INTERFACIAL REACTIONS IN LAYERED COMPOSITES OF Nb – Al₂O₃ AND Nb (1% Zr) – Al₂O₃ IN HIGH-TEMPERATURE ANNEALING

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INTRODUCTION

Layered composites of Nb – Al₂O₃ are widely used in high-temperature and vacuum engineering because of the closeness of the temperature coefficients of linear expansion of Nb and Al₂O₃. The interaction between niobium and alumina at high temperatures is described in many publications. For example, the works [1 – 3] present a thermodynamic analysis of the system Nb – Al₂O₃, the works [4 – 6] present data of model experiments on tablets made of powder mixtures, the works [7, 8] describe studies of the interaction between niobium and a liquid oxide, and the works [9 – 14] concern contacting layers of a metal and a ceramics. For the most part the results of the mentioned studies agree quite well.

The present paper is devoted to the processes of interaction in high-temperature vacuum annealing that occur in layered composites of a corundum ceramics with commercial niobium materials, namely, pure niobium obtained by electron-beam remelting and an Nb (1% Zr) alloy.

METHODS OF THE EXPERIMENT

In most cases the initial objects of our study had the form of coaxial tubes with an outer diameter of 20 mm consisting of two thin-walled metal shells with an intermediate ceramic layer up to 500 µm thick. The ratio of the thickness of the external shell to that of the internal one was equal to 0.7. In one case the shells were made of high-purity niobium obtained by electron-beam remelting, and in the other the shells were made of ÉLN-1 niobium alloy containing 1 wt.% zirconium and 0.1 wt.% carbon. The initial material for the ceramic layer was dehydrated Al₂O₃ of analytically grade in both cases. The test pieces were fabricated by a combined method that included plasma deposition of a ceramic layer followed by placement in a metal shell and high-temperature isostatic pressing in a high-purity argon medium [15, 16]. The pressing temperature was 1920 K, and the pressing pressure was 25 MPa with a hold of 3 h under the pressure. The pressed pieces were cut into thin rings by a diamond cutter. The end faces of the rings were ground using SiC powders of different dispersity, polished by diamond pastes and a high-dispersity powder of chromium oxide, and then subjected to electrochemical polishing in a mixture of lactic, sulfuric, and hydrofluoric acids in a proportion of 3 : 2 : 1 at a current density of 0.15 – 0.20 A/cm². Then the specimens were annealed in vacuum in the range of 1770 – 2070 K; before and after the annealing the specimens were weighed on an analytical balance. After the annealing the specimens were cut in half by a diamond cutter. Both faces of each ring were again subjected to the described procedure. As a result, the polished section at one face of the ring characterized the state of the central part of the studied specimen after annealing (closed position), and that at the other face characterized the state of its end part that directly contacted the vacuum in the annealing (open position).

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Carbon in niobium at room temperature is low [21], it is concentrated mainly in carbide segregations. Thus, the microstructure and phase composition of the metal shells and the ceramic layer do not change qualitatively in the annealing of the test pieces and the quantitative changes are insignificant.

The main changes caused by the annealing were localized in a narrow light band on the interface of the ceramics and the metal shells; its width was 180 µm. Microprobing of the specimens with niobium before the annealing showed that aluminum and oxygen diffused from the ceramics into the niobium within the light band. In the specimens with the alloy oxygen penetrating the metal matrix seemed to be bound by zirconium and segregated in the form of ZrO₂, because the microprobe did not find an elevated oxygen background within the light band, while the diffraction data showed that the niobium alloy had lost zirconium. At the same time we did not detect a noticeable increase in the content of ZrO₂ segregations. It seems that the new segregations were very finely disperse (2 - 5 nm by the data of [22]) and partially coherent with the matrix of the alloy (more detailed results for the initial specimens are described in another work; here we devote most attention to the changes in the specimens due to the additional annealing).

A cross section of a fragment of an end face of a specimen after annealing in vacuum (10⁻² - 10⁻³ Pa) at 2070 K for 3 h is presented in Fig. 1. Quite unexpectedly, the faces that had been in direct contact with the vacuum medium (open position) turned out to have deep narrow grooves 3 on the boundary separating the metal 1 and the ceramics 2 (see Fig. 1) that were 50 - 100 µm wide and up to 1 mm deep, while the mass of the entire specimen changed by 50 - 70 mg. It seems that in the annealing process these regions intensely underwent reactions that gave volatile products:

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\begin{align*}
\text{Al}_2\text{O}_3 &= 2\text{Al}(g) + 3\text{O}(g), \quad (1) \\
\text{Al}_2\text{O}_3 &= \text{Al}(g) + \text{AlO}(g) + 2\text{O}(g), \quad (2) \\
\text{Nb} + \text{O} &= \text{NbO}(s, g), \quad (3) \\
\text{Nb} + 2\text{O} &= \text{NbO}_2(s, g). \quad (4)
\end{align*}
\]

Under normal conditions reactions (1) and (2) give a very low yield. By the data of [23], at 2070 K the partial pressure in the gas phase of Al (or O) amounts to 10⁻² - 10⁻⁴ Pa, and the partial pressure of AlO is an order of magnitude lower. Since the specimens were annealed with continuous removal of the products of reactions (1) - (4), this shifted the equilibrium of the reactions to the right, i.e., intensified the interaction, as has been observed in a study of specimens in the form of porous pressings [5 - 7].

Since the geometric profile of the grooves changes in the annealing process, we used the total change in the mass of the specimens for comparison. The obtained values of the rate of loss of mass correspond to data of thermodynamic calculations [2] and experimental results [5]. It can be seen...