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Effect of Ti, Nb, and Ti + Nb Coatings on the Bond Strength-Structure Relationship in Al/Al_2O_3 Joints

Marzanna Ksiazek, Maria Richert, Aam Tchorz, and Lukasz Boron

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There is a growing interest in metal-ceramic bonding for wide range of applications in electronic devices and high technology industry for fabrication of metal matrix composites and bonding of ceramic components to metals. The object of the work was to study the effect of Ti, Nb, and Ti + Nb thin films deposited by PVD method on alumina substrates on structure and bond strength properties of Al/Al_2O_3 joints. The joints were fabricated using the results of a wetting experiment and the sessile drop method at a temperature of 1223 K in a vacuum of 0.2 MPa for 30 min of contact. The structure of the metal/ceramic interface was investigated using scanning electron microscopy. The elemental distribution at the metal-ceramic interface was analyzed using energy dispersive x-ray spectroscopy. Transmission electron microscopy was also used to investigate some aspects of the metal/ceramic interface. The bond strength properties of joints were measured using shear test. The shear strength results demonstrated significant improvement of shear strength of Al/Al_2O_3 joints due to the application of Ti + Nb thin film on alumina substrate. Microstructural investigations of the interface indicated that Al/coating/Al_2O_3 couples have diffusion transition interface which influences the strengthening of these joints. A conclusion could be drawn that the presence of thin film layers changes the character of interaction and leads to the formation of new reaction products in the bonding layer.

Keywords coatings, joining, surface engineering

1. Introduction

The growing popularity of technical solutions that offer metal-ceramic joints is mainly due to the fact that we obtain a combination of materials characterized by different structures and physico-chemical properties. Therefore metal-ceramic joints are widely used by different sectors of industry as both functional and structural materials (Ref 1). When bonding together alumina and metals, the main problem is to ensure reliable joints. It is well known that in the liquid phase technology of metal-ceramic joint fabrication, applying the deposition of thin metallic films on ceramic surface can improve wetting, interface structure, and bonding strength properties of metal-alumina joints (Ref 2-4). The increase of bond strength is due to hardening of metal-ceramic interface through formation of intermediate diffusion-type layers. Yet, we should remember that a strong and fast bond between the metal and the ceramic material can be produced only when the system has proper wettability, i.e., the ability to coat the surface of ceramics with a continuous film of metal. This is possible, on one hand, through control of the temperature- and time-related parameters of the bonding process and, on the other, through optimizing of this process by metallization of the ceramic material surface. The purpose of this work was to study the effect of Ti, Nb, and Ti + Nb thin film on alumina on the bond strength properties and interface structure in Al/Al_2O_3 joints.

2. Experimental Procedure and Materials

The following materials were used in the investigations: aluminum (99.9999 wt.%) and polycrystalline alumina acting as a substrate, fabricated at the Faculty of Materials Science and Ceramics, University of Science and Technology in Kracow. The polycrystalline alumina substrates were prepared from powders of the following starting composition: 99.9085% α-Al_2O_3, 0.009% CaO, 0.053% SiO_2, 0.0029% MgO, 0.023% Fe_2O_3, and 0.0036% Na_2O. Blocks ($\varnothing 17 \times 25$ mm) were produced by casting in molds under pressure (200 MPa) and sintered at the temperature 1923 K for 2 h. Substrates ($\varnothing 17 \times 5$ mm) were cut from sintered blocks using a diamond saw. The alumina substrate was characterized by the following physical and mechanical properties: porosity—almost 0%, density—3.8 g/cm^3, Young's modulus—300 GPa, Poisson ratio—0.24.

To produce a bond between the ceramic substrate and the metal, a wettability experiment was carried out by the sessile drop method. The wettability experiment was carried out at the temperature of 1223 K for of 30 min in dynamic vacuum of

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Marzanna Ksiazek, Aam Tchorz, and **Lukasz Boron**, Complex of Research Laboratories, Foundry Research Institute, 73 Zakopianska St., 30-418 Krakow, Poland; and **Maria Richert**, University of Science and Technology, 30 Mickiewicza Ave., 30-059 Krakow, Poland. Contact e-mail: marzena@iod.krakow.pl.

0.2 MPa, heating with furnace from ambient temperature to 1223 K the metal-alumina couple in contact. After wettability examinations, the Al/Al_2O_3 couple was cooled at a rate of 10 K/min to reduce the effect of thermal stresses.

Metal specimens weighing 0.20 g were used in the tests. The samples of Al_2O_3 substrates of $\varnothing 17 \times 5$ mm dimensions were polished with diamond paste of 1 μm grain size to the surface roughness of about 0.3 μm. As a next step, onto the alumina substrates, the films of Ti (800 nm thick), Nb (1000 nm thick), and Ti + Nb (900 nm thick) were deposited separately by PVD method. Films were deposited by sputtering in argon gas atmosphere Ti and Nb from metallic target and Ti + Nb from mosaic target onto different substrates such as Corning glasses and alumina, depending on the requirements imposed by further applications, including determination of the film thickness and composition. The film thickness was measured mechanically by means of the Taly Step Profilometer. The thin film composition was determined by x-ray diffraction (XRD). The weight ratio of Nb/(Nb + Ti) was found to be equal to 0.625 (62.5 wt.%).The specimens of both the metal and the ceramics without the deposited films were washed for 5 min in an ultrasonic cleaner directly before being placed in a vacuum apparatus.

On joint specimens examined by the sessile drop method, the bond strength was next tested by a shear method (modified push-off technique). In this technique, the solidified sessile drop specimens are carefully bisected perpendicular to the drop-substrate interface at the mid-plane of the contact circle by means of automatic precision cut-off machine Accutom 50 and the shear test is done on one half of the specimen. Additionally, the other half of the same bisected droplet may be used to carry out detailed structure and chemistry characterization of interfaces formed under conditions identical to the corresponding wettability test Ksiazek et al. (Ref 5). The bond strengths were determined using an INSTRON 1115 machine with a special holder, and with automatic recording of the applied load versus the corresponding displacement up to failure under constant displacement rate of 1 mm $\min^{-1}$. The advantage of this procedure is the possibility to shear the drops with less than 90° contact angles that allows to studying the systems with different wetting properties. The shear strength was calculated by dividing the applied load by the initial substrate interfacial area measured under 10× magnification using an AMSLER magnifying system.

The structure was examined on specimens after the wettability test (metal drop-ceramic substrate couple) using optical microscopy, scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The examinations of structure were restricted to the areas adjacent to metal-ceramic interface. The bond structure morphologies present in the interface were determined by SEM on a STEREOSCAN 420 scanning microscope with analysis of the metal-ceramic interface chemical composition done on an EDS LINK ISIS 300 x-ray microanalyzer. The application of x-ray microanalysis enabled the linear, local, and surface distribution analyses to be carried out in the examined microregions of metal-ceramic interface. Detailed structural examinations of the joints were also carried out on a JOEL 2010 ARP TEM equipped with energy dispersive x-ray spectrometer (EDS). The TEM examinations of the structure of metal-ceramic joints were made on thin foils prepared in a Gatan PIPS691V3.1 ion thinner by standard methods, i.e., by cutting out 3 mm diameter discs, thinning by dimpler, and ion polishing (Ref 6). The hardness at the interface of the joints was measured using Micro-Vickers hardness tester under a vertical loading of 10 g. Hardness was measured along the metal drop-ceramic substrate interface at a distance of 5 μm from the border of the joint. For every sample 5-7 measurements were taken.

3. Results and Discussion

The results of shear tests made on $Al/coating/Al_2O_3$ joints are shown in Fig. 1. The deposition of coating, both Ti and Nb, on the ceramic substrate deteriorates the shear strength of Al/Al_2O_3 joints fabricated at the temperature of 1223 K. This proves rather poor strength of the $Al/Ti/Al_2O_3$ and $Al/Nb/Al_2O_3$ joints respective of Al/Al_2O_3 joint, and consequently the formation of bond between Al and Al_2O_3 characterized by lower strength. For $Al/Ti/Al_2O_3$ joint, the maximum shear stress is 38 MPa, while for the Al/Al_2O_3 joint (without coating) fabricated at the same temperature, the shear stress of 47 MPa has been obtained. It is interesting to note that Nb as a coating for Al_2O_3 substrate reduces slightly the shear strength of an Al/Al_2O_3 joint. The maximum shear stress of an $Al/Nb/Al_2O_3$ joint is 43 MPa. On the other hand, the deposition of Ti + Nb coating on Al_2O_3 substrate increases the shear strength of an Al/Al_2O_3 joint by about 14%. From the history of the shear curves plotted for $Al/Nb/Al_2O_3$ and $Al/Ti + Nb/Al_2O_3$ joints it follows that within the shear zone the process of hardening is proceeding much more quickly (short flow range on the curve). In $Al/Ti/Al_2O_3$ joint, the shear curve is characterized by a relatively long-range shear path with the stress growing mildly to decrease later. Wettability studies show that molten Al wets uncoated and coated alumina with thin film of Ti at 1223 K. A contact angle of 79° and 42° is attained in the Al/Al_2O_3 and

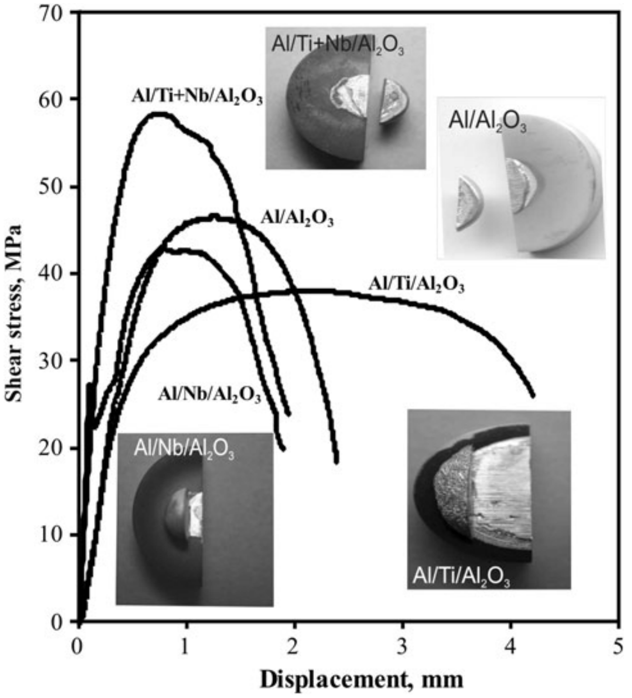

Fig. 1 Shear stress as a function of displacement for the Al/Al_2O_3, $Al/Ti/Al_2O_3$, $Al/Nb/Al_2O_3$, and $Al/Ti + Nb/Al_2O_3$ sessile drop samples obtained after wettability test at 1223 K

$Al/Ti/Al_2O_3$ couples, respectively. There is no significant difference in the angles recorded on Al_2O_3 coated with thin films of Nb and Ti + Nb at 1223 K ($\Theta = 108°$). It is worth noting that, applied onto ceramic material, the Nb and Ti + Nb coatings have improved the wettability at higher temperature (1323) and, compared to the base system (Al/Al_2O_3) at the same temperature, reduced the contact time necessary to obtain this wettability (Ref 7, 8).

Macroscopic examinations of the specimens of Al/coating/Al_2O_3 joints were also carried out. From the observation that metal was present in Al_2O_3 after fracture it can be concluded that failure takes place in the metal with the interface remaining untouched (Fig. 1). It should be emphasized that the deformation and plastic properties in the regions near the interface (on the Al side) play an important role in the interface fracture process. This best proves the metal-ceramic bond quality.

The structural examinations revealed changes in structure and chemical composition of the interface, responsible for the mechanical properties of Al/coating/Al_2O_3 joints. The results of these examinations carried out on the Al/coating/Al_2O_3 joint by optical microscopy and by SEM and TEM are shown in Fig. 2 to 4. The examinations carried out at a magnification of 500× revealed within the Al/coating/Al_2O_3 joint interface the formation of a discontinuous zone of the new phases, marked in the structural images with arrows (Fig. 2a, 3a, 4a). On the other hand, structure examinations at large magnifications (Fig. 2b, 3b, 4b) have proved the formation of new Ti-, Nb-, and oxygen-rich phases within the metal-ceramic interface during wettability test. Local analysis of the chemical composition of these phases indicates that these are the precipitates of Al_3Ti and Al_3Nb (Fig. 2b, point 1 the precipitates of high Al and low Ti concentration; also Fig. 2c, a map showing the distribution of concentration of the elements like oxygen, aluminum, and titanium; and Fig. 3b, point 1 the precipitates of high Al and low Nb concentration). This fact is consistent with the results of an analysis of the double-phase equilibrium systems of Al-Ti and Al-Nb (Ref 9), and of the Al_2O_3 precipitates (points 1 and 3 in Fig. 3b and 4b, respectively). The Al_2O_3 precipitates occur in large amounts within the $Al/Nb/Al_2O_3$ and $Al/Nb + Ti/Al_2O_3$ joints interface. It should be stressed that Al_2O_3 precipitates nucleate on the substrate surface from Al drops supersaturated with oxygen after the wetting process during cooling has been completed due to the dissolution of Al_2O_3 substrate in the drop and formation of oxygen-saturated solution in liquid aluminum during the wettability test. The presence of Al_2O_3 crystals, which have much better adherence to the interface, results in better hardening of this zone. Therefore, in an $Al/Ti/Al_2O_3$ joint, the large and hard precipitates of Al_3Ti present in soft aluminum matrix are not capable of hardening the zone of interface so effectively as the

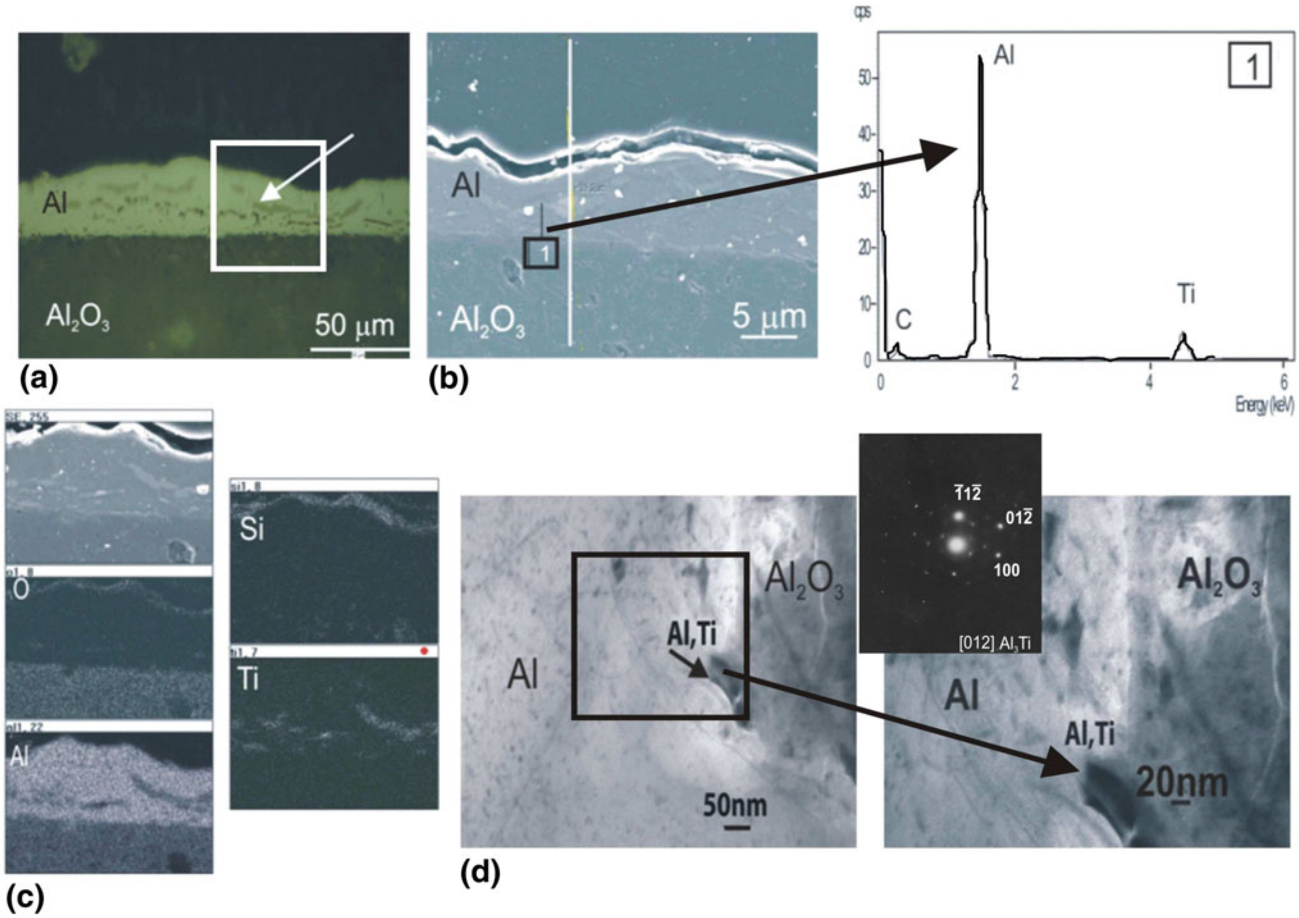

Fig. 2 Structural examination of the $Al/Ti/Al_2O_3$ couple (1223 K, 30 min): (a) optical micrograph corresponding to peripheral part of Al drop, (b, c) SEM analysis of the interface with corresponding EDS spectrum taken from the marked point 1—Al_3Ti precipitates in Al drop, and oxygen, aluminum, silicon, and titanium x-ray maps, and (d) TEM analysis of interface under different magnifications of the marked regions showing Al_3Ti precipitates

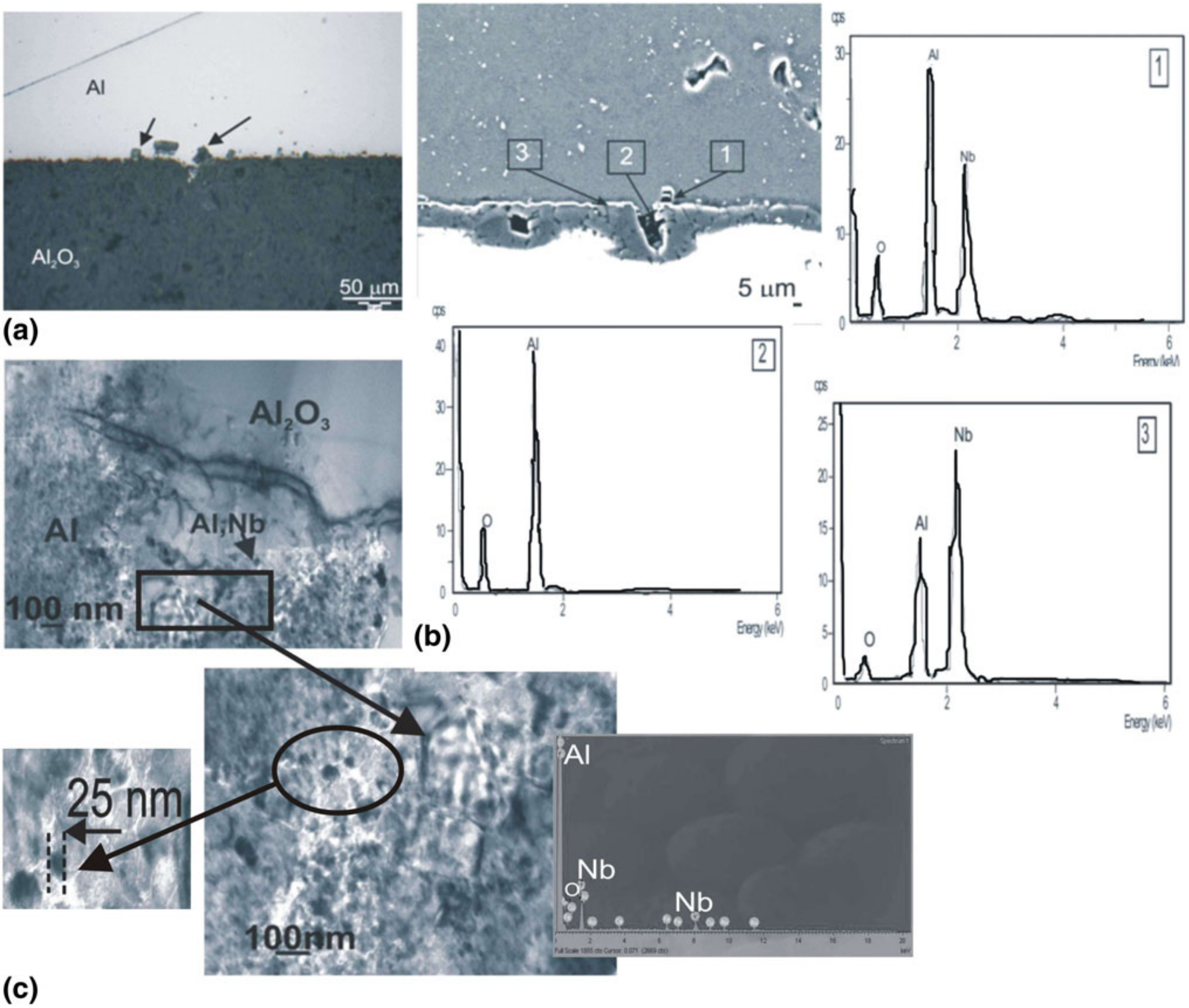

Fig. 3 Structural examination of the Al/Nb/Al_2O_3 couple (1223 K, 30 min): (a) optical micrograph corresponding to central part of Al drop, (b) SEM analysis of the interface with corresponding EDS spectra taken from the marked points 1—Al3Nb precipitates at the drop-side interface, 2—Al_2O_3 precipitates in the metal penetrated region in the substrate-side interface, 3—undissolved Nb coating at the interface, and (c) TEM analysis of interface under different magnifications of the marked regions showing the presence of a new phase (with the grain size ranging from 25 to 100 nm) of composition similar to Al_3Nb

fine and more evenly distributed Al_2O_3 crystals in Al/Ti + Nb/Al_2O_3 and Al/Nb/Al_2O_3 joints.

High-accuracy structural examinations carried out by the high-resolution electron microscopy where, using EDS technique, the local chemical composition in the most interesting elements of the structure of a metal-ceramic interface was analyzed, revealed partial dissolution of Ti, Nb, and Ti + Nb coatings in liquid Al and the formation, due to reactive diffusion, of new products of reaction in the form of the precipitates of Ti- and Nb-rich phases. In Al/coating/Al_2O_3 joints, the phases rich in both Ti and Nb occur in the form of highly dispersed precipitates of size comprised in the range of 10-100 nm (Fig. 2c, 3c). The detailed TEM studies accompanied with EDS analysis indicate the local of presence of Ti and Nb elements. By measuring the diameter of the particles (such as a measurement is shown in Fig. 3c) estimated the size of precipitates was estimated. Occasionally, precipitates of the size comprised in a range of 100-300 nm are also present (Fig. 4c).

The results of the measurements of microhardness should be connected with level of strengthening of contact area between metal and ceramic and so with quality and reliable of metal-ceramic joints. It is interesting to note that the values of microhardness obtained in an Al/Al_2O_3 joint with coating are higher than the analogical values obtained at the same temperature for the joint with non-modified Al_2O_3 substrate surface. For the joints of Al/Al_2O_3, Al/Ti/Al_2O_3, Al/Nb/Al_2O_3, and Al/Ti + Nb/Al_2O_3 type, obtained at $T = 1223$ K, the mean hardness values in the area of the interface (at a distance of approximately 5 µm from the metal drop-ceramic substrate interface) amount to 60 ± 4, 540 ± 22, 240 ± 12, and 640 ± 32 µHV0.1, respectively. Al/Al_2O_3 joints follow a general structure-property relationship with higher hardness for applying coating including titanium. From this observation it is concluded that the microhardness

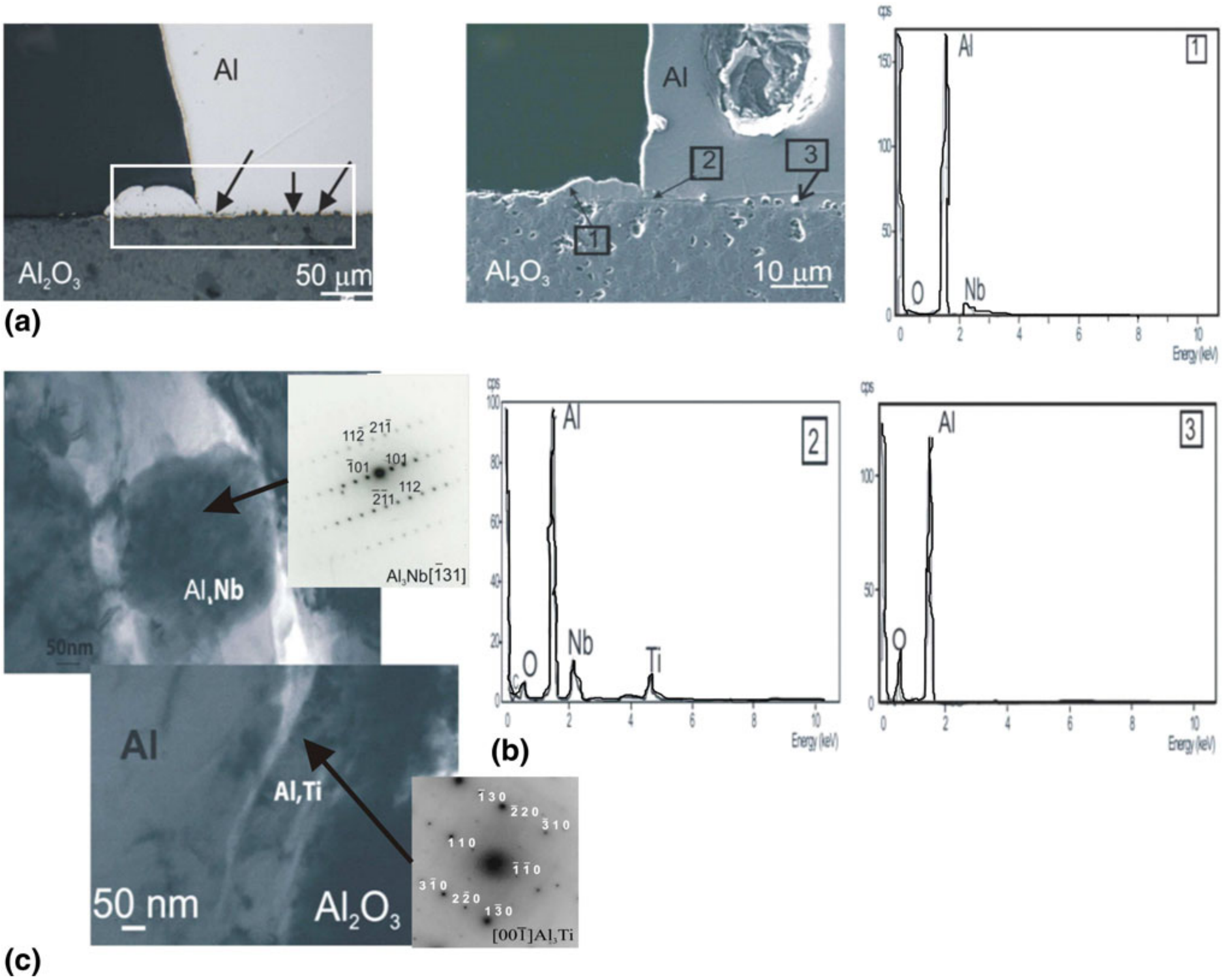

Fig. 4 Structural examination of the Al/Ti + Nb/Al_2O_3 couple (1223 K, 30 min): (a) optical micrograph corresponding to peripheral part of Al drop, (b) SEM analysis of the interface with corresponding EDS spectra taken from the marked points 1—surrounding Al containing Nb, 2—Al-Ti-Nb precipitates at the interface, 3—Al_2O_3 crystals at the drop-side interface (c) TEM analysis of the Al/Ti + Nb/Al_2O_3 interface showing an interaction leading to the formation of new phases containing Nb and Ti

values are better correlated with the formation of an Al_2O_3 and size and distribution of Ti- and Nb-rich phases in the region of the interface. This can be due to the volume fraction of Al_3Ti formed during wettability test at 1223 K, estimated to be larger than that of Al_3Nb. This fact proves that by depositing the coating onto an Al_2O_3 substrate, the metal-ceramic interface undergoes a very obvious hardening.

The comparative studies and examinations of the typical features of a layered system of Al/coating/Al_2O_3 and Al/Al_2O_3 reveal the crystals of new phases precipitating at a relatively high temperature in the metal-ceramic interface, combined with microhardness growth. The presence of the precipitates of these new phases, especially of those based on niobium and titanium, proves the occurrence of reactive diffusion during the process of bond formation, which—as a consequence—makes the interface harden by precipitation. Good plastic properties of the contact boundary combined with high degree of hardening are due to the nature of the precipitate-matrix interface, to the precipitates deformability, and to the crack propagation rate slowed down within the area of high residual stresses near the phase boundary.

4. Summary and Conclusions

The results of the experimental research give the following conclusions:

1. Modification of Al_2O_3 substrate surface by deposition of the thin layers of Ti, Nb, and Ti + Nb:
   - Increases the hardness of an Al-Al_2O_3 interface. The systems with coating are characterized by good adherence to the substrate resulting from the diffusive nature of bond.
   - Ensures good mechanical properties of the joint. This is proved by the topography of a fracture surface, which shows that shear occurs in metal due to plastic degradation while the interface area remains basically untouched.
2. The examinations of the interface structure carried out by light microscopy, SEM and TEM in joints of Al/coating/

Al_2O_3 produced at $T = 1223$ K have revealed partial dissolution of Ti, Nb, and Ti + Nb coating in liquid aluminum and formation (due to reactive diffusion) of the new products of reaction, which appear as precipitates of the Al_3Ti and Al_3Nb phases, playing an important part in the simultaneous hardening and plastification of interface, giving consequently joints of higher quality.

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