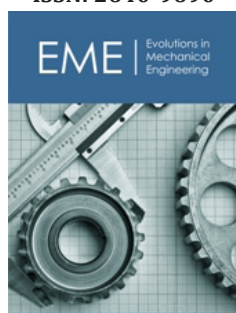


Heat-Resistant Coating of Molybdenum and Tungsten Compounds with Silicon and Carbon on The Surface of Layered Nb/(Si-B) Composite

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Abstract

Using diffusion welding under pressure of multilayer packages with a powder coating of molybdenum, tungsten and silicon, heat resistant multilayer composites $\sim 35 \times 40 \times 2-3$ mm based on niobium with hardening niobium compounds with carbon and boron and heat-resistant coatings on the surface were obtained. Carbon in the Nb-alloy and coating fell from the CO-atmosphere in the chamber for welding and graphite gaskets located between the package and the punches.

Keywords: Niobium, Layered composite, Heat resistance, Heat-resistant coating, Molybdenum silicide, Tungsten silicide, Solid-phase sintering

Introduction

Any material and a metal material in particular, intended to be operated at high temperatures, is subject to gaseous corrosion when interacting with the environment. Only noble materials have the natural ability to resist gas corrosion, called heat resistance. But there can be no talk of their widespread use in industry. Therefore, protective coatings and alloying are used to protect the surface from corrosion.

The classic way to the development of heat-resistant materials was doping Fe-, Ni-alloys, including steels, with chromium. The positive effect lies in the formation of $(\text{Fe}, \text{Cr})_2\text{O}_3$ chromium oxide on the surface of steel, for example. Chromium alloyed steels are successfully used for operation at temperatures up to 1100 °C. The surface of steel with chromium becomes even more heat-resistant, if it is doped insignificant, up to 1%, the amount of yttrium. The unique properties of that combine strength at high temperatures, heat resistance, long-term strength under static and variable loads are alloys based on Ni-Al system. However, the low melting point limits their operating temperature slightly above 1100 °C.

Refractory metals, their alloys, composite materials, which are developed on the basis of them, and, in particular, layered composites have high heat-resistant properties at temperatures above 1150 °C [1]. But they are unstable against gas corrosion. For a chemically active metal, such as niobium and other refractory metals, the problem of its protection against gas corrosion cannot be solved by doping. Therefore, in the late 50s and early 60s of the last centuries, it became clear that research on the development of protective coatings would be more promising [2]. Among them were coatings of niobium aluminide, zinc, a mixture of alumina powders and thorium dioxide, molybdenum silicide, zirconium boride, etc. Interesting were also attempts to create a two-layer coatings and bimetal Nb-alloy/Chromium [3].

Coating methods depended on the shape, size and purpose of the coated parts. Claddings, deposition from the gas phase, immersion into the melt, diffusion saturation, and fusion were used. For the latter method, a plasma torch was effectively used. It was noted [4] the promise of plasma coatings in space technology. They were particularly resistant to low environmental pressure and high temperatures, that is, under conditions similar to the return of a spacecraft to Earth. Protection of refractory materials against gas corrosion at high temperatures of 1100-1600 °C, as well as adjacent issues of the fragility of the protective layer and the

strength of its adhesion to the base metal, have been and remain the most urgent in the problem of heat resistance. Its solution will greatly expand the scale of the use of refractory metals and high-heat-resistant alloys [2] based on them. In the meantime, in order to protect against gas corrosion, it is necessary to use more inert gases, where possible, as a working medium [5].

In this work, for heat-resistant layered composites based on niobium, strengthened by its compounds with silicon and boron [6], it is proposed to use heat-resistant silicide coatings of molybdenum and tungsten. The first experiments on the development of a solid-phase method for the production of these coatings in a single process with the formation of a composite layered structure are presented.

Assembly Procedure and Diffusion Welding of Coated Packages

The initial multilayer packages for the production of heat resistant composites were assembled from Nb-foils 60 microns thick, with a unilateral suspension (Si-B)-coating. Suspensions are concentrated suspensions of fine powders in organic liquids. As it polyvinyl butyral was used in its work. Coatings based on it dried in the air. For the (Si-B)-coating, a powder mixture of silicon and boron in the ratio Si/B = 3 was used, and for a coating of Molybdenum, Tungsten and Silicon-a powder mixture of composition 44% Mo-44%W-12 wt. %Si, corresponding to one of the phases Novotny.

Packages were assembled from U-shaped elements in which Nb-foils had one-sided (Si-B)-coatings. One of the coatings turned out to be outside the element, the other - inside it (Figure 1). With such an assembly sequence, as shown in the figure, the assembled package had one Nb-surface without coating, and another surface with (Si-B)-coating, which was covered with a separate niobium foil. The final operation was the application of (Mo-W-Si)-coatings on both surfaces of the packet see Figure 1.

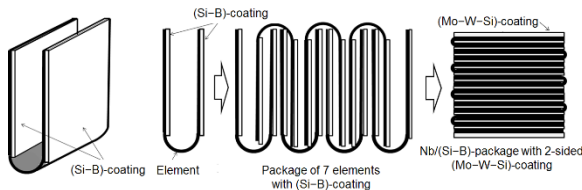


Figure 1: Assembly scheme of a multilayer package of U-shaped elements made of Nb-foils with a single-sided (Si-B)-coating. Right is Nb/(Si-B)-package with outer (Mo-W-Si)-coatings, ready for diffusion welding.

Thus, in the assembled state, the package had 15 layers of niobium ($7 \times 2 + 1 = 15$) alternating with 14 layers of silicon with boron, the content of which in the package was 15,5 wt.%, and the outer layers of molybdenum, tungsten and silicon (7,8 wt.%). Next, the package was subjected to diffusion welding under pressure (Figure 2), during which the composite layered structure was formed, and a heat-resistant coating was formed on its surface. Carbon penetrated into the coating due to gaskets 4 of thermally split graphite [7], located between the package and the punches see Figure 2.

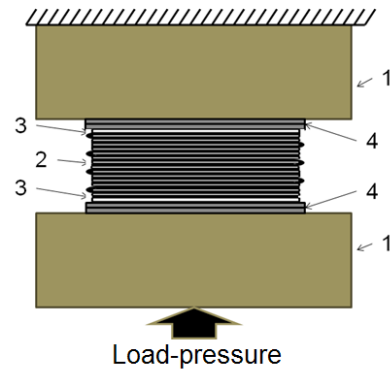


Figure 2: Diffusion welding of Nb/(Si-B)-package with outer (Mo-W-Si)-coatings:

1 - fixed and movable punches, 2 - pack of Nb-elements with (Si-B)-coatings, 3 - (Mo -W -Si)-coatings, 4 - thermally split graphite gaskets.

Microstructure

In Figure 3 shows the coating formed on the surface of the composite after diffusion welding at 1400 °C and a pressure of 7,4 MPa for 1 hour. The coating thickness is ~60 microns. It looks quite dense, without transverse cracks and is in good contact with the composite-substrate. Between the coating and the volume of the composite with a layered structure, an intermediate layer ~10 microns thick is visible.

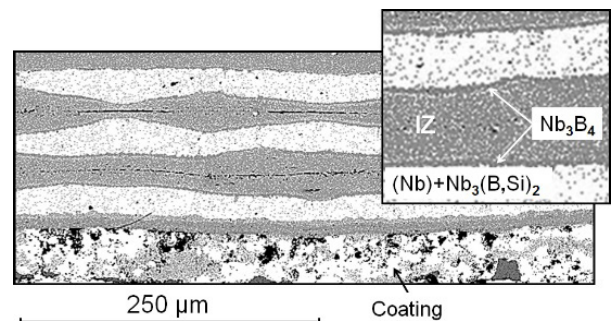


Figure 3: A fragment of the microstructure of the composite with a protective coating.

The layered structure of the composite consists of light layers that inherit Nb-foil and gray layers of the interaction zone (IZ) of Nb-foils with (Si-B)-coatings. According to X-ray spectral analysis, the light layers had the composition of the eutectic region of the Nb-B state diagram $Nb_{65,0}(B_{33,2}Si_{1,8})_{35,0}$ and the structure of the (Nb)-solid solution (dominant phase) and the $Nb_3(B, Si)_2$ intermetallic compound (solid solution of Si in boride Nb_3B_2) in the form of small inclusions of light gray color. These layers represent the viscous-plastic component of the composite. The layers of the interaction zone are identified as intermetallic $Nb_3(B, Si)_4 = Nb_{2,92}(B_{2,35}Si_{1,73})_{4,08}$ (solid solution of silicon in boride Nb_3B_4) and should perform a strengthening function in the composite. Between layers with (Nb)-matrix and layers of diffusional IZ a significantly thinner (about 3 μ m) layer is again boride Nb_3B_4 , but with very low silicon content- $Nb_{3,01}(B_{3,96}Si_{0,03})_{3,99}$.

Three phases were found in the coating composition (Figure 4):

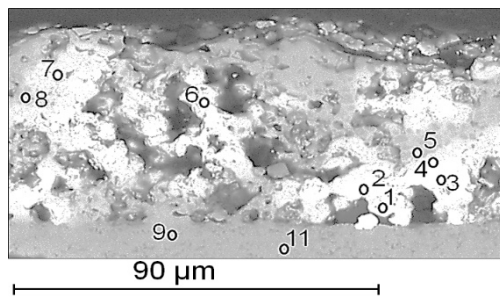


Figure 4: The microstructure of the coating on the surface of the composite: 1-9 and 11 - numbers of the spectra.

A. Carbide-silicide of molybdenum and tungsten with the composition $(\text{Mo}_{30.4}\text{W}_{15.7})_{46.1}(\text{Si}_{27.7}\text{C}_{26.2})_{53.9}$, which can be represented as equiatomic intermetallic compound $(\text{Mo}_{0.61}\text{W}_{0.31})_{0.92}(\text{Si}_{0.55}\text{C}_{0.53})_{1.08} = (\text{Mo, W})(\text{Si, C})$;

B. Compound with the composition $(\text{Mo}_{37.8}\text{W}_{2.3}\text{Nb}_{0.6})_{40.7}\text{Si}_{34.8}\text{C}_{24.5})_{59.3}$, which at this stage of diffusion welding contains up to ~3 at.% W and Nb and can be identified as a silicide $(\text{Mo, Me})(\text{Si, C})_2 = (\text{Mo}_{1.14}\text{Me}_{0.08})_{1.22}(\text{Si}_{1.04}\text{C}_{0.74})_{1.78}$ or molybdenum carbide $(\text{Mo, Me})(\text{C, Si}) = (\text{Mo}_{0.76}\text{Me}_{0.06})_{0.82}(\text{C}_{0.48}\text{Si}_{0.70})_{1.18}$, where Me is W and Nb;

C. Unused tungsten (light phase), which is still quite a lot.

The layer of the composite adjacent to the coating is niobium carbide with Mo, W and Si dissolved in it. Its average composition $(\text{Nb}_{41.5}\text{Me}_{1.4})_{42.9}(\text{C}_{51.3}\text{Si}_{5.8})_{57.1}$ is close to the monocarbide $(\text{Nb, Me})(\text{C, Si})_{1-x} = (\text{Nb}_{0.83}\text{Me}_{0.03})_{0.86}(\text{C}_{1.03}\text{Si}_{0.11})_{1.14}$, where Me is Mo and W.

Conclusion

A. During diffusion welding, 1400 °C for 1 hour, none of the Novotnaya phases of the stoichiometric compositions $(\text{Mo, W})_5\text{Si}_3\text{C}$ or $(\text{Mo, W})_5\text{Si}_2$ not yet formed most likely due to low temperature and short time of the welding. However, already obtained compounds

with molybdenum and tungsten are heat resistant. The experiment showed that the interaction between the refractory elements Mo and W with carbon and silicon is quite active.

B. This pilot experiment highlighted another possibility of the solid-phase technology developed by us, which consists in obtaining a heat-resistant coating from refractory compounds of molybdenum and tungsten compounds on the surface of the Nb/(Si-B) composite at the same time as obtaining its heat-resistant layered structure.

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