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STRUCTURE AND PROPERTIES OF WEAR-RESISTANT MATERIALS BASED ON Co–Mo–Cr–Si–B ALLOYING SYSTEM

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The aim of the work was to study the structure and properties of Co–Mo–Cr–Si–B alloying system for the case of its application as a wear-resistant material for hardening the contact surfaces of blades of ship gas turbine engines. The studies were performed with application of the methods of high-temperature differential thermal analysis, electron microscopy, X-Ray micro and X-Ray structural analyses. Hardness and microhardness of phase components were measured, adhesion activity of experimental alloys was investigated using the sessile drop method. It is shown that experimental compositions have a balanced structure based on solid solution of cobalt alloyed with molybdenum and chromium, with hardening by complex silicides, borides and carbides, have acceptable mechanical properties and melting temperature below the temperature of irreversible softening of high-temperature nickel alloys, and are characterized by high adhesive activity, which creates favourable prerequisites for their use in ship gas turbine construction. 10 Ref., 1 Table, 4 Figures.

Keywords: *high-temperature nickel alloys, wear-resistant materials, structure phase composition, hardness, melting temperature, adhesive activity*

An important problem in marine engineering is the need to increase the effectiveness, reliability and service life of gas turbine engines. These parameters are primarily determined by the intensity of wearing of contact surfaces of blades, which are in the most severe operating conditions. In this connection, the materials and technologies of hardening the contact surfaces require development of new advanced solutions.

At present, there exists a rather wide selection of wear-resistant materials, which can be deposited on the contact surfaces with melting or without melting of the base material [1]. In this case, the decisive criteria of adaptability-to-fabrication of wear-resistant materials are their melting temperature and possible methods of deposition. Under the conditions of specific production, the above criteria can have mutually exclusive action that essentially complicates selection of optimum compositions and technologies [2].

In ship gas turbine construction high-temperature nickel alloys of ChS88U-VI, ChS70U-VI and other types are used for manufacturing the turbine blades. These alloys are hardened by disperse precipitates of γ'-phase $Ni_3(Al, Ti)$ which is prone to coagulation during contact interaction at high temperatures that creates favourable conditions for increase of wearing intensity, also due to intensification of the processes of oxidation of the surface layer, which is depleted in alloying elements.

These alloys are practically unweldable by the traditional methods of fusion welding, so that their heating temperature should not exceed 1210–1220 °C at deposition of wear-resistant material. Otherwise, an irreversible lowering of base metal strength is observed, caused by degradation of γ'-phase and cracking in the deposition area [1]. In this connection, the alloy which hardens the contact surface, at deposition in the liquid state should have the melting temperature not higher than 1210–1220 °C. At higher intrinsic melting temperature it can be joined to the base, for instance, by brazing. However, the turbine blade design does not always allow application of this effective method.

Thus, it is convenient to classify wear-resistant materials for ship gas turbines into two groups by their melting temperature: below and above 1210–1220 °C.

An extremely complicated problem is development of alloys, which belong to the first group, have the required level of wear resistance at working temperatures (up to 900 °C) and can stand short-term thermal loads at up to 1150 °C temperature «pulses» that is close to the conditions of γ'-phase dissolution in the base metal.

The known alloys of the first group include, for instance, KBNKhL-2 composition, which has the melting temperature at the level of 1070–1090 °C that does not allow the alloy to stand short-term heating up to temperatures of 1150 °C [3].

All the other known nickel- and cobalt-based alloys can be included into the second group, for instance VZhL-2, VKNA-2M [4], V3K-r [5], Stellite 12

[6], Kh30N50Yu5T2 [7], Kh25N10V8 [4], KhTN-61 [8], KhTN-62 [9], Tribaloy T-800, T 400, T 401 alloys [10], etc. The above-listed alloys have melting temperature above 1220 °C which makes their application extremely difficult at deposition on contact surfaces of blades of ship gas turbine engines by surfacing.

The main technological process, which is used for deposition of wear-resistant materials in enterprises of SC GTRPC «Zorya»–«Mashproekt», is the method of oxy-acetylene flame spraying without base metal melting. Additional fluxing of the surface by PV-200 flux is used, in order to increase the adhesive activity of the process. The surfacing process is accompanied by an insignificant dissolution of base metal to the depth of up to 0.1 mm that guarantees formation of a common transition zone, which is responsible for the bond strength. Thus, physicochemical and metallurgical processes, which run during the surfacing process, have a lot of common features with that of brazing. In this case, adhesion activity of surfacing materials is extremely important.

In this connection, the objective of our work was development of a high-temperature material with the required level of wear resistance at working temperatures (up to 900 °C), with melting temperature below 1210–1220 °C, which would have satisfactory adhesion activity for ship high-temperature nickel alloys and could stand the temperature and dynamic conditions of their operation, that is an urgent problem.

The National University of Shipbuilding together with SC GTRPC «Zorya»–«Mashproekt» developed promising wear-resistant high-temperature materials KMKh and KMKhS which satisfy the above requirements [2].

KMKh and KMKhS alloys were developed on the base of Co–Mo–Cr–Si classical system with additional alloying by boron and chromium carbide [2]. Alloy matrix is a solid solution of cobalt (β-modification) alloyed by molybdenum and chromium, which readily withstands contact and thermal loads up to temperatures of 1000 °C, inclusive. Simultaneous addition of silicon and boron allows at the melting stage lowering the alloy temperature to the required level and at the same time significantly increasing their adhesion activity. After melt solidification, boron and silicon actively form a uniformly distributed, thermodynamically stable highly-dispersed hardening phase, which consists of complex silicides and borides (CoB, Mo_2B, MoSi, CoSi) that imparts the required wear resistance level to the alloys. X-Ray structural analysis was performed in DRON-3 diffractometer. Additional presence of chromium carbide (Cr_2C_6) in KMKhS alloy somewhat lowers its melting temperature compared to KMKh alloy and stabilizes its structure and properties.

Test alloys were produced by induction melting in vacuum of the order of 10^{-2} Pa with subsequent annealing at the temperature of 1100 °C for 1 h. The characteristic electronic structure of the alloys is shown in Figure 1. Both the alloys demonstrate the regular two-phase structure, the density and uniformity of which increases at transition from KMKh alloy to KMKhS alloy. The hardness of KMKh alloy is equal to approximately $HV10$ – 710–715, that of alloy KMKhS is $HV10$ – 735–740. Average microhardness $H\mu_{50}$ of phase components of alloy KMKh is equal to 4771 MPa (Figure 1, region 1) and 2365 MPa (region 2), and for alloy KMKhS it is 661 MPa (region 3) and 3213 MPa (region 4), respectively.

Distribution of concentrations of alloying elements in phase components of test alloys was determined using scanning electron microscope-microanalyzer REMMA 102-02. The results are given in the Table. Analysis of obtained results of distribution of alloying elements in phase compositions showed that the base of cobalt-based alloys, up to 67 wt.% for KMKh alloy and 59 wt.% for KMKhS alloy, additionally contains from 4 up to 11 % molybdenum and from 25 up to 26 % chromium, with slight alloying with silicon of up to 2.5 wt.%. The hardening phase, contrarily, simultaneously with lowering of base level of cobalt alloying to 50 wt.% and of chromium, to 16 wt.%, also contains an increased concentration of molybdenum, up to 33 wt.% and of silicon, up to 9 wt.%, that pro-

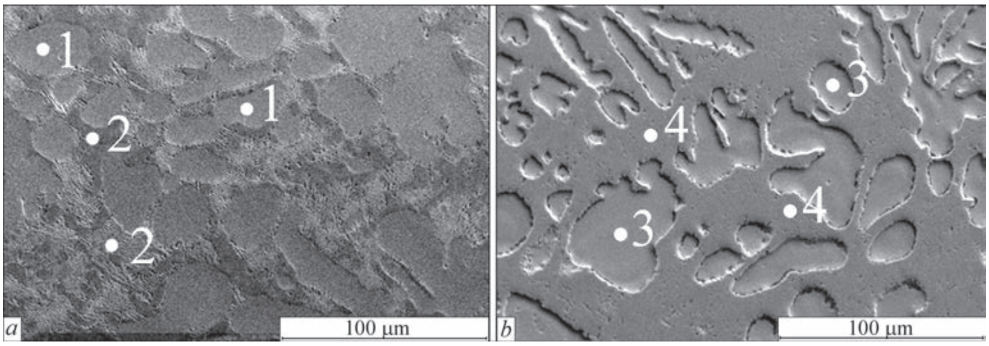

Figure 1. Electronic structure of KMKh (*a*) and KMKhS (*b*) alloys (for description of 1–4 see the text)

Alloying element concentration in phase components of test alloys in keeping with Figure 1

Region number	Alloying element				
	Co	Mo	Cr	Si	Ni
1	50.78–46.03 47.62 (48.41)	33.60–26.37 31.3 (29.99)	16.60–12.25 13.83 (14.43)	7.75–6.25 7.24 (7.0)	–
2	68.25–63.73 67.01 (65.99)	8.37–4.55 5.49 (6.46)	26.11–24.98 25.69 (25.55)	2.11–1.52 1.81 (1.82)	–
3	46.06–45.33 45.78 (45.70)	32.23–29.79 30.70 (31.01)	14.01–12.22 13.24 (13.12)	8.78–8.55 8.70 (8.67)	1.81–1.45 1.58 (1.63)
4	59.06–56.41 57.7 (57.74)	9.15–11.96 10.61 (10.56)	26.38–25.67 26.18 (26.03)	2.98–2.64 2.81 (2.81)	3.06–2.35 2.71 (2.71)

Note. Numerator — max and min value, wt.%, denominator mean value, wt.% (at.%).

motes formation of complex-alloyed hardening phase (CoB, Mo_2B, MoSi, CoSi). The base of the alloys and hardening phases contain the same chemical elements as those in the alloy composition, in different proportions, that ensures their good structural compatibility and smooth change of physical properties at transition through the interphase. Boron and carbon concentration was not determined in the work, in connection with limited capabilities of the used equipment.

Alloy melting temperature was determined by the method of high-temperature differential thermal analysis. Characteristic thermograms of melting and crystallization of alloys KMKh and KMKhS are given in Figure 2. Data of thermal analysis (DSC) are indicative of the fact that at preservation of an optimum ratio of silicon and boron in the alloys, KMKh and KMKhS alloys have only one thermal effect in the heating and cooling curves. The above effect determines the solidus temperature for KMKh alloy on the level of 1185–1190 and 1165–1170 °C for KMKhS alloy. At deviation from the recommended ratio, the stability of phase composition is disturbed, and there is the possibility of phase reaction running with formation of nonequilibrium phases. It results in appearance of additional effects on the thermal curves that leads to increase or lowering of the alloy melting temperature and formation of a wider interval of crystallization that is undesirable.

Adhesion activity of KMKh and KMKhS alloys was studied by the sessile drop method at melting in

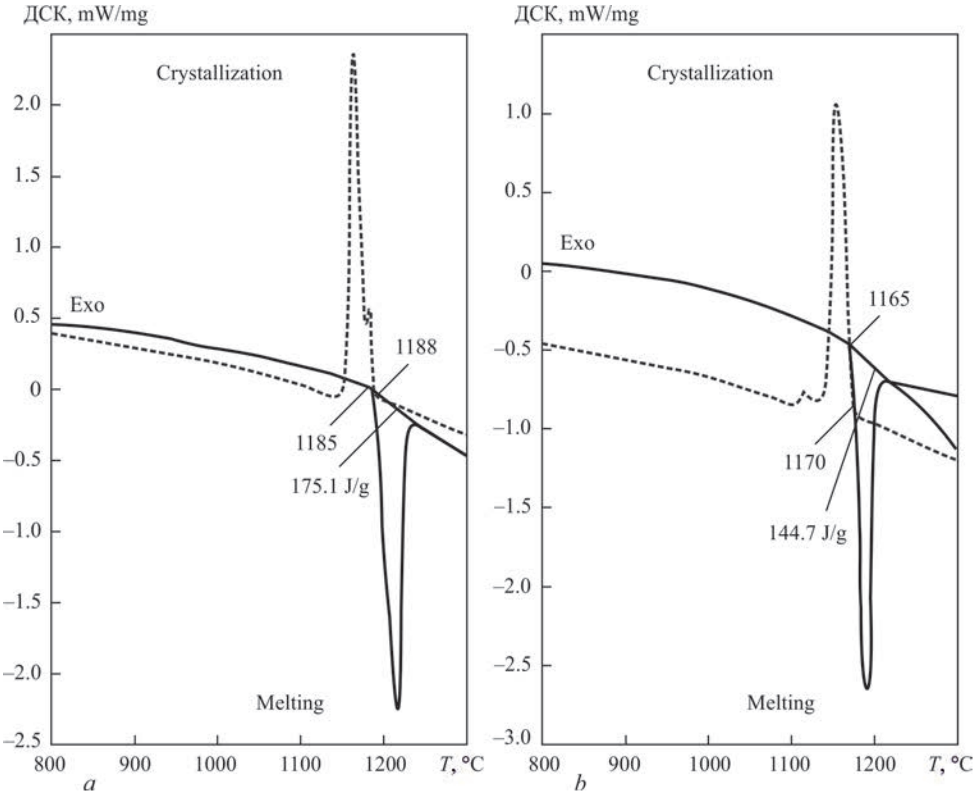

Figure 2. Differential scanning calorimetry of samples of KMKh (*a*) and KMKhS (*b*) alloys

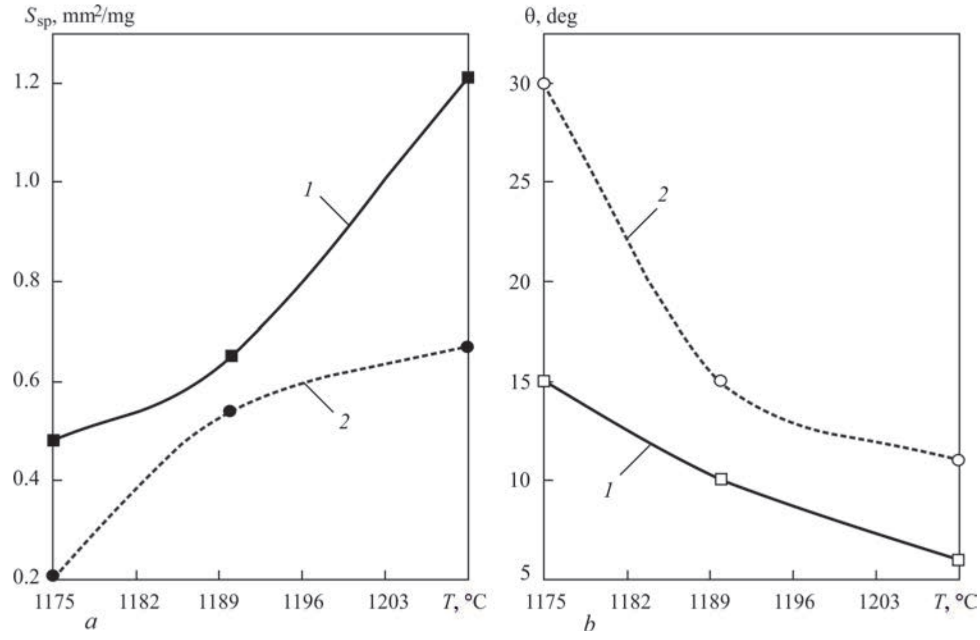

Figure 3. Dependence of specific spreading area S_{sp} (*a*) and wetting angles θ (*b*) of KMKhS (*1*) and KMKh (*2*) alloys on temperature

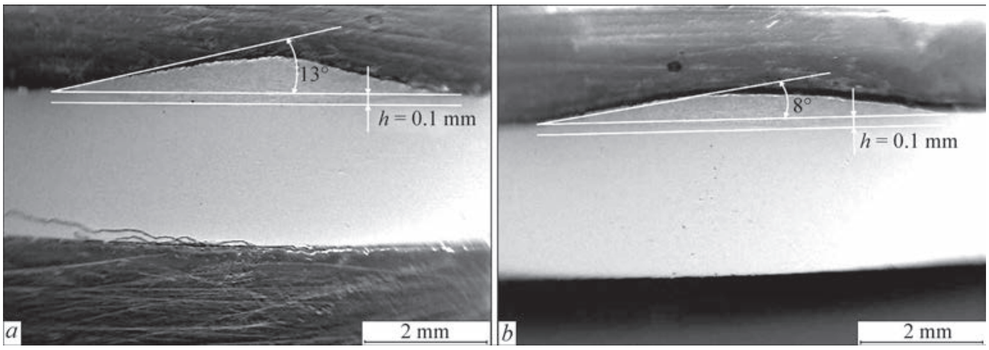

Figure 4. Characteristic macrostructure of the zone of interaction of KMKh (*a*) and KMKhS (*b*) alloys with VZh 98 alloy ($T = 1210$ °C)

the vacuum of the order of 10^{-2} Pa on the substrate of standard high-temperature nickel alloy VZh 98. The time of soaking at temperatures from 1175 to 1210 °C was 3 min. Measurements of specific area of spreading and angles of wetting for the above experimental conditions are shown in Figure 3. Characteristic macrostructure of the zone of interaction of KMKh and KMKhS alloys with high-temperature alloy VZh-98 is shown in Figure 4.

Analysis of the obtained results showed that at heating temperatures of 1175–1185 °C both the alloys have insufficiently stable wetting and spreading characteristics, the scatter of measured values being more than 15 %. Wetting angles exceed 12° for KMKhS alloy and 20° for KMKh alloy that is insufficient in terms of adaptability to fabrication.

Starting from the temperature of 1190 °C, both the alloys demonstrate high adhesion activity in the specified working temperature range of surfacing (1190–1210 °C). The most stable steady characteristics of wetting and spreading for both the test alloys are fixed in the temperature range of 1190–1195 °C. Wetting angles are within the range of 13–15° for KMKh alloy and 8–10° for KMKhS alloy. Specific spreading areas exceed 0.5 mm²/mg for both the alloys, that is more than sufficient in terms of adaptability-to-fabrication, and creates favourable prerequisites for their industrial application. Good adhesion with the substrate material is observed in the entire temperature range without formation of brittle intermetallic components. Here, the dissolution depth remains minimum right up to the temperature of 1210 °C and does not exceed 0.1 mm (see Figure 4) that guarantees preservation of the deposited metal properties and minimizes its effect on the base metal. More over, the melting temperature of both the alloys increases the critical heating temperature of turbine blades to 1150 °C during possible short-term overspeeding in operation, and does not exceed the limit admissible short-term heating temperature of high-temperature nickel alloys of ChS88U-VI type (1210–1220 °C) that is a mandatory requirement to the properties of new adhesion-active surfacing materials.

Conclusions

1. Structure of KMKh and KMKhS alloys consists of solid solution of cobalt (β-modification) alloyed with molybdenum and chromium with hardening by complex silicides and borides (CoB, Mo_2B, MoSi, CoSi), KMKhS alloy additionally contains chromium carbide (Cr_2C_6).

2. Melting temperature determined by the method of differential thermal analysis, is equal to 1185–1190 °C for KMKh alloy, and 1165–1170 °C for KMKhS alloy.

3. KMKh and KMKhS alloys are characterized by high adhesion activity relative to high-temperature alloy VZh 98. Steady characteristics of wetting and spreading are fixed at temperatures above 1190–1195 °C. For KMKh alloy the wetting angles are equal to 13–15°, for KMKhS — 8–10°. Specific spreading areas exceed 0.5 mm^2/mg.

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