

Study of the phase composition of silicide coatings, based on layered Nb–Mo structures, obtained by vacuum-arc deposition

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Abstract. A multilayer composite ~1000 μm in thickness, formed by niobium and molybdenum layers (number of layers $n = 230$), is obtained by vacuum-arc deposition with subsequent siliconization of the surface layers at a temperature of 1200 °C. Layer-by-layer phase analysis is performed by X-ray diffraction and scanning electron microscopy. It is found that in the surface layers ~130 μm in thickness, single-phase silicides $(\text{Nb}_x\text{Mo}_{1-x})\text{Si}_2$ are formed with the hexagonal C40 structure (Strukturbericht designations). Alternating layers of solid solutions based on niobium and molybdenum with a body-centered cubic (BCC) lattice are observed within the composite. The formation of solid solutions caused by heating of the coating leads to convergence of the values of the linear thermal expansion coefficient and Young's modulus at the interface between the layers.

1. Introduction

Multilayer coatings of alternating metal or ceramic layers are attracting increasing attention because of their excellent mechanical properties, such as high hardness, adhesion strength and toughness, and wear resistance, and relatively low levels of residual stress [1–3]. These properties are the result of deviation of the crack path due to the presence of a soft metal layer in conjunction with an obstacle in the form of a solid ceramic layer; the ability to create favorable residual stress gradients; a decrease in the bending stress resulting from better load distribution in a layered material compared to a monolithic material; and the branching of cracks because of different values of the elastic moduli of the layers. Therefore, investigations of the formation of silicide coatings based on layered structures obtained by the ion-vacuum deposition of alternating layers of niobium and molybdenum, followed by saturation of the surface layers with silicon, are of considerable scientific and practical interest, which is selected as the topic of this paper.

2. Experimental

To obtain a multilayer coating, an NNV-6.6-II setup equipped with three vacuum-arc evaporators was selected. A 5VMTs niobium alloy and molybdenum (MCh grade) were used as evaporated materials (cathode materials). The coatings were deposited on a cylindrical substrate of copper (M1 grade) mounted in a mandrel. The chamber was evacuated to a residual pressure of $P = 0.33 \cdot 10^{-3}$ Pa; argon was introduced to a pressure of $P = 3\text{--}4$ Pa; and the surface of the samples was purified in the glow



discharge plasma at a voltage of 1.1 kV for 30 min. After purification, the argon pressure was reduced $P = 4 \cdot 10^{-1}$ Pa, and the sample was heated by an electron beam. Then, layers of niobium and molybdenum were sputtered alternatively at a substrate bias voltage of $U = 40$ V to form a layered metal composite approximately 1 mm in thickness. The thickness of the molybdenum layer was 1 μm , and the niobium layer was 3–4 μm thick. The copper substrate was then removed by selective chemical etching, and the composite was subjected to diffusion siliconization at 1200 $^{\circ}\text{C}$ for 10 h.

3. Results and discussion

Figure 1 shows a cross-sectional structure of the multilayer coating, which testifies to the absence of cracks and bundles in alternating layers of molybdenum and niobium. Figure 1(b) shows a few traces of the droplet phase.

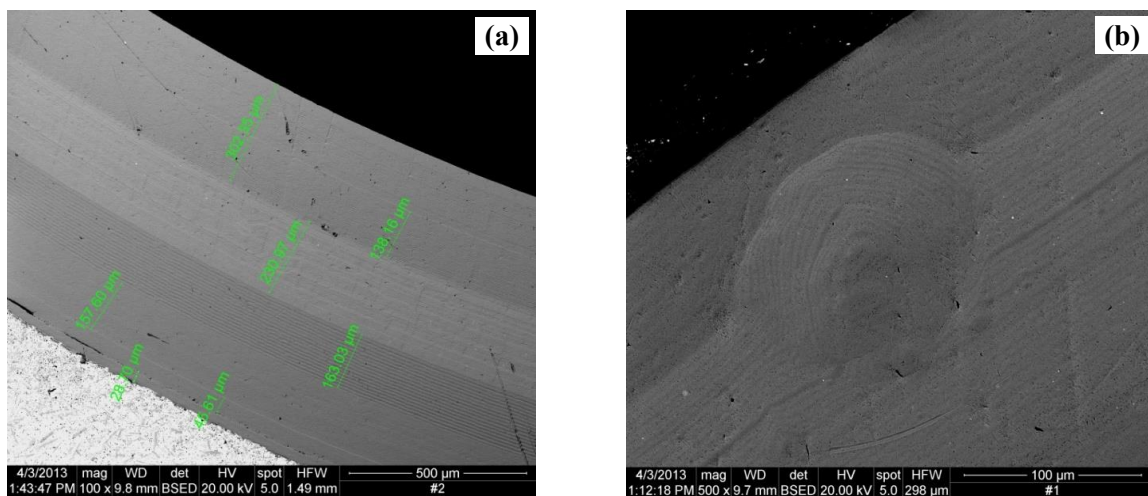


Figure 1. The structure of the cross section of the coating (a) and droplet phase region (b) recording in the reflected electrons, the thickness of the surface indicated "siliconized" coating layers.

A diffraction pattern obtained from an assembled sample is shown in figure 2. In the diffraction pattern, there are reflections of a BCC phase located between the reflections of Mo and Nb, but shifted respectively toward smaller and larger values of the Bragg diffraction angles. Such a shift in reflections indicates that during siliconization ($T = 1200$ $^{\circ}\text{C}$) a substitutional solid solution is formed by the interdiffusion of metal atoms between adjacent layers.

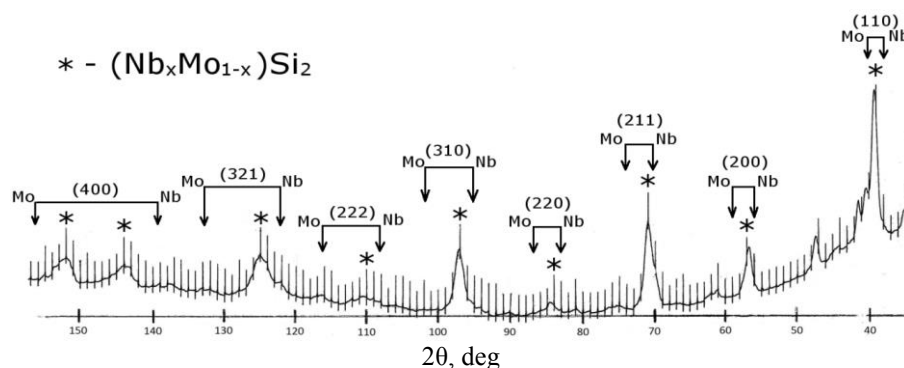


Figure 2. Diffraction pattern of the assembled sample of Nb–Mo solid solutions; arrows indicate the positions of the reflections of pure niobium and Mo.

In the diffraction pattern of the surface layer, there are all reflections of the NbSi_2 phase without exception corresponding to the ICDD-2003 database, and there are no extraneous reflections (figure 3),

which is very rare in such complex non equilibrium systems as multilayer vacuum-arc coatings, particularly those subjected to high-temperature siliconization. Therefore, we can assume that there are no other silicides in the surface layer. The mean values of the composition of the solid-solution phases with a predominance of niobium (solid solution A) and molybdenum (solid solution B) were estimated by averaging over all available reflections in the diffraction pattern, taking into account the texture and proportions of the two phases for each reflection according to equation

$$C_{\text{Mo}} = \frac{1}{n} \sum_{i=1}^n (C_{\text{Mo}}^A P_i^A f_i^A + C_{\text{Mo}}^B P_i^B f_i^B), \quad (1)$$

where C_{Mo}^A and C_{Mo}^B are the molybdenum concentrations in solid solutions A and B, respectively; P_i^A and P_i^B are the pole densities of the i -th reflex in solid solutions A and B, respectively; f_i^A and f_i^B are the volume fractions of solid solutions A and B.

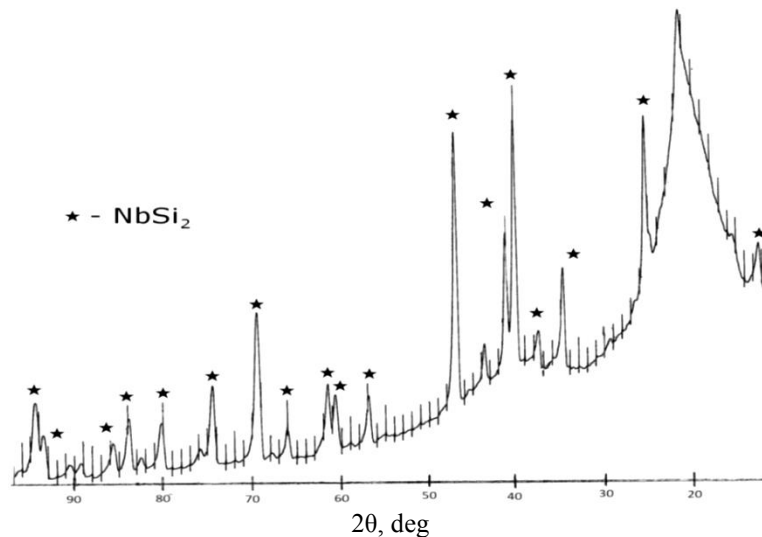


Figure 3. Diffraction pattern obtained from the outer surface of the sample after siliconization.

X-ray diffraction studies have shown that as a result of the diffusion siliconization at 1200 °C of a Nb–Mo layered composite ($n = 230$, $T \sim 1000 \mu\text{m}$) with alternating metal layers in the surface region $\sim 130 \mu\text{m}$ in thickness, single-phase silicides $(\text{Nb}_x\text{Mo}_{1-x})\text{Si}_2$ with the hexagonal C40 structure are formed. The single phase structure of the silicide, formed from bicomponent solid solutions of Mo and Nb, corresponds to the pseudobinary state diagram of NbSi_2 – MoSi_2 and is characteristic of a number of similar systems MoSi_2 – XSi_2 (where $X = \text{Ta}$, Ti , Ir , Zr , V or Cr) [4, 5]. All of these elements except molybdenum form silicides with the C40 structure, this structure is metastable only for MoSi_2 , and the stable silicide forms the tetragonal C11b structure. The pseudobinary state diagrams of MoSi_2 – XSi_2 are characterized by a wide homogeneity range of solid solutions of the C40 structure and relatively narrow two-phase and single-phase regions of the C11b structure. This explains the presence of the coating of single-phase silicide C40 in the surface layer, despite the significant concentration of molybdenum in the initial coating: the ratio of the metal components corresponds to the composition of $\text{Nb}_{0.62}\text{Mo}_{0.38}$.

4. Conclusions

A multilayer Nb–Mo coating ($n = 230$) with a thickness of $\sim 1 \text{ mm}$ is obtained by vacuum-arc deposition.

It was found that in the surface layers ~130 μm in thickness silicides $(\text{Nb}_x\text{Mo}_{1-x})\text{Si}_2$ are formed with the hexagonal C40 structure.

The rest of the coating section by heating accompanying siliconizing process formed of alternating layers of BCC solid solutions based on Nb and Mo nominal composition $\text{Nb}_{0.75}\text{Mo}_{0.25}$ (78 %) and $\text{Nb}_{0.18}\text{Mo}_{0.82}$ (22 %), respectively.

Acknowledgments

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