

NANOSTRUCTURED MATERIALS

EFFECT OF METALLIC NANOCOATINGS DEPOSITED ON SILICON OXIDE ON WETTING BY FILLER MELTS

II. EFFECT FROM THE ANNEALING OF NANOCOATINGS DEPOSITED ON SiO₂ ON THEIR STRUCTURE AND INTERACTION WITH THE OXIDE

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The sessile drop method using capillary melt cleaning was employed in the experiment to study the effect of metallic nanocoatings (single Ti, Nb, and Mo coatings and binary Ti–Cu, Nb–Cu, and Mo–Cu coatings with a copper layer of constant thickness) on the wetting of silicon oxide by Pb–15 wt.% In melt in $1 \cdot 10^{-3}$ Pa vacuum at 500 °C after their annealing at 900 °C. The metallic coatings were applied by electron beam evaporation in vacuum. The binary coatings were produced by sequential deposition of layers. The dependences of contact angle on coating thickness show that the ‘threshold’ thickness is determined by the annealing temperature of the coating or, in other words, its structure. The threshold coating thickness for different metals depends on their chemical affinity to oxygen. When freshly applied and annealed single Mo, Nb, and Ti coatings are wetted, their threshold thickness increases from 70 to 80 nm for the titanium coating, from 63 to 70 nm for the niobium coating, and from 50 to 60 nm for the molybdenum coating. The structure of Cu, Ni, Mo, Cr, Nb, and Ti coatings annealed at 600, 900, and 1200 °C was studied. The initial (freshly deposited) metallic coatings showed high integrity. The coatings became dispersed after annealing and their integrity decreased with increasing temperature. The dispersed metallic coatings formed ‘islands’ of various shapes, round shape being predominant, depending on the chemical affinity of the coating metal to oxygen. The so-called ‘solid’ wetting was observed. The shape of the islands is determined by equilibrium between the metal–substrate attraction forces (interaction, adhesion) and the very strong surface tension of the metal (at such a small coating thickness). To use metallic coatings for brazing quartz with aluminum alloys, coatings of adhesive metals (Mo, Cr, Nb, Ti) should be annealed at temperatures of 900–1000 °C with a holding time of 10 min. The coating thickness should be within the threshold range.

Keywords: metal nanocoatings, silicon oxide, wetting, annealing, coating dispersion.

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INTRODUCTION

Current advances in science and technology require fundamentally new materials, such as nanomaterials, to be developed. The relevance of nanomaterials was justified in detail in the previous paper of the series [1]. We should only note that nanocoatings and nanofilms need to be studied to improve the wetting of refractory oxide materials by metallic (filler) melts and improve the effect of annealing on structural features of nanocoatings and their interaction with the substrate.

The objective is to determine how the surface of oxide materials is modified when metallic nanocoatings are immobilized by absorption and examine how annealing of metallic nanocoatings influences their wetting by filler melts.

EXPERIMENTAL PROCEDURE

Wetting was studied by the sessile drop method using capillary melt cleaning in the experiment [2] in 2×10^{-3} Pa vacuum at 500°C. The hard phase was presented by silicon oxide substrates (KV quartz glass with 99.95% SiO₂). The substrates were preliminary polished to 0.01 μm surface roughness. Prior to depositing coatings, the substrates were cleaned with acetone and alcohol and annealed in vacuum at 1100°C for 60 min. In the experiments, we used In of grade 000 and Pb of grade OVCh. Indium was preliminary melted at 1000°C and lead at 650°C in graphite crucibles and then filler melts of lead with 15 wt.% In were further melted.

Single and binary nanocoatings were applied using molybdenum, iodide-refined titanium, and electrolytic vanadium, niobium, chromium, nickel, and copper. Metals for the first coating layer (Ti, Nb, Mo) were chosen so that the filler–coating solubility was virtually zero. Moreover, these metals had different chemical affinities to oxygen, determining the adhesion with silicon oxide.

The coatings were applied to substrates by electron beam evaporation in vacuum. To produce binary coatings, a layer of an adhesive metal (Ti, Nb, Mo) was deposited first and then the next layer was deposited onto the metal-coated surface. Copper of grade V3 (99.995% purity) was chosen for the second layer. The reference coating thickness was measured differently: optically employing a 3D Micron Alpha Optical Profiler, with a special quartz thickness meter located directly in the deposition area, and using the procedure described in [3, 4]. The coating quality was verified with an XJL-17 metallographic microscope.

The coatings applied to SiO₂ were annealed in $2 \cdot 10^{-3}$ Pa vacuum at 600, 900, and 1200°C. The annealed samples were examined using JCM-6700 and JCM-5000 scanning electron microscopes and a Nano Scope III atomic force microscope.

EXPERIMENTAL RESULTS AND DISCUSSION

Annealing of metallic nanocoatings on silicon oxide and the effect of annealing on interaction processes, structural features, and wetting behavior in the substrate–coating–melt system are of particular research interest. Annealing of metallic coatings deposited on silicon oxide should activate interaction between the coating metal and oxide. The papers [3, 5–7] studied how annealing influenced the wetting behavior, but the samples were annealed and wetted simultaneously at the same temperatures (900–1150°C). In our experiments, the samples were wetted at 500°C and the first layer was annealed at 900°C. The literature [3, 5, 8] and our studies [6] focusing on the structure of annealed coatings indicate that adhesive metals actively interact with silicon oxide at 900°C and the substrate surface remains about 50% occupied.

We studied how the Pb–15 wt.% In melt wetted single Ti, Nb, and Mo coatings applied to silicon oxide and binary Ti–Cu, Nb–Cu, and Mo–Cu coatings with the copper layer of constant thickness ($\delta = 100$ nm) after annealing at 900°C. The results are presented in Fig. 1.

The dependences of contact angle on coating thickness show that the ‘threshold’ thickness is determined by the coating annealing temperature or, in other words, coating structure. In the case of a freshly applied and annealed single Ti, Nb, or Mo coating, the ‘threshold’ thickness increases from 70 to 80 nm for the Ti coating (Fig. 1a), from 63 to 70 nm for the Nb coating (Fig. 1b), and from 50 to 60 nm for the Mo coating (Fig. 1c). The coating thickness increases through interaction in the coating–silicon oxide systems at the annealing temperature. The metallic coating

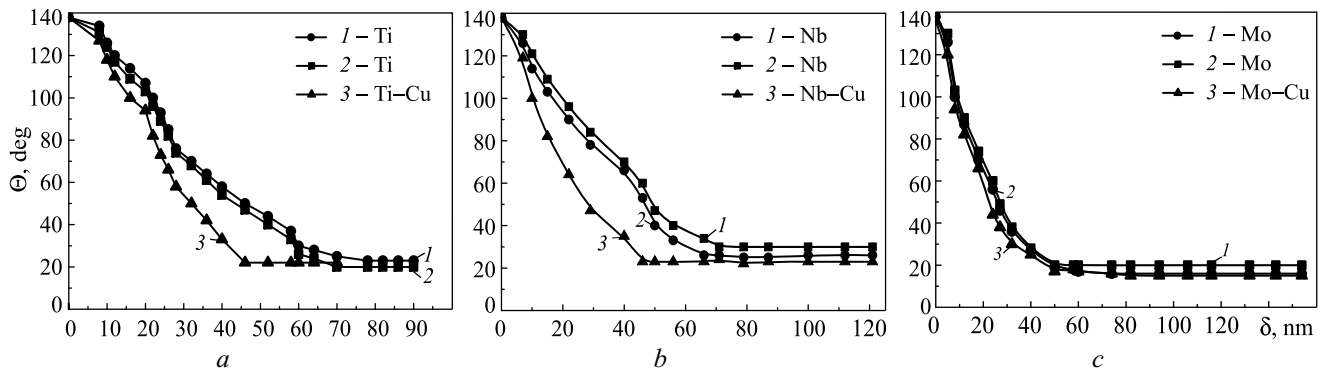


Fig. 1. Wetting of the Ti and Ti-Cu (a), Nb and Nb-Cu (b), and Mo and Mo-Cu (c) coatings deposited on SiO_2 by the Pb-15% wt. In melt before (2) and after (1, 3) annealing of the first layer at 900°C

is wetted better than the interaction products. The wetting of a single molybdenum coating and binary molybdenum coating with the second layer (copper) deposited onto the annealed first molybdenum layer does not substantially differ. The reason is that copper poorly interacts with molybdenum and fully dissolves in the melt. In the case of Nb-Cu, when copper more readily interacts with the first metal layer, the wetting of the binary niobium coating is better than that of the single coating. This can be explained by insignificant mutual dissolution of niobium and copper and the fact that the coating remains two-layer and copper is wetted better than niobium. The wetting behavior of the binary Ti-Cu coating improves because it is thicker than the single one.

As already noted, the structure of the metallic coating applied to the oxide plays an important and, in many respects, crucial role for coating wetting by the melt. The metals of coatings deposited on silicon oxide can be divided into the following groups according to their interaction with the oxide:

- metals with low affinity to oxygen (inert to oxygen)—nickel and copper;
- metals with high affinity to oxygen (adhesive to oxygen)—titanium, niobium, and chromium;
- molybdenum, as an individual group, which forms silicides and oxides at high heating temperatures.

We analyzed the structure of Cu, Ni, Mo, Cr, Nb, and Ti coatings 100 nm thick after annealing at 600, 900, and 1200°C (Fig. 2). The initial (freshly applied) metallic coatings show high integrity. The coating integrity decreases with increasing annealing temperature. The metallic coatings become dispersed depending on temperature. The failed metallic coating forms ‘islands’ of different shape determined by the chemical affinity of coating metal to oxygen, round shape being predominant (as an axially symmetrical body like a molten droplet on a solid surface). The so-called ‘solid’ wetting is observed. The shape of the ‘islands’ is determined by equilibrium between the metal-substrate attraction forces (interaction, adhesion) and very strong surface tension of the metal (at such a small coating thickness). The ‘islands’ become elongated when the coating metal interacts with the substrate oxide and the surface tension tends to collect the ‘islands’ into a ball (lowest surface energy). The thermodynamic situation is the same as in the case of a molten metal on an oxide substrate. The higher the metal affinity to oxygen, the better the solid coating metal wets the silicon oxide substrate. The ‘islands’ become spread droplets, i.e., the coating will occupy greater area.

The copper and nickel coatings of studied thickness annealed at different temperatures are not integral and contain multiple islands (Fig. 2). Similar results were obtained in [6] for Cu and Ge coatings annealed at 900 and 780°C, respectively. The average diameter of the ‘islands’ increased from 0 to 1350 nm after the copper coatings 0–160 nm thick were annealed at 900°C. The substrate surface acquired higher integrity and became up to 25% occupied. The contact angles of ‘solid’ wetting of silicon oxide were determined: 136–138° for Cu and 140–143° for Ge. The contact angles larger than 90° indicate that the island coatings do not wet the quartz substrate.

The nickel coatings annealed at 900°C become dispersed after holding for 10 min. When the annealing temperature increases to 1200°C (Fig. 2), the ‘islands’ become rounded ‘solid’ droplets and the oxide surface is occupied by about 10% (Fig. 3). Copper and nickel do not wet oxides [8]: chemical interaction is zero in the metal–

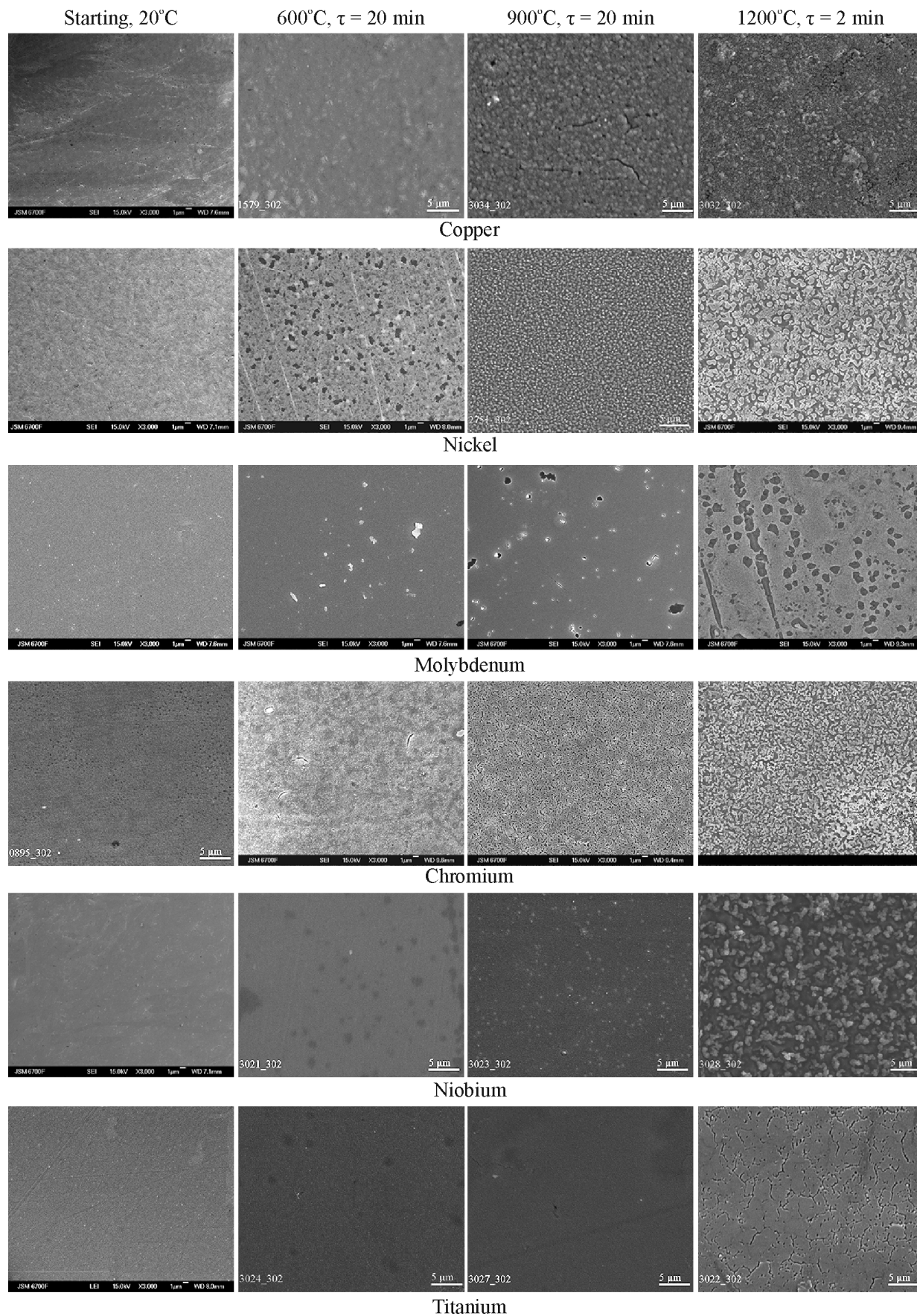


Fig. 2. Structure of the coatings 100 nm thick deposited on SiO₂: starting and annealed in different conditions

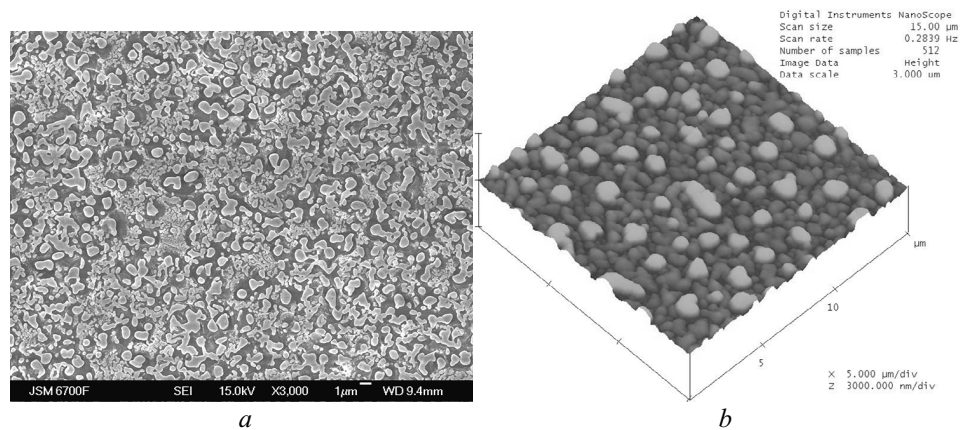


Fig. 3. Nickel coating 100 nm thick on silicon oxide annealed in vacuum at 1200°C for 2 min: a) scanning microscope image, $\times 3000$, and b) atomic force microscope image

quartz system. The ‘islands’ should be shaped as metal droplets that do not wet the oxide nor do they spread over its surface. The spread ‘solid’ droplets have greater thickness (height) than the coating deposited after annealing seemingly because the ‘island’ droplets form ‘solid’ contact angles larger than 90° .

Annealing of single coatings (Cr, Nb, Ti) with high affinity to oxygen showed that they became dispersed at temperatures above 900°C (Fig. 2). When annealing temperature increases, the dispersion intensifies and the coatings break into ‘islands’ in 5 min at 1200°C (Fig. 4). The annealed metal coatings of small thickness represent islands. The shape of the islands should correspond to the shape of metal droplets spread in ‘solid’ wetting. The coating integrity (or silicon oxide surface occupancy) is determined by the amount of the sprayed adhesive metal and constitutes 30–50% at the coating thickness in question. The greater thickness (height) of the spread ‘solid’ droplets after annealing (compared to the deposited coating thickness) found in the papers [9, 10] seems to be associated with the formation of island droplets with ‘solid’ contact angles smaller than 90° . The paper [3] studies the adhesion of freshly deposited and annealed Mo and V coatings on the SiO_2 substrate using a sliding indenter. Annealing of the thin Mo and V coatings increased their adhesion to silicon oxide as compared to the freshly deposited ones. This can be explained by interaction of the Mo and V coatings with the oxide. Annealing of the Mo coatings does not significantly improve adhesion at 600°C compared to the freshly deposited samples and increases it at 900°C . The adhesion of thin V films to SiO_2 increases already at 600°C .

Therefore, bonding of adhesive metals to the oxide after annealing depends on their reactivity, i.e., on their affinity to oxygen. In our case, the reactivity should increase in the $\text{Mo} \rightarrow \text{Cr} \rightarrow \text{Nb} \rightarrow \text{Ti}$ row; the Gibbs energy for the formation of oxides increases likewise. The same dependence is observed in ‘liquid’ wetting of oxides by these metals.

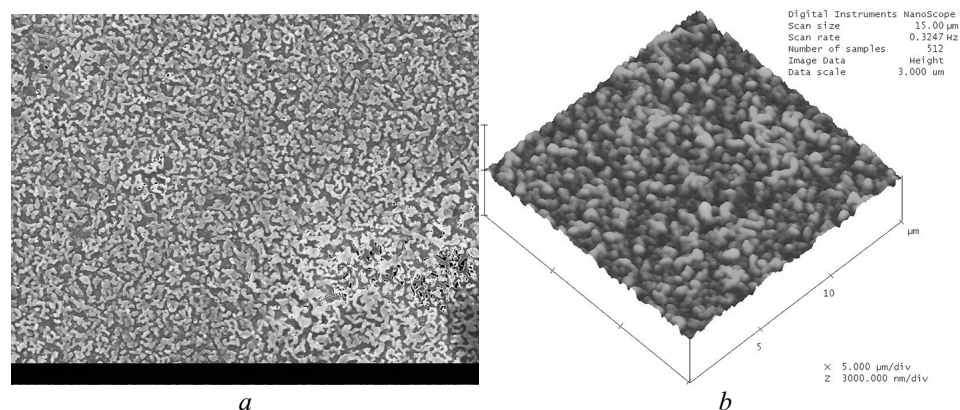


Fig. 4. Chromium coating 100 nm thick on silicon oxide annealed in vacuum at 1200°C for 5 min: a) scanning microscope image, $\times 3000$, and b) atomic force microscope image

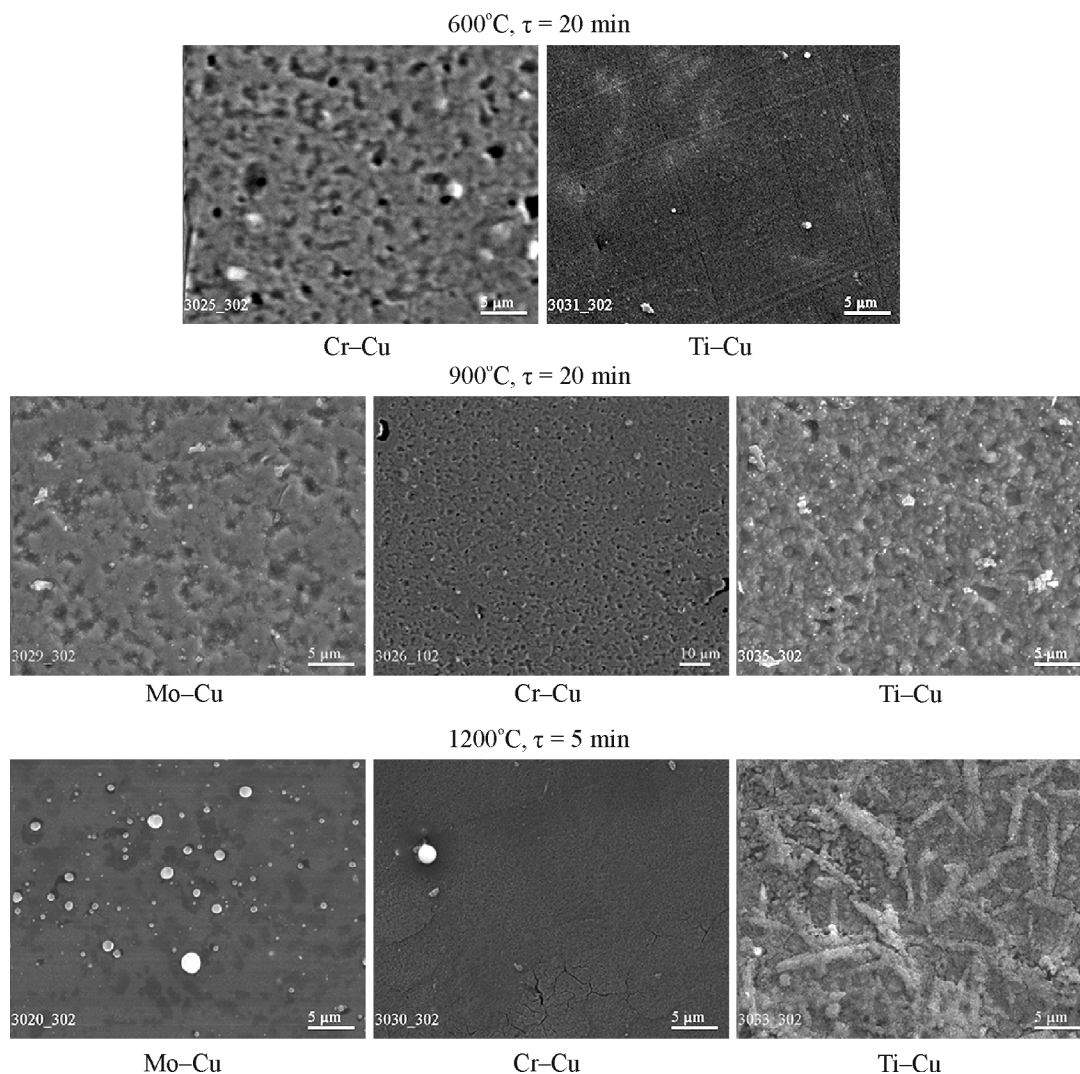


Fig. 5. Structure of binary coatings deposited on SiO₂ annealed in different conditions

In the annealing of binary Mo–Cu, Cr–Cu, and Ti–Cu coatings deposited on quartz at 600, 900, and 1200°C, the ‘island’ shape and coating integrity depend on interaction of metals in the first and second layers (Fig. 5). The effect of the second (copper) layer ($\delta = 100$ nm) on the structurization of island films is determined by the interaction and dissolution of copper in the first layer after annealing. The choice of metals for the Mo–Cu, Cr–Cu, and Ti–Cu coatings is due to their different interaction [11, 12]. The Ti–Cu system is characterized by the greatest interaction between the components (there are four intermetallics). The interaction between components is weaker in the Cr–Cu system (insignificant solid-state solubility of components, no intermetallics) and the weakest in the Mo–Cu system (zero solid-state solubility, significant liquid-state miscibility of components).

The dissolution of copper in chromium and titanium (and the formation of titanium–copper intermetallics) in the Cr–Cu and Ti–Cu systems decreases the activity of chromium and titanium relative to silicon oxide and, hence, affects ‘solid’ wetting. No interaction or mutual dissolution of components is observed in the Mo–Cu system. The quartz surface occupancy and island shape after annealing are determined only by the amount of metals deposited in the first layer both for the binary and single coatings.

The wetting of the metallic coating deposited on the oxide surface by filler melt is defined by the following factors: coating thickness (amount of deposited metal) and structure (integral, insular), affinity of the coating metal to oxygen (film–substrate adhesion determining the shape of islands and the ease of dispersion), dissolution of the coating in the melt, and wettability of the adhesive metal coating.

CONCLUSIONS

The dependences of contact angle on coating thickness show that the ‘threshold’ thickness is determined by the coating annealing temperature or, in other words, coating structure. When freshly applied and annealed single Ti, Nb, and Mo coatings are wetted, their ‘threshold’ thickness increases from 70 to 80 nm for the Ti coating, from 63 to 70 nm for the Nb coating, and from 50 to 60 nm for the Mo coating. The contact angle decreases linearly with increasing coating thickness from the values peculiar to SiO₂ to those formed by the filler melt on compact metal coating.

Bonding of adhesive metals to the oxide after annealing depends on their reactivity, i.e., on their affinity to oxygen. The reactivity should increase in the Mo → Cr → Nb → Ti row; the Gibbs energy for the formation of oxides increases likewise. The immobilization (adhesion bonding) of metallic coatings on the substrate is determined by contact interaction between the coating metal and silicon oxide.

The wetting of the metallic coating deposited on the oxide surface by filler melt is defined by the following factors: coating thickness (amount of deposited metal) and structure (integral, insular), affinity of the coating metal to oxygen (film–substrate adhesion), dissolution of the coating in the melt, and wettability of the adhesive metal coating.

To use metallic coatings for brazing quartz with aluminum alloys, adhesive metal coatings (Mo, Cr, Nb, Ti) should be annealed at 900–1000°C and a holding time of 10 min. The thickness of the coatings should be within the ‘threshold’ range. Freshly deposited Cu and Ni coatings up to 10 nm thick are preferable for the second layer.

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