for gearwheels, which would possess twofold wear resistance than carbonized steels. In order to achieve this goal, the idea has emerged to create a monolithic high-alloy high-carbon steel that, in contrast to similar steels that have been designed as tool steels, would be structural steel. Therefore, it should possess a specific set of properties, such as hardness, fatigue strength, bending strength, and impact toughness, which can be achieved by combination of a certain amount of carbides and of carbon content in the martensite matrix. Works [11-17] are devoted to developing monolithic material for gearwheels of aircraft modules in order to replace currently applied materials obtained via chemical-thermal treatment.

The task of this work was to choose the composition and amount of the carbide phase and the content of carbon in martensite that will provide the required level of mechanical properties. The main difficulty is that the steel has to be used that was subjected to lowtemperature tempering. Taking this into account, the

[†] Deceased.

Heat	Content of alloying elements, wt $\%$			
	С	Cr	V	
1	1.40	5.9	5.4	
2	1.70	5.9	6.0	
3	2.00	5.9	6.2	
4	1.40	5.6	2.7	
5	1.67	9.4	6.0	
6	1.90	7.8	9.2	

 Table 1. Chemical composition of the heats

ratio of the alloying elements has to ensure a moderate amount of the retained austenite after tempering. The influence of the retained austenite on the structure of the alloyed steels is described in [18, 19].

EXPERIMENTAL

Six experimental laboratory heats have been studied; their chemical compositions are listed in Table 1. Ingots were prepared in open induction furnaces with the subsequent electroslag remelting. Billets that were forged to rods were subjected to step annealing. Then, samples for the investigation and mechanical testing of wear resistance, static bending, and fatigue strength were prepared.

The method of the phase physicochemical analysis of steels is described in detail in [20]. The electrolytes employed for the differential phase analysis were as follows: No. 1 contained 10% HCl and 3% citric acid in alcohol; and No. 2, 7.5% KCl and 0.5% citric acid in water.

The wear resistance was tested by the method (developed at the All-Russia Scientific Research Institute of Aviation Materials) MM 1995-5-314-2007 "Comparative Estimate of the Tribotechnical Characteristics of Steels and Alloys in Different Structural Phase States" using an I-47 friction machine. For testing there were used annular samples with the following dimensions: $\emptyset_{\text{ext}} = 28 \text{ mm}$, $\emptyset_{\text{int}} = 20 \text{ mm}$, and h = 10 mm.

The tests for static bending were carried out using a Zwick/Roel Z 100 machine according to the Russian GOST State Standard 14019-80. The testing samples were plates with dimensions of $2.5 \times 12 \times 100$ mm. The fatigue strength was determined according to the GOST 25.502-79 using an MVI611M machine on conical samples with \emptyset 14.0–7.5 mm and L = 110 mm.

RESULTS AND DISCUSSION

Choice of carbon content in martensite. Based on the results of [20], the *M*C carbide based on VC has been chosen as the main carbide of the steel. Particles of the eutectic and secondary carbide have sizes of $8-10 \mu m$ and less than 5 μm , respectively. They are uniformly distributed over the martensite matrix (Fig. 1).

The carbon content in the martensite is highly important for the mechanical properties of the steel. Since the hardness is mainly provided by a large amount of carbides, the martensite has to be low- or medium-carbon (0.25-0.35 wt %).

In order to choose the content of carbon in martensite, the phase composition and hardness of three heats with a constant chromium content (5.9 wt %) and different vanadium contents in the range of 5.4-6.2 wt % and carbon contents 1.40-2.00 wt % have been analyzed (Table 1, heats 1, 2, and 3,). The results of the investigation have demonstrated that, with increasing carbon concentration in the steel, the content of vanadium carbide increases from 6.3-7.4 wt % (Fig. 2). After quenching, the carbon content in martensite increases from 0.23 to 0.53 wt %, while the hardness increases from 60 to 61 *HRC* (Fig. 3). Then, *M*C carbide is alloyed with chromium in the amount of only





Fig. 1. Microstructure of steels of heats with (a) vanadium carbide $[\alpha + MC]$ and (b) with a greater amount of chromium carbide than that of vanadium $[\alpha + MC + M_7C_3]$.





Fig. 2. Effect of carbon content in Kh6F6 steel on the amount of vanadium carbide content (after quenching and tempering at 250° C).

0.75-1.0 wt %, its major part is in the solid solution, i.e., 5.00-5.15 wt %.

To ensure low and medium carbon contents in the martensite, the steel should be alloyed with 5.5-6.0% vanadium and 1.4-1.7% carbon. The upper limit of the carbon concentration of 2% is unacceptable both for technological reasons and in view of the negative influence on the properties.

Choice of the ratio between chromium and the vana**dium content.** The case of a chromium content in the steel higher than that of vanadium has been studied, i.e., heat 4 (Table 1). This experiment has been implemented taking into account that, the chromium carbide is necessary to enhance the carbide amount and the vanadium carbide, wear resistance. The choice of an optimal upper chromium content has to be made taking into account its positive effect on the wear resistance, the negative effect on the structural homogeneity, and the effect on heating technology for quenching. The latter is caused by the fact that the lower temperature of the chromium-carbide dissolution narrows the range of heating temperatures used for quenching for maximum hardness. This is also proved by the data shown in Fig. 4. In heat 4 (Table 1), with a chromium content higher than that of vanadium (5.6 wt % Cr and 2.7 wt % V), upon increasing the quenching temperature to higher than 1000°C, the dissolution of the



Fig. 3. Effect of carbon content in Kh6F6 steel on carbon concentration in solid solution and on hardness (after quenching and tempering at 250° C).



Fig. 4. Dependence of the hardness of steel and the amount of carbide for heats 1 and 4 on temperature of heating for quenching (tempering at 180° C).

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Heat	Quenching temperature, °C	VC, wt %	Content of elements in martensite, wt %			
			V	Cr	Мо	C (calculated)
1	1100	7.0	0.45	5.00	0.45	0.23
2	1150	6.7	0.95	5.15	0.65	0.32
3	1150	7.4	0.75	4.90	0.60	0.53
5	1150	8.4	0.45	8.00	0.50	0.20

 Table 2. Content of alloying elements in the martensite after heating for quenching

Table 3. Mechanical properties of high-carbon Kh6F6 steel and VKS-5 (16Kh3MVF) carbonized steel

Heat	Carbide phase		σ. MPa	Degree of wear 10^{-9}
	carbide type	amount, wt %	Ubend, WII a	Degree of wear, 10
2	VC	6.7	2380	6.55
4	$VC + Cr_{23}C_6$	12.2	—	-
VKS-5	Fe ₃ C	15–17 (in the surface layer	1800	13.5

chromium carbide occurs, along with an increase in the degree of austenite alloying and, therefore, a decrease in the temperature of the finish of the martensite transformation. After quenching, since the content of austenite in the matrix is high (up to 70%), the hardness of the steel decreases lower than the required values, i.e., to 52 *HRC*. Thus, since the steel should be used after low-temperature tempering at $180-250^{\circ}$ C, after quenching, it should contain less than 10-15% retained austenite. Taking this into account, the chromium content in the steel should not be greater than that of vanadium.

In heat 3 (Table 1), which is characterized by approximately the same contents of both elements, vanadium has a higher carbide-forming ability, and the *M*C carbide based on VC is formed, which has low solubility even at elevated temperatures, thus ensuring high values of hardness after quenching. The dependence of the hardness on the quenching temperature becomes less pronounced upon heating to 1200° C. Therefore, the heating for quenching for optimal hardness is performed in a wide temperature range.

The choice of the main type of the carbide, i.e., the MC carbide based on VC_{0.88}, particles of which are uniformly distributed over the martensite, ensures low index of carbide heterogeneity. Mechanical properties of the Kh6F6 steel are determined by the parameters of the phase composition, i.e., by the amount of the carbide phase and by the martensite composition.

Because of the formation of a large amount of carbides, the chemical composition of the martensite differs substantially from the initial chemical composition of the steel (Table 2). To provide the required level of hardness higher than 60 *HRC* after tempering at $180-250^{\circ}$ C, the Kh6F6 steel should have the following chemical composition: 1.4-1.9 wt % carbon, 5.46.2 wt % vanadium, 5.4–5.9 wt % chromium, and 0.9-1.0 wt % molybdenum.

This chemical composition ensures that, after quenching from 1150° C into icy water, there will be 8– 10 wt % carbide VC and 10–15% retained austenite. After binding the alloying elements into carbides, the depleted matrix, namely, austenite before quenching or martensite after quenching, has the following chemical composition: 0.23–0.53 wt % carbon, 4.9– 8.0 wt % chromium, 0.45–0.95 wt % vanadium, and 0.45–0.65 wt % molybdenum (Table. 2). Note that, due to the increased carbon content in the steel itself and in the martensite after quenching, the chemical composition of the steel of heat 3 does not meet the specified requirements.

The vanadium content of 0.45-0.95 wt % in the martensite of the steels of the studied compositions enhances the strength upon static bending by 30% compared to carbonized steels subjected to cementation with the same carbon content in the martensite (Table 3). Despite the fact that there are no compressive stresses in the surface layer, the values of the fatigue strength are close to the minimum level that is characteristic of carbonized steels (Table 3).

The replacement of the type of the carbide (cementite in the steels saturated with carbon) for the VC carbide resulted in a twofold wear resistance compared to 16Kh3MVF (VKS-5) steel with an even smaller amount of carbides (Table 3). The presence in the martensite of up to 8.00 wt % chromium, 0.65 wt % molybdenum, and 0.75 wt % vanadium allows one to classify Kh6F6 steel as a heat-resistant steel. Therefore, it was of interest to determine the mechanism of the steel strengthening upon high-temperature tempering. Three experimental heats, namely, 2, 3, and 6 have been studied. The temperature of heating for quench-

Heat	Carbide type	Carbide amount, wt %	Hardness, HRC		
			after heating for quenching	after tempering	
2	M_3 C + M_7 C ₃	5.8	62	63	
3	M_3C	7.6	62	65	
6	M_7C_3	1.45	62	62	

Table 4. Phase composition and hardness of heats of the Kh6F6 steel after triple high-temperature tempering

ing was 1150°C; triple tempering has been performed at 530° C for 1 h.

After quenching, the steels contain 8-10 wt % vanadium carbide, which has the following chemical composition: (V₇₅₋₇₉, Cr₁₁₋₁₄, Fe₇₋₉, Mo₂₋₃)C_{0.88}. The chemical composition of the anode sediments separated after tempering from the heats changed compared to the as-quenched state, namely, the vanadium and molybdenum content changed negligibly, whereas the iron and chromium content increased by a factor of 1.5–3.

According to XRD data on the anode sediment of heat 6, the phase precipitated from the martensite is a chromium-based carbide M_7C_3 . To determine the carbide content and ensure the correctness of the calculated data (calculation of the difference in concentration after the heating for quenching, and after the triple tempering according to PPCA data), a physicochemical analysis of the differential phase has been carried out. Based on an analysis of the data, the carbide content precipitated upon high-temperature tempering is 1.5 wt %; the chemical composition is (Cr₅₆Fe₃₇V₄Mo₃)₇C₆.

For the most complete precipitation of cementite alloyed with chromium and vanadium, which can be only partially passivated in electrolyte 1, the differential analysis was repeated using electrolyte 2, which is specially applied for the passivation of carbides of the cementite type. The XRD analysis showed the presence of cementite. The type, amount, and chemical composition of carbides precipitated from the martensite upon triple high-temperature tempering are listed in Table 4. The carbide precipitation upon tempering results in the decomposition of the retained austenite; its content in the heats is no more than 5%.

The precipitation of the disperse particles of alloyed cementite and chromium carbide upon high-temperature tempering favors an increase in hardness to 63–65 *HRC*, which can positively affect the wear resistance. Thus, after high-temperature tempering, Kh6F6 steel can be employed as heat- and wear-resistant material.

CONCLUSIONS

(1) Based on the results of the phase physicochemical analysis, data on the composition and amount of the carbide phase and chemical composition of the martensite of the high-carbon Kh6F6 steel have been obtained, which allowed determination of the alloy-ing-element concetration limits for the steel. To obtain the hardness level greater than 60 *HRC* after tempering at $180-250^{\circ}$ C, the alloying limits of the steel have to be as follows: 1.4–1.9 wt % carbon, 5.4–6.2 wt % vanadium, 5.4–5.9 wt % chromium, and 0.9–1.0 wt % molybdenum.

(2) The application of steel subjected to low-temperature tempering requires that after heating for quenching the content of the retained austenite be no more than 10-15%. Due to this fact, the chromium content should not exceed the vanadium content.

(3) The mechanical tests carried out have demonstrated advantages of the new steel over carbonized steels in wear resistance and bending strength with the fatigue strength retained.

(4) The mechanism of the secondary strengthening of the steel upon high-temperature tempering has been determined to be due to the additional precipitation of M_3C and MC_3 carbides. The application of high-temperature tempering is justified for articles that are required to possess both high wear and heat resistance.

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