Heat Resistance of Laminated Niobium- and Molybdenum-Based Composites with Coatings

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Heat Resistance of Laminated Niobium- and Molybdenum-Based Composites with Coatings

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Abstract—The heat resistance of composite materials fabricated by diffusion welding under pressure and consisting of alternating layers of niobium, molybdenum, and Nb30Ti or Nb0.1C alloy or layers of Nb–Al, Ti–Al, or Mo–Al intermetallics has been studied. Two types of coatings, namely, ZrO_2–Y_2O_3 sol–gel coating or electrochemical chromium–diamond coating, are deposited onto composite samples. The samples are subjected to heat resistance tests in air at temperatures of 800 and 1000°C. Nb30Ti/Al composite samples with a chrome–diamond coating demonstrate the highest heat resistance, which is several orders of magnitude higher than the heat resistance of uncoated niobium samples.

Keywords: laminated composite, intermetallics, sol–gel method, ZrO_2–Y_2O_3 coating, chrome–diamond coating, heat resistance

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INTRODUCTION

The materials of the parts operating at high temperatures in aggressive environments must meet stringent hot strength, heat resistance, and corrosion resistance requirements. Refractory metals, in particular, niobium and molybdenum, and alloys based on them are promising from this point of view [1]. Heat-resistant laminated composite materials based on niobium and molybdenum can be an alternative to cast alloys. A group of the authors of this article is developing a series of such materials designed for operating temperatures up to 1300–1450°C [2–6]. Their strength, fracture toughness, and creep resistance are at the level of modern requirements for heat-resistant structural materials operating over a wide temperature range [7].

A wider practical application of the developed heat-resistant laminated composites is possible when their heat resistance is increased, in particular, due to coatings. Coatings based on refractory oxide ZrO_2 are potentially capable of providing operating temperatures at a level of 1400–1500°C [7, 8]. Acceptable life characteristics and an increase in the operating temperature are thought to be provided by wear- and corrosion-resistant chrome coatings modified by diamond nanoparticles [9–12].

The work is exploratory in essence, and its purpose is to estimate the influence of the chosen types of coatings and their deposition conditions on the heat resistance of laminated composite materials based on niobium and molybdenum.

EXPERIMENTAL

Laminated composite materials were fabricated by diffusion welding of assembled stacks under pressure. The following stacks were assembled by alternating niobium (made of Nb30Ti and Nb0.1C alloys or Nb) or molybdenum foils with aluminum foils: Nb30Ti/Al (total of 51 or 201 foils), Nb0.1C/Al (51 foils), Nb/Al (51 foils), Mo/Al (201 foils). The thicknesses of the Nb30Ti, Nb0.1C, Nb, and Mo foils were 40–50 μm and the Al foil thickness was 10 μm. The external foils in the stacks were made of the niobium or molybdenum-based materials.

A stack was placed in a special high-temperature vacuum chamber (vacuum was 1.3×10^{-4} MPa) between graphite punches, through which a load was transferred. Diffusion welding of the stacks containing niobium-based foils was carried out at a pressure of 14 MPa and a temperature of 1300°C for 1 h, and that of the Mo/Al stacks, at 10 MPa and 1500°C for 1 h. As a result, 30 × 50-mm composite workpieces 1.5 mm (in the case of 51 foils in a stack) or 5 mm (in the case of 201 foils) were prepared.

The outer surfaces of the workpieces were cleaned of defects, which formed, in particular, as a result of contact of the stacks with the graphite punches. Samples in the form of 1.5 × 20 × 25 mm plates were then spark-cut from the 1.5-mm-thick workpieces, and samples in the form of 5 × 5 × 50-mm rods were spark-cut from the 5-mm-thick workpieces.

Two types of coatings were deposited onto the entire sample surface after chemical etching: a sol–gel coating based on Y_2O_3-stabilized ZrO_2 or an electrolytic chromium–diamond coating. The ZrO_2–Y_2O_3 coating was deposited onto Nb30Ti/Al, Nb0.1C/Al, and Nb/Al plate samples, and the chrome–diamond coating was deposited onto Nb30Ti/Al and Mo/Al rod samples.

The preparation of a zirconium oxalate sol involved the dissolution of 0.1 M $ZrOCl_2·8H_2O$ (Alfa Aesar) in 31 mL absolute ethyl alcohol and the homogenization of the solution in a magnetic stirrer for 30 min at room temperature. As the hydrolysis process progressed, 0.8 mL nitric acid was added to the mixture drop by drop. The process continued until the solution became transparent. To stabilize the solution, acetylacetone was added to it. A solution of yttrium nitrate $Y(NO_3)_3$ (Alfa Aesar) in 0.3 mL HNO_3 was then prepared and homogenized for 15 min. The homogenized solution was then added to the previously prepared Zr-containing sol–gel in the ratio 8 mol % Y_2O_3 : 92 mol % ZrO_2 drop by drop for 30 min. The resulting stable and transparent sol–gel was used to deposit coatings onto the composite samples.

The sol–gel coating was deposited by centrifugation in an Ossila Spin Coater L2001A3 setup at room temperature, a centrifuge rotation speed of 1300 rpm, and a process time of 30 s. Five sol–gel layers with intermediate drying in a drying cabinet at 120°C in an air atmosphere were deposited onto the composite samples degreased in ethanol. Heat treatment was then performed in a VEB EIectro Bad Frankenhausen LM 312.11 furnace in an air atmosphere with a gradual controlled temperature rise to 350°C; the holding time at this temperature was 10 h.

The chrome–diamond coating was deposited by an electrolytic method. For this purpose, an aqueous suspension, which contained 10% diamond nanoparticles and was preliminarily activated in an ultrasonic bath, was added to a standard chromium electrolyte (CrO_3 : H_2SO_4 = 100 : 1). The composite rods were used as a cathode. The process was performed at an electrolyte temperature of 55°C and a current density of 50 A/dm^2 for 50 min.

Heat resistance tests were carried out in a SNOL 10/10 laboratory furnace with iron–chromium–aluminum heaters in calm air. The experiment consisted of a series of cycles involving heating to a selected temperature, holding at this temperature (annealing), and air cooling. The experiment was stopped when erosion of the composite material, which had lost its coating, was observed. The annealing temperature was 800°C, and the samples that passed the tests at this temperature were subjected to additional annealing at 1000°C. After each cycle, the sample was weighed accurate to 1 mg on a DEMCOMD L-203 balance. The heat resistance was determined as the change in the sample mass Δm during annealing divided by its surface area S, $q = \Delta m/S$. For comparison, the heat resistance of the samples made of commercial-purity pure niobium and molybdenum without coatings was determined.

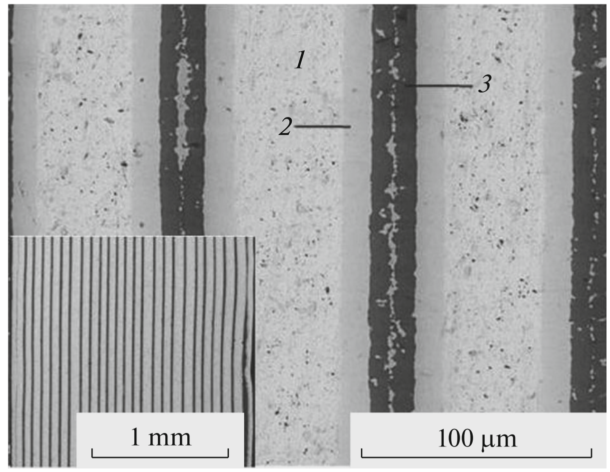

Fig. 1. Structure of the Nb30Ti/Al (cross section) composite material: (*1*) Nb30Ti alloy and (*2*, *3*) Nb–Al and Ti–Al intermetallics, respectively.

RESULTS

Figure 1 shows the typical structure of the prepared composites. The structure and properties of the developed laminated composites were described in detail in [4, 5]. Note that the contribution to the strength of such structures is mainly made by alloy and intermetallic layers, and fracture toughness is provided by the ductility of alloys, the alloy–intermetallic interface, and the interface between various intermetallics. Intermetallics also significantly increase the creep resistance and, having a relatively low density, positively affect the specific characteristics of composite materials in general.

After annealing, a scale, the character of which depended on the type of base and coating, was detected on the sample surface (Fig. 2). All composite samples with coatings were superior in heat resistance to the samples without coatings, and the heat resistance of the samples with the ZrO_2–Y_2O_3 coating was lower than the samples with the chrome–diamond coating in almost the entire time range (Figs. 3, 4). For example, after annealing at 800°C for 60 min, the

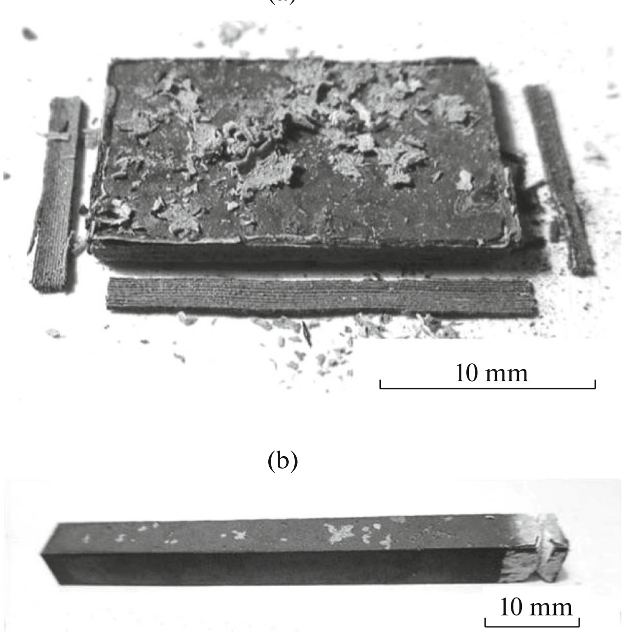

Fig. 2. Appearance of Nb30Ti/Al samples (a) with a ZrO_2–Y_2O_3 coating after annealing at 800°C for 1.5 h and (b) with a chromium–diamond coating after annealing at 800°C for 5 h and additional annealing at 1000°C for 5 h.

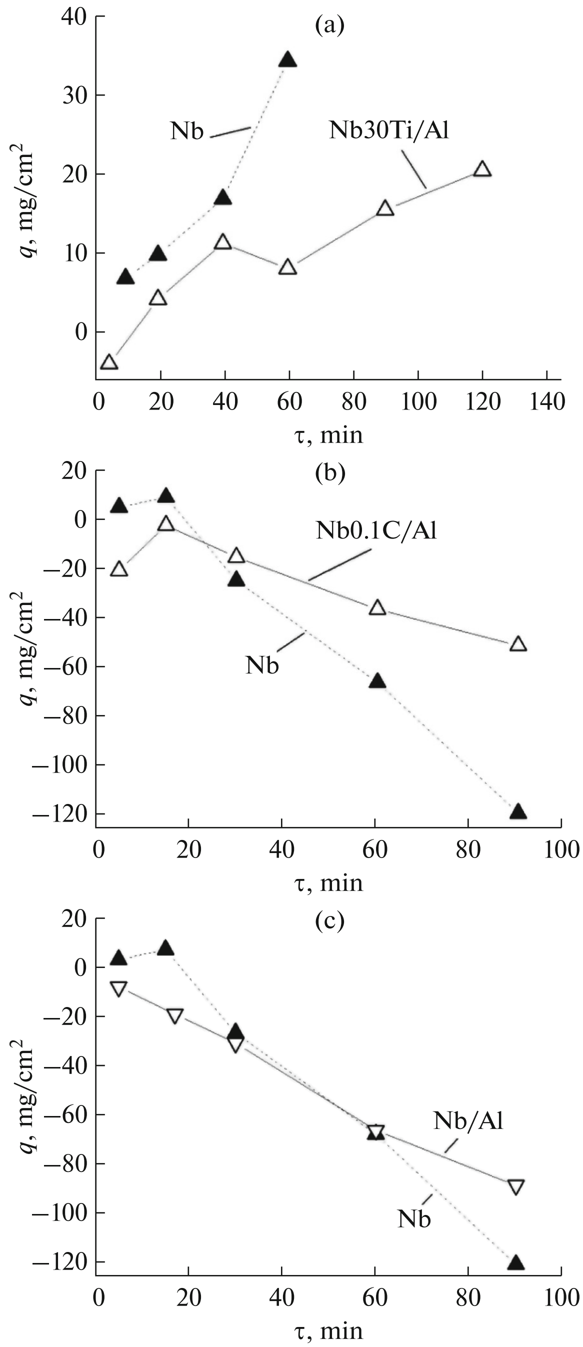

Fig. 3. Specific changes in the mass q of samples (a) Nb30Ti/Al, (b) Nb0.1C/Al, and (c) Nb/Al with a ZrO_2–Y_2O_3 coating and pure uncoated Nb vs. the time τ of annealing at 800°C.

change in the specific gravity of the samples coated with ZrO_2–Y_2O_3 was 8.1 mg/cm^2 for Nb30Ti/Al (see Fig. 3a), 37 mg/cm^2 for Nb0.1C/Al (see Fig. 3b), and 65 mg/cm^2 for Nb/Al (see Fig. 3c). The different type of dependences in Fig. 3a is associated with the fact that the samples were weighed with a scale.

No change in the specific gravity of the Nb30Ti/Al samples with the chrome–diamond coating was detected at the same temperature and annealing time (see Fig. 4a), and the change for the Mo/Al samples with the chrome–diamond coating was 12 mg/cm^2 (see Fig. 4b). Subsequent annealing at 1000°C also showed better stability of the Nb30Ti/Al sample: its specific gravity changed by 1.1 mg/cm^2 in 60 min (see Fig. 4a). The change in the specific gravity of the Mo/Al sample was 478 mg/cm^2 (see Fig. 4b). Erosion of both the coating and the Mo/Al sample was noted. It should be noted that the scale formed on Mo/Al was almost completely volatilized during annealing, which is due to the low oxidation resistance of molybdenum.

CONCLUSIONS

(1) We fabricated Nb30Ti/Al, Nb0.1C/Al, and Nb/Al composites in the form of plates with a ZrO_2–Y_2O_3 sol–gel coating and composite samples in the form of rods made of Nb30Ti/Al and Mo/Al composites with an electrochemical chromium-based coating containing diamond nanoparticles.

(2) The results of heat resistance tests in an air atmosphere at temperatures of 800 and 1000°C demonstrate that the heat resistance of all composite samples with coatings exceeds the heat resistance of Nb and Mo samples without coatings.

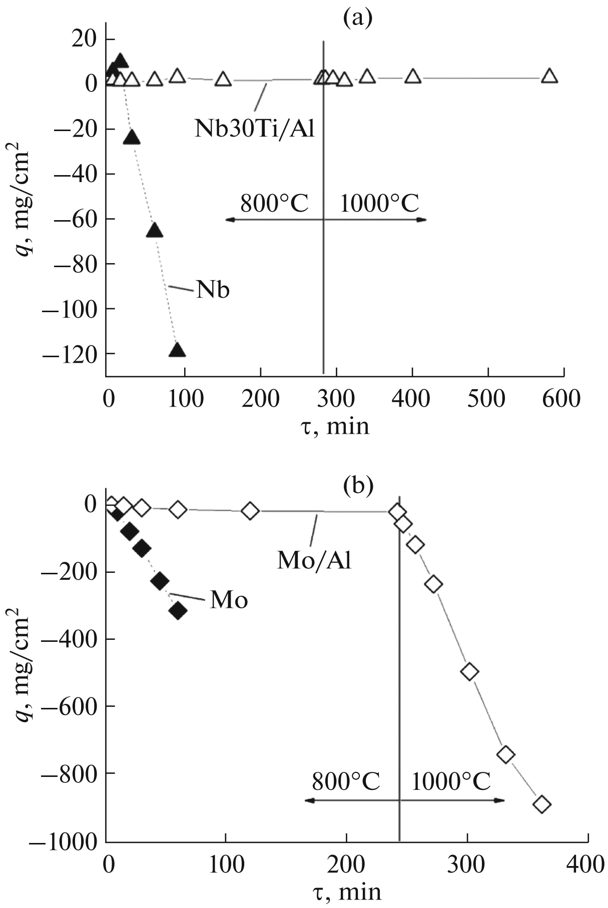

Fig. 4. Specific changes in the mass q of samples (a) Nb30Ti/Al and (b) Mo/Al with a chromium–diamond coating and pure uncoated Nb or Mo vs. the time τ of annealing at 800 and 800 + 1000°C.

(3) The highest heat resistance was demonstrated by the Nb30Ti/Al sample with a chrome–diamond coating: the total specific change in its mass during heat resistance tests at 800°C, 5 h + 1000°C, 5 h was 1.3 mg/cm^2.

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CONFLICT OF INTEREST

The authors declare that they have no conflicts of interest.

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