

# Wetting and Interface Microstructure in the System of Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> Based Ceramics/Nb-Containing Melts

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**Abstract:** Wettability and interface microstructure were studied for Nb-containing melts in the contact with ceramic oxide materials of Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> system. Ni-40.5 at.%Nb and Au-(0-20) at.%Nb alloys were investigated as prospective alloys for high temperature brazes. Ceramic samples ranged in composition from pure Al<sub>2</sub>O<sub>3</sub> to pure SiO<sub>2</sub>. The wettability was measured by the sessile drop method. Microstructure of the oxide/metal interface was investigated by scanning electron microscopy and X-ray diffraction methods. The results showed that contact angles decreased with the increase of SiO<sub>2</sub> content in the solid substrate for all the melts. Al<sub>2</sub>O<sub>3</sub> was dissolved insignificantly in the melts under study. SiO<sub>2</sub> formed intermediate chemical compounds at the interface with the melts: NbO, Nb<sub>6</sub>Ni<sub>6</sub>O and Nb<sub>5</sub>Si<sub>3</sub> with the Ni-based melt and NbO<sub>2</sub>, Nb<sub>2</sub>O<sub>5</sub> with the Au-based melt. Obtained results allow consideration of Nb alloys under study as high-temperature brazes for the Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> materials.

**Keywords:** Oxides, adhesion, wetting, niobium.

## 1. INTRODUCTION

Nb is a prospective metal for high temperature brazing of oxide ceramic materials. It possesses fairly high chemical affinity to oxygen and can be applied as an adhesion-active additive to inert brazing alloys. It should be noted that chemical affinity of Nb to oxygen is lower than that of Ti. This should prevent the formation of thick intermediate phase layers between filler metal and the ceramic and so should promote joint strength. Brazes, containing Nb as an adhesion-active element, have not yet been developed for oxide materials brazing.

Nowadays joining with Nb is performed most often by diffusion bonding. Ample research has been performed on investigation of mechanical properties and interface microstructures of diffusion-bonded alumina/niobium assemblies. Detailed review of the results on this subject can be found in [1-2]. In many cases, copper interlayer was applied to promote the Nb/Al<sub>2</sub>O<sub>3</sub> joint strength [1-2]. No reaction products were observed in the works [1, 3-5] after joining of niobium with single crystal alumina or polycrystalline alumina of high purity. NbO<sub>x</sub> layer was detected at the single crystal alumina/niobium interface in the work [6]. However, niobium silicides were observed at the niobium interfaces with low purity polycrystalline alumina [1, 7-9].

Literature data on the wettability of oxide materials by Nb-containing melt are not available except works [10-11]. According to [10], contact angle of Cu-1.4at.%Nb melt decreases to 20° on Al<sub>2</sub>O<sub>3</sub> substrate after 5 hours of exposure at 1150°C. Though, such low value of the contact angle can

be also referred to the melt evaporation during the long high-temperature test. According to [11], Nb improves wettability of Al<sub>2</sub>O<sub>3</sub> by medium Mn steel at the temperature 1600°C. Contact angle of the steel decreases from ca. 90° to ca. 37° with the addition of ~1.15 wt. % Nb.

Adhesion mechanism between pure niobium and aluminum oxide was discussed in the theoretical works [12, 13]. The authors showed the dominating role of the Nb-O bonds comparatively to Nb-Al bonds at the Al<sub>2</sub>O<sub>3</sub>/Nb interface. These theoretical findings are supported by the experimental detection of the NbO<sub>x</sub> layer at the single crystal alumina/niobium interface [6]. The nature of the bond for the SiO<sub>2</sub>/Nb systems has not been considered in the literature.

The purpose of the present work was to investigate the wettability, adhesion and interface microstructure of chosen Au-Nb and Ni-Nb melts in contact with Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> oxide materials (Fig. 1) and finding prospective Nb-containing alloys for the brazing of the oxides. The alloys for the study were chosen after consideration of the corresponding binary phase diagrams [14] and preliminary experimental investigations of some alloys with good Nb solubility and relatively low melting temperatures. Eutectic composition was chosen on the Ni-Nb phase diagram (Ni-40.5 at.%Nb, melting point 1175 °C). Several compositions were chosen on the Au-Nb phase diagram in the range 0-20 at.%Nb (Au-0.9 at.%Nb, melting temperature ~1070 °C; Au-4.5 at.%Nb, melting temperature ~1140 °C; Au-7.5 at.%Nb, melting temperature ~1150 °C; Au-10 at.%Nb, melting temperature ~1200 °C; Au-20 at.%Nb, melting temperature ~1320 °C).

Capillary and contact phenomena at the interaction of Ni-Nb and Au-Nb melts with Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> materials are of practical and theoretical interests due to wide applications of these oxides in industry (high temperature insulators, refractory materials etc.).

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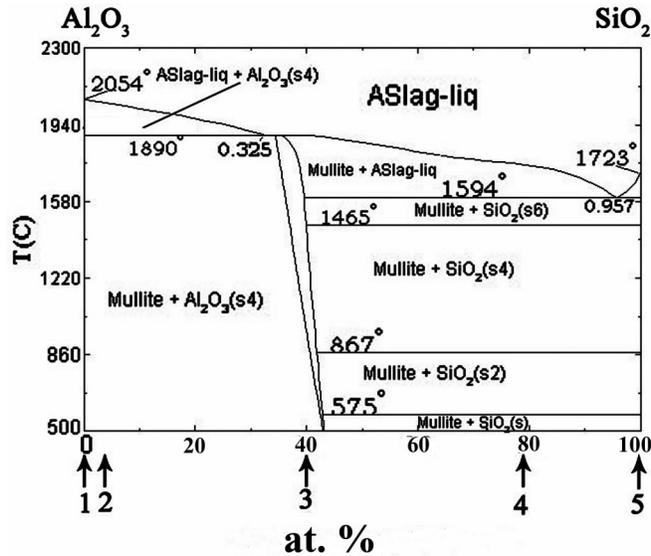


Fig. (1). Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> binary phase diagram and the solid substrate compositions (1 - sapphire, 2 - ceramic VK-94-1, 3 - mullite, 4 - hard porcelain, 5 - quartz glass).

## 2. EXPERIMENTAL TECHNIQUES

Modified equipment [15] was employed to perform wettability tests and surface tension measurements. Experiments were performed in vacuum  $\sim 1\text{-}3 \times 10^{-3}$  Pa. Reported contact angles were measured by the sessile drop method during  $\sim 30\text{-}60$  min isothermal exposure at the temperatures 1100-1350 °C. Also, advancing and receding contact angles were observed for several systems during immersion of the oxide plate into the melt with subsequent its extraction at the experimental temperature. Size of the immersed plates was  $\sim 20 \times 5 \times 1.5$  mm.

Interface microstructure was studied for some samples by optical microscopy, scanning electron microscopy (SEM) and X-ray diffraction methods (XRD). Superprobe 733 and X-ray diffractometer of DRON type were used for the study. SEM images were taken from the cross-sections of solidified sessile drop samples or from a surface of the Au-7.5 at.%Nb/SiO<sub>2</sub> sample. X-ray patterns were taken from the surface of the oxide for the Au-7.5 at.%Nb/SiO<sub>2</sub> sample and from powder of reaction products for the Ni-40.5 at.%Nb/SiO<sub>2</sub> sample. Detailed description of the sample preparations for the XRD analysis will be given in the chapters 3.1.2 and 3.2.2.

Oxide substrates ranged in composition from pure Al<sub>2</sub>O<sub>3</sub> to pure SiO<sub>2</sub> (Fig. 1): leucosapphire (Al<sub>2</sub>O<sub>3</sub>), ceramic VK-94-1 (92Al<sub>2</sub>O<sub>3</sub> - 5SiO<sub>2</sub>, at.%), mullite (60Al<sub>2</sub>O<sub>3</sub> - 40SiO<sub>2</sub>, at.%), hard porcelain (20Al<sub>2</sub>O<sub>3</sub> - 77SiO<sub>2</sub>, at.%), quartz glass (SiO<sub>2</sub>). Ceramic VK-94-1, mullite and hard porcelain contained insignificant amounts of other oxides than Al<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub>. The influence of these other oxides on the wettability was insignificant due to their low concentration. All substrates were polished up to Ra $\sim 0.01$   $\mu\text{m}$  prior to the tests and were cleaned ultrasonically with acetone and alcohol.

Vacuum melted niobium (99.9%), gold (99.99%) and electrolytic nickel (99.99%) were used for the study. Ni-40.5 at.%Nb alloy was prepared preliminary by co-melting the

components. Au-Nb alloys (Au-0.9 at.%Nb, Au-4.5 at.%Nb, Au-7.5 at.%Nb, Au-10 at.%Nb, Au-20 at.%Nb) were co-melted in situ during the wettability tests. Drop masses were  $\sim 200\text{-}500$  mg.

The work of adhesion was calculated using the equation:

$$Wa = \sigma_{lv} (1 + \cos\theta) \quad (1)$$

where  $Wa$ - work of adhesion,  $\sigma_{lv}$ - surface tension of the melt,  $\theta$ - contact angle.

Surface tension for the Ni-40.5 at.%Nb melt was measured at 1250-1300 °C by the large drop method.

Surface tension of the Au-Nb melts was calculated at 1300 °C using equation for an ideal solution [16]:

$$\sigma = \sigma_i + (RT/\omega_i) \ln(x_{i\omega}/x_i) \quad (2)$$

where  $\sigma$  is the surface tension of the solution,  $\sigma_i$  is the surface tension of a pure component  $i$ ,  $R$  is the gas constant,  $T$  is temperature,  $\omega_i$  is the area occupied by a mole of the component  $i$  as a monomolecular layer,  $x_i$  and  $x_{i\omega}$  are molar parts of the component  $i$  in a bulk of the solution and in the surface layer respectively. Surface tension data for pure liquid Au and Nb were taken from [17] (1137 mJ/m<sup>2</sup> and 1840 mJ/m<sup>2</sup> respectively).

## 3. RESULTS

### 3.1. The Wettability and Contact Interaction of Ni-40.5 at.%Nb Alloy with Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> Oxides

Fig. (2) presents data on the wettability of the oxides by the melt depending on SiO<sub>2</sub> content in the solid substrate (1250 °C). The wettability improves with the increase of SiO<sub>2</sub> content in the oxide from  $\sim 90^\circ$  for Al<sub>2</sub>O<sub>3</sub> to  $\sim 9^\circ$  for SiO<sub>2</sub>.

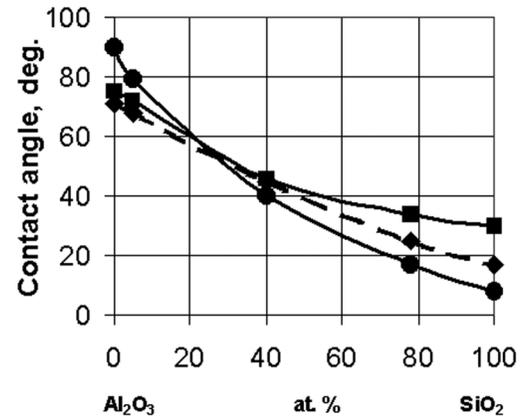


Fig. (2). Wettability of the Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> oxides by Nb-containing melts in dependence on SiO<sub>2</sub> content in the oxide (● - Ni-40.5 at.%Nb, 1250 °C; ■ - Au-10 at.%Nb, 1250 °C; ◆ - Au-20 at.%Nb, 1320 °C).

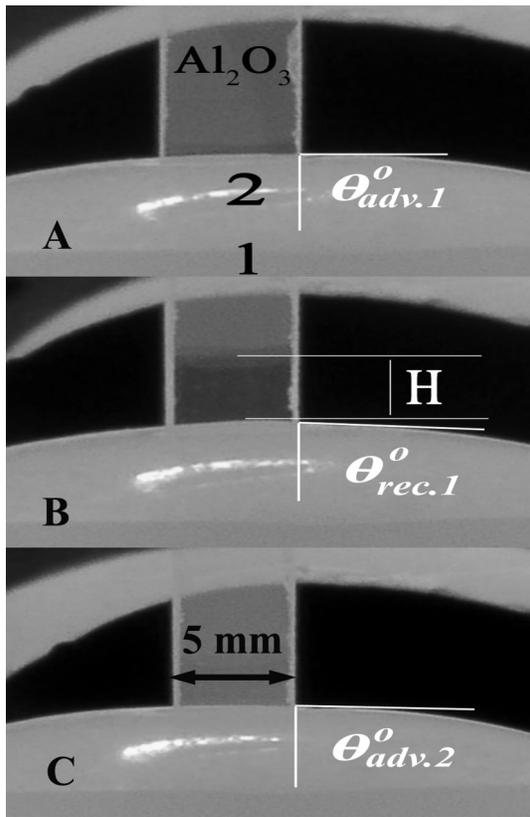
Surface tension was measured for the Ni-40.5 at.%Nb melt at 1250-1300 °C. The 1610 mJ/m<sup>2</sup> value was obtained.

The detailed study was performed for the Ni-40.5 at.%Nb/Al<sub>2</sub>O<sub>3</sub> and Ni-40.5 at.%Nb/SiO<sub>2</sub> systems.

#### 3.1.1. Ni-40.5 at.%Nb/Al<sub>2</sub>O<sub>3</sub> System

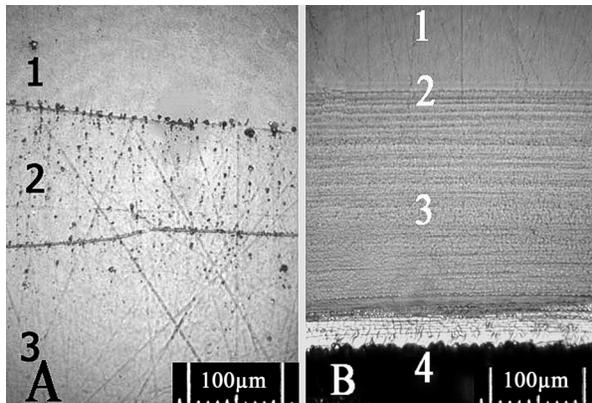
Contact angle of the melt on sapphire was  $93 \pm 3^\circ$  at the melting point (1175 °C). The further heating up to 1250 °C resulted in minor contact angle decrease to  $90 \pm 3^\circ$ .

Advancing and receding contact angles were observed at 1250 °C at the immersion and extraction of the vertical sapphire plate into the melt. Hysteresis of the advancing and receding contact angles was insignificant  $\sim 3\text{-}6^\circ$  (Fig. 3).



**Fig. (3).** Wettability of the vertical sapphire plate by Ni-40.5at.%Nb melt at 1250 °C: (A) the initial plate immersion, advancing contact angle  $\theta_{adv.1}$ , 1- alumina crucible, 2- melt; (B) the plate extraction, receding contact angle  $\theta_{rec.1}$ , H- length of the extracted plate; (C) the second plate immersion  $H_1 < H$ , advancing contact angle  $\theta_{adv.2}$ .

Image of the sapphire surface subjected to 45 min contact with the melt at 1250 °C is shown on Fig. (4A). Optical Light Microscopy observations revealed the evidences of the slight dissolution of the oxide in the melt.

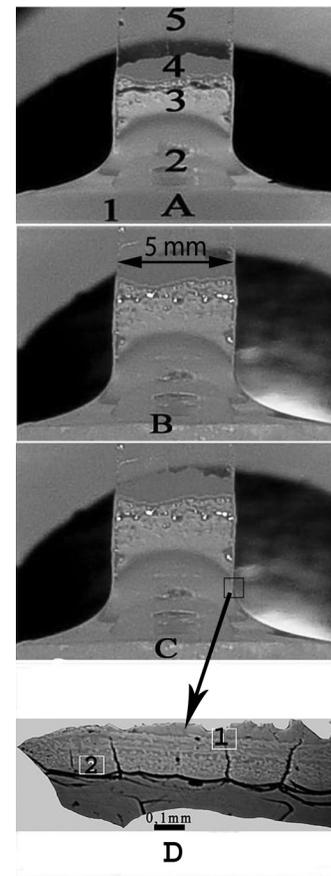


**Fig. (4).** Top view of sapphire substrates subjected to 45 min contact with the melts at 1250 °C: (A) with Ni-40.5at.%Nb melt, (B) with Au-7.5at.%Nb melt, 1- the surface, which was not in the contact with the melt, 2- the perimeter of the wetting, 3- the wetting zone, 4- the edge of the Au-7.5at.%Nb drop.

### 3.1.2. Ni-40.5at.%Nb/SiO<sub>2</sub> System

Temperature dependence of the contact angle was registered. The contact angle was  $27 \pm 3^\circ$  at the melting point (1175 °C) and decreased to  $9 \pm 2^\circ$  with temperature rise to 1250 °C.

Advancing and receding contact angles were observed at 1250 °C at the immersion and extraction of the vertical quartz plate into the melt. Advancing contact angle  $\sim 9^\circ$  was formed within 3-5 min after the immersion (Fig. 5A). The formation of a layer of solid reaction products was observed at the perimeter of the wetting after  $\sim 5$  min of the isothermal exposure (Fig. 5A, zones 3-4). The layer of the reaction products grew with time and enhanced significantly the roughness of the plate (Figs. 5B, C). Excessive plate roughness did not allow the measuring of the receding contact angle. Interface reaction products were formed in macro quantities and detached from the quartz surface after cooling. A typical detached part of the reaction products is presented on the Fig. (5D).



**Fig. (5).** Wettability of the vertical quartz glass plate by Ni-40.5at.%Nb melt at 1250 °C: (A)  $\tau=5\text{ min}$ , 1- alumina crucible, 2- the melt, 3- the interaction products, 4- a view of the interaction products through the glass, 5- the plate without the melt; (B)  $\tau=15\text{ min}$ ; (C)  $\tau=30\text{ min}$ ; (D) a typical fragment of the reaction layer detached from the quartz after cooling, 1- the melt/interaction products boundary, 2- the quartz glass/interaction products boundary.

The detached reaction products were collected and powdered for further investigation by XRD analysis. The

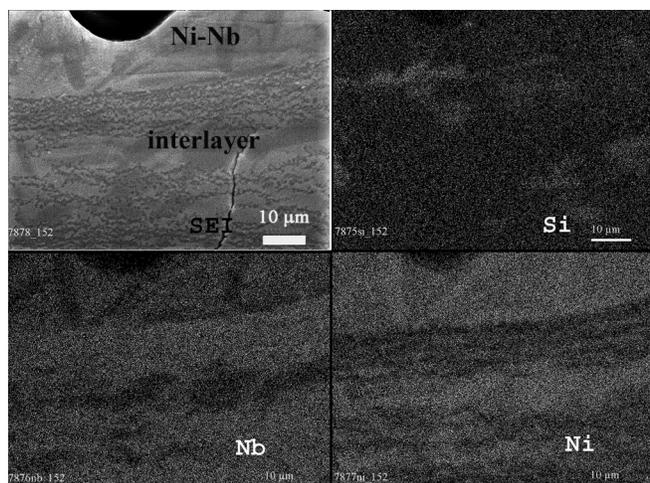
main components, which have been revealed in the powder, are listed below as well as their crystal lattice parameters:

- Nb<sub>6</sub>Ni<sub>6</sub>O - ~34wt.%, a = 1,11809 nm (cubic structure),
- NbO - ~ 9.3wt.%, a = 0,42182 nm (cubic structure),
- Nb<sub>5</sub>Si<sub>3</sub> - ~ 11,2 wt.%, a = 1,00313 nm, c = 0,51872 nm (tetragonal structure),
- SiO<sub>2</sub> (Q) - ~ 3,4%, a = 0,49052 nm, c = 0,54040 nm (hexagonal structure);
- NbNi<sub>3</sub> - ~11,8wt.%, a - 0,5215 nm, b = 0,42636 nm, c = 0,45329 nm (rhombic structure),
- Nb<sub>7</sub>Ni<sub>6</sub> - ~ 30,5 wt.%, a = 0,48759 nm, c = 2,65400 nm (tetragonal structure).

It should be noted that Nb<sub>6</sub>Ni<sub>6</sub>O is an isostructural phase with lattice parameters similar to Nb<sub>3</sub>Ni<sub>2</sub>Si phase [18-19]. Structure Nb<sub>6</sub>Ni<sub>6</sub>O is more probable for the case under the study due to molar balance of interface reaction products. Namely, general molar ratio Si/O should be ~1/2 for all interaction products (similar to molar Si/O ratio for SiO<sub>2</sub>).

SEM investigations were performed for the cross-sections of two regions of the interaction layer: 1) melt/interaction products boundary; 2) quartz glass/interaction products boundary (areas 1 and 2 on the Fig. (5D) respectively).

Element distributions at the melt/interaction products boundary showed (Fig. 6) that interface possessed layered structure with alterations of Nb-rich and Ni-rich regions and includes Si-rich regions.



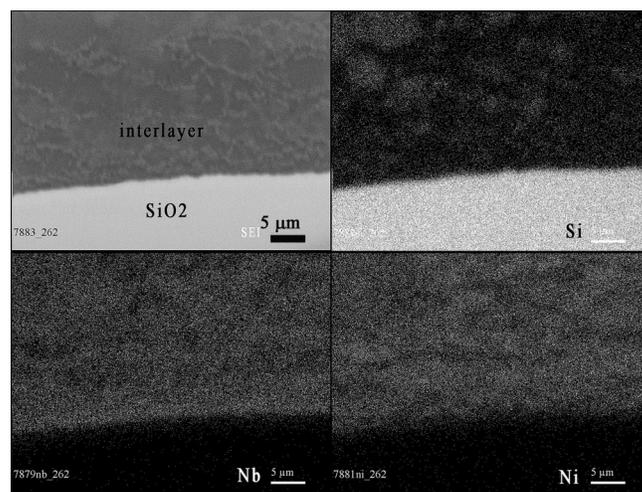
**Fig. (6).** SEI image of the interface microstructure for SiO<sub>2</sub> in contact with Ni-40,5at%Nb melt and corresponding elemental X-ray maps (the melt/interaction products boundary).

Similar element distributions were observed at the quartz glass/interaction products boundary (Fig. 7). The difference from the above interface is a more uniform distribution of Nb and Ni and higher Si content.

### 3.2. The Wettability and Contact Interaction of Au-Nb Alloys with Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> Oxides

The wettability of the oxides by Au-10 at.%Nb and Au-20 at.%Nb melts is plotted in Fig. (2) as a function of the SiO<sub>2</sub> content in the solid substrate. The wettability improves with the increase of SiO<sub>2</sub> concentration in the oxide, which is

similar to the data for the Ni-40.5 at.%Nb melt. Contact angles decrease from ~75° and ~71° on sapphire to ~30° and ~18° on quartz glass with additions of 10 at.%Nb and 20 at.%Nb respectively.



**Fig. (7).** SEI image of the interface microstructure for SiO<sub>2</sub> in contact with Ni-40,5at%Nb melt and corresponding elemental X-ray maps (SiO<sub>2</sub>/interaction products boundary).

Values of the surface tension 1160 mJ/m<sup>2</sup> and 1226 mJ/m<sup>2</sup> at 1300 °C were obtained by calculations for Au-10 at.%Nb and Au-20 at.%Nb melts.

The detailed study was performed for the Au-Nb/Al<sub>2</sub>O<sub>3</sub> and Au-Nb/SiO<sub>2</sub> systems.

#### 3.2.1. Au-Nb/Al<sub>2</sub>O<sub>3</sub> System

Table 1 presents concentration and temperature dependencies of the contact angles for the Au-Nb melts/sapphire systems. Wettability improves with the increase of Nb concentration in the melt. Contact angles decrease slightly with the temperature rise.

Insignificant movement of the drop of the Au-7.5 at.%Nb melt over sapphire surface was observed at 1250 °C when the time of the isothermal exposure exceeded 30 minutes. The movement led to the appearance of a drop trace on the oxide surface. Usually the dimension of the drop trace was ~0.2-0.3 mm. The drop trace was investigated with Optical Light Microscopy. Indications of sapphire dissolution were observed (Fig. 4B).

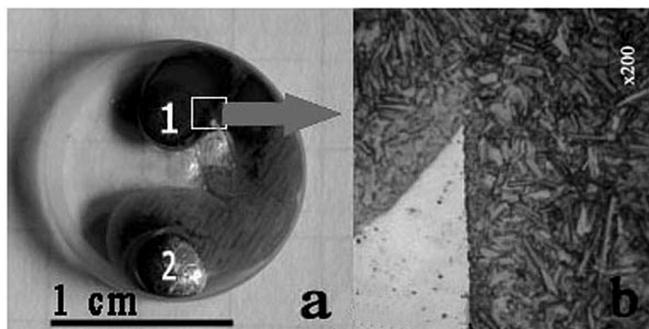
**Table 1.** Wettability Contact Angles (Degrees) of Au-Nb Melts on Sapphire and Quartz Glass

		Nb, at%			
		0,9	4,5	7,5	10
Sapphire	1150°C	130	90	90	-
	1250°C	130	88	76	75
Quartz glass	1150°C	-	48	-	-
	1250°C	-	46	45	30

#### 3.2.2. Au-Nb/SiO<sub>2</sub> System

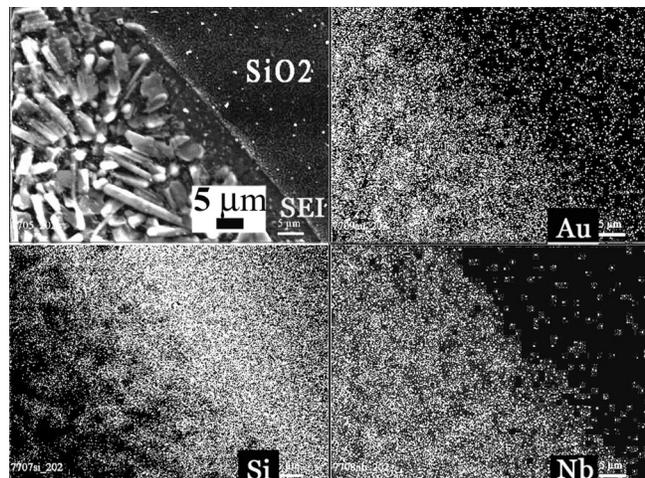
Data on the wettability of SiO<sub>2</sub> by Au-Nb melts are also listed in the Table 1. Similar to Al<sub>2</sub>O<sub>3</sub>, contact angles decrease with the increase of Nb concentration in the melt.

The movement of the Au-7.5 at.%Nb melt over SiO<sub>2</sub> surface was observed at 1250 °C and isothermal exposure exceeding 30 minutes. The movement of the drop on the SiO<sub>2</sub> surface was more pronounced than on the Al<sub>2</sub>O<sub>3</sub> surface. Macro-trace of the drop (~1 cm) was observed after ~45 minutes of the exposure (Fig. 8). Composition and structure of the drop trace were investigated in detail to define interaction products formed directly at the experimental temperature.



**Fig. (8).** Top view of the of the Au-7.5at.%Nb drop trace on SiO<sub>2</sub> surface: (a) the drop moved from position 1 to position 2 at 1250 °C,  $\tau=45$  min ; (b) optical light image of the area 1 microstructure,  $\times 200$ .

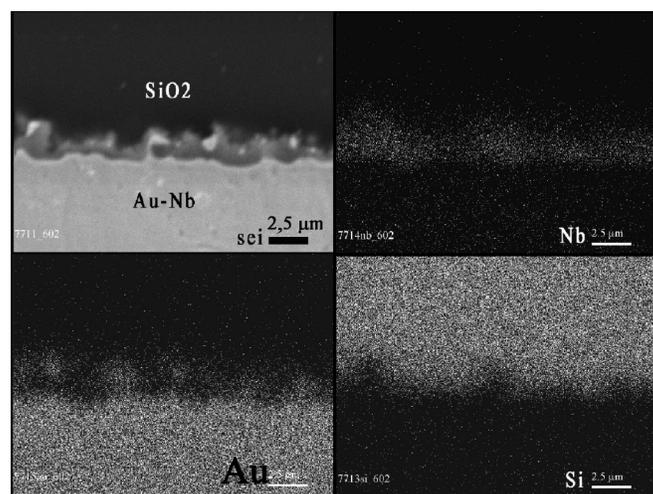
SEI image of the drop trace is presented on the Fig. (9). It demonstrates that the interaction products were formed in the shape of elongated crystals on SiO<sub>2</sub> surface. X-ray elemental maps revealed the expected presence of Nb, Au and Si in the interaction layer.



**Fig. (9).** Top view (SEI image) of the Au-7.5at.%Nb drop trace at the boundary with quartz glass and corresponding elemental X-ray maps.

X-ray phase analysis from the surface of the drop trace showed, that the main surface phase is NbO<sub>2</sub> (tetragonal crystal system,  $a = 1,36483$  nm,  $c = 0,59642$  nm). Nb<sub>2</sub>O<sub>5</sub> phase ( $a = 2,11676$  nm,  $b = 0,38542$  nm,  $c = 1,92306$  nm,  $\beta = 120,2210$  degrees) and Au traces were also observed in the region under study.

Elemental maps for the cross-section of the Au-7.5 at.%Nb/SiO<sub>2</sub> sessile drop sample showed segregation of Nb at the melt/quartz interface (Fig. 10).



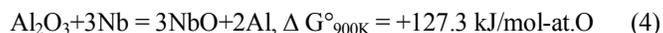
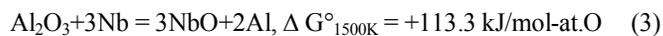
**Fig. (10).** SEI image of the interface microstructure for SiO<sub>2</sub> in contact with Au-7.5at.%Nb melt and corresponding elemental X-ray maps.

#### 4. DISCUSSION

High temperature wettability of oxides by liquid alloys is usually accompanied by chemical interaction at the solid/liquid interface. Chemical interaction means dissolution of the oxide in the wetting melt, formation of solid reaction products at the interface, etc. Wettability level and work of adhesion mainly depend on the Gibbs energy decrease during such interaction. Though, they can be also promoted by the metallic type of chemical bond of solid interaction products adjacent to the interface [15, 20, 21].

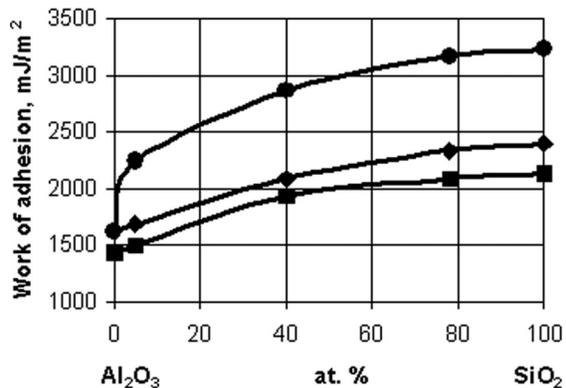
Au, Ni/Al<sub>2</sub>O<sub>3</sub> and Au, Ni/SiO<sub>2</sub> systems are well known as non-reactive systems with contact angle exceeding  $\sim 120^\circ$  [21]. Nb has been added to Au and Ni melts in the present work to promote chemical interaction of the melts with the substrates and thus to promote the wettability.

Experimental results showed that Nb improves the wettability of sapphire by Au and Ni melts (Fig. 2), though the contact angle values exceed  $60^\circ$ . It should be noted that Au-Nb and Ni-Nb melts similarly interact with Al<sub>2</sub>O<sub>3</sub>. Some dissolution of the oxide was evident (Fig. 4). New chemical compounds were not observed at the interfaces. Obviously, chemical reactions at the interface and so the formation of new compounds are hampered with high thermodynamic stability of the aluminum oxide. The expected interface reactions possess high positive values of the Gibbs energies and cannot proceed [22, 23]:



The following physico-chemical explanation can be proposed to clear positive influence of Nb on the wettability of Al<sub>2</sub>O<sub>3</sub> by Au and Ni melts. Au-Nb and Ni-Nb melts dissolve Al<sub>2</sub>O<sub>3</sub> (Fig. 4). The dissolution leads to transition of some oxygen from the substrate to the melts. This oxygen participates further in the formation of niobium-oxygen clusters in the melts [21]. Chemisorption of the clusters at the interfaces promotes the wettability. It can be supposed that Ni-based and Au-based alloys possess the similar work

of adhesion to sapphire (Fig. 11) due to the similar interface interaction with it.



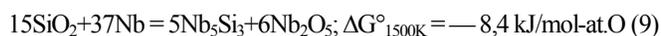
**Fig. (11).** Work of adhesion of the Nb-containing melts to the Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> oxides in dependence on SiO<sub>2</sub> content in the oxide (● - Ni-40.5at.%Nb, 1250 °C; ■ - Au-10at.%Nb, 1250 °C; ◆ - Au-20at.%Nb, 1320 °C).

The work of adhesion increases with the increase of SiO<sub>2</sub> content in the substrate (Fig. 11). That results from an intensification of the chemical reactivity at the interface due to lower thermodynamic stability of SiO<sub>2</sub> comparatively to Al<sub>2</sub>O<sub>3</sub>. Data on the microstructure investigation revealed the formation of new chemical compounds at the Au-Nb and Ni-Nb interfaces with SiO<sub>2</sub>.

It is necessary to note that thermodynamic affinity of silicon to oxygen is still higher than that of niobium and the reaction below is not thermodynamically favorable [23]:



However, there are reactions with the simultaneous formation of niobium oxides and silicides, possessing negative values of the Gibbs energies [23]:



Thus, silica can react with Nb-containing melt with the simultaneous formation of niobium oxide and silicide. Such processes are thermodynamically favorable.

Indeed, the data of the SEM observations and X-ray phase analysis showed that both Au- and Ni-based melts react with the SiO<sub>2</sub> substrate intensively. The reaction products, corresponding to the equations (7-9), were revealed at the interfaces. Namely, Ni-40.5 at.%Nb/SiO<sub>2</sub> interface contains NbO and Nb<sub>5</sub>Si<sub>3</sub>. Au-7.5 at.%Nb/SiO<sub>2</sub> interface contains NbO<sub>2</sub> and Nb<sub>2</sub>O<sub>5</sub> (Nb silicides were not detected which can be attributed to their dissolution in the melt).

Additional research was performed on the wettability of Nb<sub>5</sub>Si<sub>3</sub> substrates by Ni-40.5 at.%Nb melt to prove that the formation of the interface compound with metallic type of chemical bond promotes the wettability. Nb<sub>5</sub>Si<sub>3</sub> for the tests was obtained by melting the components in electro-arc furnace in purified Ar atmosphere. The obtained slab was cut into plates ~10x13 mm. The plates were polished and annealed in vacuum 10<sup>-3</sup>Pa at 1250 °C prior to the experiments. The results showed that Nb<sub>5</sub>Si<sub>3</sub> is wetted well by the melt. The contact angle was ~25° at melting

temperature (1175 °C) and decreased to ~13±2° with the temperature rise to 1250 °C. So, the formation of the Nb<sub>5</sub>Si<sub>3</sub> (compound with metallic type of chemical bond) at the interface assists the wettability.

Obviously, good wettability and high work of adhesion, observed for the (Ni-Nb)/SiO<sub>2</sub> system, result from complex action of two factors: 1) the decrease of the Gibbs energy during interface interaction; 2) the formation of the metallic compounds Nb<sub>6</sub>Ni<sub>6</sub>O, NbO, Nb<sub>5</sub>Si<sub>3</sub> at the interface that promote the wettability. In contrast to the Ni-based melt, Au-based melts form NbO<sub>2</sub> and Nb<sub>2</sub>O<sub>5</sub> oxides that are rather ionic compounds and so do not assist the wettability. The contact angle and the work of adhesion for the (Au-Nb)/SiO<sub>2</sub> system are defined by the chemical reactivity (the Gibbs energy decrease) during the interface interaction.

The hypothetical explanation can be proposed to interpret the differences in the interface product compositions formed by the Au-based and Ni-based alloys. Au-based melts contained less Nb, than Ni-based melts. Also, the oxygen removal from the contact zone was more problematic for the Au-based melt than for the Ni-based melt as the solubility of oxygen in Ni exceeds significantly its solubility in Au. Lower solubility of oxygen in Au led to comparatively higher oxygen concentration at the contact zone Au-Nb/SiO<sub>2</sub> than at the contact zone Ni-Nb/SiO<sub>2</sub>. Higher oxygen concentration in combination with lower concentration of niobium resulted in the formation of Nb oxides with higher oxygen content at the boundary with Au-based melt (NbO<sub>2</sub> and Nb<sub>2</sub>O<sub>5</sub>) comparatively to oxides with lower oxygen content at the boundary with Ni-based melt (Nb<sub>6</sub>Ni<sub>6</sub>O and NbO).

The intensive movement of the Au-7.5 at.%Nb drop over SiO<sub>2</sub> surface was observed during long isothermal exposure at 1250 °C (Fig. 8). Probably the movement results from the different wettability of lower and higher Nb-oxides by the melt. Namely, lower niobium oxides are formed at the initial stage of the wettability. These oxides are wetted well by the melt. Later, a saturation of the oxides with oxygen takes place and their wettability decreases [15, 20]. Any chaotic contact of the drop with “fresh” SiO<sub>2</sub> surface leads to the formation of a new layer of the lower oxides, which is wetted better by the melt. Advancing contact angle onto the new-formed surface is lower than receding contact angle from previously formed interface, which initiates the drop displacement. Probably, the movement of the drop is hardly noticeable at short time of the isothermal exposure due to insufficient time for the saturation of the reaction products with oxygen.

Therefore, the work of adhesion for the systems under study depends on the type of chemical interaction at the interface and type of the solid interface interaction products. The formation of the different oxides at the interfaces Ni-40.5 at.%Nb/SiO<sub>2</sub> and Au-7.5 at.%Nb/SiO<sub>2</sub> results from the different solubility of oxygen and the different Nb content in the melts.

## CONCLUSION

1. The wettability of oxide materials of the Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> system by Ni-40.5 at.%Nb and Au-(0-20) at.%Nb melts was investigated. The wettability improves and the work of adhesion increases with the increase of

- SiO<sub>2</sub> content in the oxides. That is explained by the more intensive chemical interaction of the melts with SiO<sub>2</sub> possessing the lower thermodynamic stability than Al<sub>2</sub>O<sub>3</sub>.
- SiO<sub>2</sub> reacts with the melts with the formation of the following compounds: Nb<sub>5</sub>Si<sub>3</sub>, Ni<sub>3</sub>Nb, NbO, Ni<sub>6</sub>Nb<sub>6</sub>O with the Ni-40.5 at.%Nb melt; NbO<sub>2</sub>, Nb<sub>2</sub>O<sub>5</sub> with the Au-7.5 at.%Nb melt. Al<sub>2</sub>O<sub>3</sub> is dissolved insignificantly in the both melts.
  - The work of adhesion and the wettability for the silica-containing oxides depend not only on the chemical reactivity during the interface interaction, but also on the type of solid interaction products formed at the interface. Namely, Ni-40.5 at.% Nb melt forms compounds with rather metallic type of chemical bond (Nb<sub>5</sub>Si<sub>3</sub>, Ni<sub>6</sub>Nb<sub>6</sub>O, NbO) which additionally promote the wettability and the work of adhesion.

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#### CONFLICT OF INTEREST

None declared.

#### REFERENCES

- J. T. McKeown, J. D. Sugar, R. Gronsky, and A. M. Glaeser, "Effects of impurities on alumina-niobium interfacial microstructures", *Mater. Charact.*, vol. 57, pp. 50-57, July 2006.
- R. A. Marks, J. D. Sugar, and A. M. Glaeser, "Ceramic Joining: IV. Effects of processing conditions on the properties of alumina joined via Cu/Nb/Cu interlayers", *J. Mater. Sci.*, vol. 36, pp. 5609-5624, December 2001.
- M. Florjancic, W. Mader, M. Rule, and M. Turwitt, "HREM and diffraction studies of an Al<sub>2</sub>O<sub>3</sub>/Nb interface", *J. Physiol. (Paris)*, vol. 46 (C4), pp. 129-133, August 1985.
- M. L. Shalz, B. J. Dalgleish, A. P. Tomsia, R. M. Cannon, and A. M. Glaeser, "Ceramic Joining: III. Bonding of alumina via Cu/Nb/Cu interlayers", *J. Mater. Sci.*, vol.29, pp. 3678-3690, January 1994.
- D. Knauss and W. Mader, "Chemical composition and lattice relaxation at diffusion-bonded Nb/Al<sub>2</sub>O<sub>3</sub> interface", *Ultramicroscopy*, vol. 37, pp. 247-262, August 1991.
- S. Morozumi, M. Kikuchi, and T. Nishino, "Bonding mechanism between alumina and niobium", *J. Mater. Sci.*, vol. 16, pp. 2137-2144, August 1981.
- G. Ellsner, D. Korn, and M. Ruhle, "The influence of interface impurities on fracture energy of UHV diffusion bonded metal-ceramic bicrystals", *Scr. Metall. Mater.*, vol. 31, pp. 1037-1042, April 1994.
- D. Korn, G. Ellsner, H. F. Fischmeister, and M. Ruhle, "Influence of interface impurities on the fracture energy of UHV bonded niobium sapphire bicrystals", *Acta Metall. Mater.*, vol. 40, pp. S355-360, January 1992.
- J. J. Kruzic, R. A. Marks, M. Yoshiya, A. M. Glaeser, R. M. Cannon, and R. O. Ritshie, "Fracture and fatigue behavior at ambient and elevated temperatures of alumina bonded with copper/niobium/copper interlayers", *J. Amer. Ceram. Soc.*, vol. 85, pp. 2531-2541, October 2002.
- A. P. Tomsia, E. Saiz, N. Sobczk, S. Foppiano, and R. M. Cannon, "Reactive wetting: Ridging, adsorption and compound formation", in *Second International Conference on High Temperature Capillarity*, N. Eustathopoulos and N. Sobezk1998, pp. 59-80.
- Y. U. Sirong, L. U. Yaohui, and H. E. Zhenming, "Effect of Nb on the interfacial wettability in Al<sub>2</sub>O<sub>3</sub>/medium Mn steel", *J. Mater. Sci. Technol.*, vol. 19, pp. 625-627, November 2003.
- W. Zhang, and I. R. Smith, "Stoichiometry and adhesion of Nb/Al<sub>2</sub>O<sub>3</sub>", *Phys. Rev. B*, vol. 61, pp. 16883-16889, June 2000.
- I. G. Batirev, A. Alavi, M. W. Finnis, and T. Deutsch, "First-principles calculations of the ideal cleavage energy of bulk Niobium(111)/  $\alpha$ -Alumina(0001) interfaces", *Phys. Rev. Lett.*, vol. 82, pp. 1510-1513, February 1999.
- T. B. Massalski and H. Okamoto, *Binary alloy phase diagrams*. OH: ASM International/Materials Park, 1990.
- Yu. V. Naidich, V. S. Zhuravlev, V. G. Chuprina, and L. V. Strashinskaya, "Adhesion wetting and formation of intermediate phases in systems composed of a titanium-containing melt and oxide", *Powder Metall. Metal Ceram.*, vol. 12, pp. 895-899, November 1973.
- A. A. Zhuhovitskiy, "Surface tension of solutions", *Zhurnal Fizycheskoy Himii*, vol. 18, pp. 214-233, July 1944. (in Russian)
- V. N. Eremenko, *Physical chemistry of inorganic materials*, Vol. 2. Kiev: Naukova Dumka, 1988. (in Russian).
- R. Mackay, G. J. Miller, and H. F. Franzen, "New oxides of the filled-Ti<sub>2</sub>Ni type structure", *J. Alloys Compounds*, vol.204, pp. 109-118, February 1994.
- U. I. Gladyshevskiy, Yu. V. Kuz'ma, and P. I. Kripyakevitch, "The crystal structures of Mn<sub>3</sub>Ni<sub>2</sub>Si, V<sub>3</sub>Ni<sub>2</sub>Si, Nb<sub>3</sub>Ni<sub>2</sub>Si and related Cr and Ta compounds", *J. Struct. Chem.*, vol. 4, pp. 343-355, May 1963.
- Yu. V. Naidich, V. S. Zhuravlev, and V. G. Chuprina, "Adhesion wetting and formation of intermediate phases in systems composed of a titanium-containing melt and an oxide", *Powder Metall. Metal Ceram.*, vol. 13, pp. 236-238, March 1974.
- Yu. V. Naidich, "The wettability of solids by liquid metals", in *Progress in Surface and Membrane Science*, D. A. Cadenhead and J. F. Danielli, Eds., Academic Press: New York, 1981, pp. 354-370.
- A. G. Malets, "Thermodynamic properties of the niobium aluminides", *Veszi AN BSSR, Chimiya*, pp. 127-129, May 1974. (in Belorussian).
- FACT. Fact-Web. Reaction-Web - properties of a species or chemical reaction. [Online]. Available: <http://www.crct.polymtl.ca/fact/> [Accessed June 8, 2011].

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