Available online at www.sciencedirect.com
ScienceDirect
Journal of the European Ceramic Society 28 (2008) 717–728
www.elsevier.com/locate/jeurceramsoc

# Liquid metal wettability and advanced ceramic brazing

Y.V. Naidich, V.S. Zhuravlev, I.I. Gab, B.D. Kostyuk, V.P. Krasovskyy, A.A. Adamovskyy, N.Yu. Taranets *

*Frantsevich Institute for Problems of Materials Science of National Academy of Sciences of Ukraine, 3 Krzhyzhanovski Str., 03680 Kiev-142, Ukraine*

Received 5 August 2006; received in revised form 10 July 2007; accepted 20 July 2007
Available online 22 October 2007

**Abstract**

Data are presented as to results on wettability and joining of ceramic materials performed during last years at the Frantsevich Institute for Problems of Materials Science of National Academy of Sciences of Ukraine. Wettability of ceramics by advanced filler alloys is considered to be a background for brazing alloy design. Joining techniques (brazing, diffusion welding) were developed for a number of oxide, carbide, nitride and boride ceramic materials. The data reported include specially designed filler compositions, optimized brazing parameters, mechanical properties of obtained joints as well as joint schemes and examples of manufactured details.
© 2007 Elsevier Ltd. All rights reserved.

*Keywords:* Joining; Wettability; Strength; Brazing

## 1. Introduction

Nowadays parts of modern equipment are subjected to a complex of working stresses including thermomechanical, electrophysical stresses, corrosion, etc. Requirements on their operating characteristics are quite high and can be achieved frequently by combination of different groups of materials. In particular, metals are combined with ceramics. The most popular ceramics are based on oxides, nitrides or carbides. The most reliable ways to join dissimilar materials are brazing by special metal fillers and solid phase pressure bonding ("diffusion" bonding).

High enough wettability of ceramic materials by molten metal fillers is principal requirement for successful brazing. Wettability contact angle should range from ∼5° to ∼20°. Low values of the contact angle mean high adhesion of fillers to solid phase due to high surface tension of common filler melts on the base of Cu, Ag, Sn, etc. Thermodynamic adhesion is meant here of liquid metal to the solid surface in accordance with Young's equation. High thermodynamic adhesion is the main condition for high strength of brazed joint. That follows from a correlation between thermodynamic work of adhesion to the solid phase and mechanical contact strength of solidified filler to the solid phase, which was considered earlier.[1] Also, high adhesion of gasket material to solid phase is important criterion to obtain reliable diffusion solid phase bonding. As a rule, metals are adherent to ceramics poorly. Special adhesion-active alloys have to be designed to overcome this obstacle.

In spite of intensive research on ceramic brazing during recent decades, only few processes are widely applied by industry. The following can be emphasized among them: molybdenum–manganese metallization of aluminium oxide based ceramic with subsequent brazing by usual metal fillers; quartz glass bonding for portholes of different purposes with diameter ranging from 2–3 mm to 0.5–1 m; joining of glass ceramic materials to metals by Ti-containing melts on the base of Sn, Pb, In. Two latter technologies and fillers were elaborated at the Frantsevich Institute for Problems of Materials Science NASU. Also, different companies manufacture nowadays fillers of Ag/Cu/Ti composition as a ribbon, foil or wire for various applications.

Usually, special research and technological process peculiarities need to be worked out for each particular case of brazed detail manufacture from oxide, nitride or carbide materials. Thus, research and technology development in the field of brazing (soldering) of ceramic materials to metals or to ceramics is of present interest. It can be also mentioned that methods for brazing of metals are known and used since antique times.

* Corresponding author. Tel.: +38 44 424 30 17; fax: +38 44 424 30 17.
*E-mail address:* taranets@ipms.kiev.ua (N.Yu. Taranets).

0955-2219/$ – see front matter © 2007 Elsevier Ltd. All rights reserved.
doi:10.1016/j.jeurceramsoc.2007.07.021

Technological findings in the field of ceramic brazing are of 50–60 years old only.

The main problem for the ceramic brazing is non-wettability of ceramics (non-metallic materials) by brazing alloys that are normally used for brazing of metals. The other problem is thermal expansion coefficient mismatch between ceramic and metal components of a joint. This difference generates stresses at the joint, which weakens the joint or even destroys it. Presented results are examples of solution for the mentioned problems, especially as to overcoming of non-wettability of ceramics by metals.

There are several schools in the world which made significant contribution into ceramic brazing by metal fillers. These are scientific schools of M.G. Nicholas (UK), E. Lugscheider (Germany), S.D. Peteves (Netherlands), J.A. Pask (USA).[2–5]

Purpose of the present paper is not detailed review of world achievements in the field of ceramics brazing. It is a description of research and developments, performed at the Frantsevich Institute for Problems of Materials Science of National Academy of Sciences of Ukraine in the field of brazing during last years. Peculiarity of works on brazing performed at the IPM NASU is that wettability processes are investigated initially. Obtained data are used as scientific base for subsequent brazing technology development. Fundamental investigations of the ceramic wettability by liquid metals permit to design not only liquid metal fillers but also solid metal gaskets for pressure welding.

## 2. Experimental

Wettability investigations were performed by sessele drop method in high vacuum high temperature installation described previously.[6] Apparatus is equipped with optical photo system. The main part of the apparatus is horizontal resistance furnace consisting of an alumina tube heated externally by a molybdenum resistor.

Brazing and metallization were performed in high vacuum installations equipped with observation systems. High level of vacuum was provided by both diffusion and turbomolecular pumps. Heating was provided by tungsten element resistant furnaces of different volumes (from about $10^6$ mm$^3$ to 6 m$^3$). Such difference in the volumes permitted to perform successfully brazing of small details as well as details with dimensions up to 500 mm. Some installations were equipped with mechanical or hydraulic pressure systems. All equipment was designed at the IPM NASU. Schemes and detailed description of employed equipment can be found in work.[7]

Wettability tests, metallization and brazing with active fillers were performed in vacuum $2 \times 10^{-3}$ Pa at experimental temperatures. Some technologies were performed in different vacuum conditions or in air, which will be pointed out in corresponding sections.

All ceramic materials employed in the present study were produced at the IPM NASU. Types of ceramics used for investigations were as following:

- hot-pressed $Si_3N_4$ containing 2 wt.% of $Al_2O_3$ as sintering aid;
- sintered cubic $ZrO_2$ stabilized with $Y_2O_3$ (3 at.% of $Y_2O_3$);
- sintered AlN;
- hot-pressed $B_4C$ containing 15 wt.% of $ZrB_2$ as sintering aid;
- $LaB_6$ single crystals manufactured by non-crucible inductive zone melting;
- sintered $Al_2O_3$.

Also, the following materials were employed: Super Hard Materials (SHM) produced in Russia; sapphire monocrystals produced by the Institute of Monocrystals of NASU (Charkov, Ukraine).

Ceramic samples were ground and polished prior to wettability tests up to roughness $R_a \approx 0.02$ μm with diamond powders and cleaned in acetone and ethanol. Similar procedure of surface preparation was used for samples prior to brazing or metallization. Though level of roughness was higher for these applications and ranged from ∼1 μm up to ∼0.04 μm in dependence on requirements for each particular case.

The type of the bend strength tests was three-point bend test performed on the P-0.5 testing machine with 5 kN load capacity. Span was 16 mm. Load of the top support was applied directly to the brazing gap area. The load was applied at a vertical speed 5 mm/min until applied load resulted in fracture of the specimen.

Shear strength tests were performed in the following way. Brazed sample was placed in a shear jig and stressed to destruction in the P-0.5 machine operating at a crosshead speed 5 mm/min.

Vacuum tightness tests were performed using helium leak detector PTI-7A when helium flow blew directly onto the brazed joint.

## 3. Results and discussion

### 3.1. General principles of wettability processes for non-metallic non-organic materials

High wettability of non-metallic solid body by liquid metal results from formation of interfacial chemical bonds if chemical interface reaction occurs. Energy of the reaction contributes to the work of adhesion liquid metal/solid body. That results in general correlation between wettability (contact angle) and Gibbs energy $\Delta G$ of interfacial chemical reaction. In application to liquid metal/oxide systems the reaction is the reduction of solid phase oxide by liquid metal and $\Delta G$ can be expressed as

$$\Delta G = \Delta G_1 - \Delta G_2 \quad (1)$$

where $\Delta G_1$ is Gibbs energy of liquid metal oxide formation and $\Delta G_2$ is Gibb's energy of solid phase oxide formation. Thus for oxides, the wettability is better when chemical affinity of liquid metal to oxygen is high and $\Delta G$ is less positive or becomes negative.[6] The reaction is liquid metal/nitrogen interaction for aluminium and silicon nitrides. Though, liquid metal/aluminium, silicon interaction has to be taken into account as well for these systems. For example, $\Delta G$ for AlN is expressed

as following:

$$\Delta G = \frac{1}{2}\left(\frac{1}{m}\Delta G_{Me_nN_m} - \Delta G_{AlN}\right) + \frac{1}{2}\left(\frac{1}{y}\Delta G_{Me_xAl} - \Delta G_{AlN}\right) \quad (2)$$

Where $\Delta G_{AlN}$, $\Delta G_{MenNm}$, $\Delta G_{MexAly}$ are Gibbs energies of formation of aluminum nitride, liquid metal nitride and aluminide correspondingly.Contact angle is defined by metal's affinity to carbon in the case of carbon materials wettability.

In many cases solid/liquid chemical interaction results in formation of new phase layer at the interface. For example in case of liquid metal/oxide system, the layer is an oxide of the liquid metal.

Metals that are traditionally used as filler base (Sn, Cu, Ag, Au, etc.) do not wet oxide, nitride, carbide and boride ceramics as a rule. High level of wettability can be obtained by two main ways.

### *3.1.1. Modification of liquid phase with special adhesion-active additives*

This method makes use of adsorption effect. That means that concentration of an additive is small. Volume properties of a metal change insignificantly. At the same time, wettability effect of the additive is significant as additive concentrates at the interface due to high adhesion ability.

Adhesion-active additives can be divided into two groups:

(a) Metallic elements possessing high chemical affinity to solid phase atoms (to oxygen, nitrogen, carbon, etc.). Addition of these elements to "neutral metals" (such as Cu, Sn, Ag, Au, Ni, etc.) provides occurring of interfacial chemical reactions. Ti, Sc, V, Zr, Cr can be distinguished among the most active additives. They promote wettability for both ionic and covalent solids (Figs. 1–3 and Table 1).

(b) Non-metallic elements with high affinity to electron—O, S, Se, Cl. These elements improve wettability by metals (Cu, Ni, Ag, Pb, etc.) of solids possessing ionic chemical bond (oxides, sulphides, salts) (Fig. 4). The reason for the improvement is the following. Electronegative element accepts electrons of solvent metal atoms. This leads to formation of positive metal ions. Positive ions interact with oxide anions by means of Coulomb forces and wettability improves. In this way oxygen improves wettability by copper of oxides, fluorides and other ionic compounds. Oxygen is particularly effective in Ag–Cu alloys.[8]

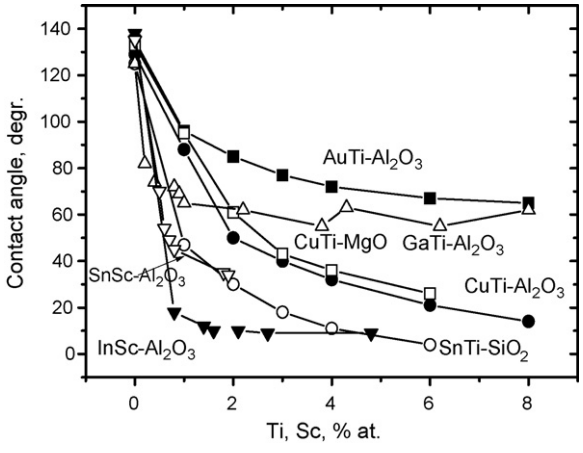


Fig. 1. Wettability of oxide ceramics by liquid metals with additions of Ti and Sc at 700 °C (InSc–$Al_2O_3$), 900 °C (SnSc–$Al_2O_3$), 1000 °C (SnTi–$SiO_2$), 1050 °C (GaTi–$Al_2O_3$) and 1150 °C (CuTi–MgO, CuTi–$Al_2O_3$, AuTi–$Al_2O_3$).

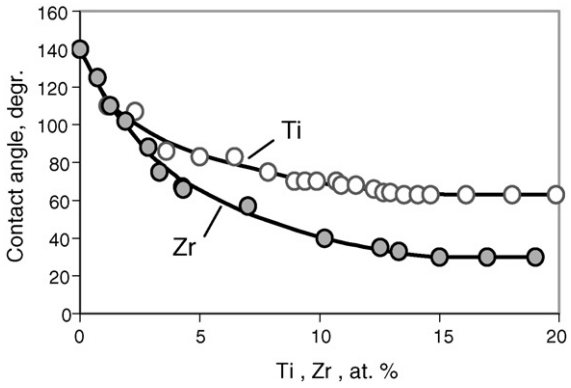


Fig. 2. Influence of Ti and Zr on wettability of zirconia by Cu–Ga melts at 1150 °C.

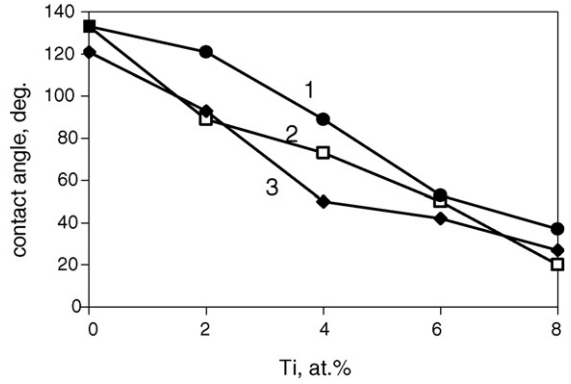


Fig. 3. Influence of Ti on wettability of nitride ceramics by Cu–Ga melts at 1150 °C (1 and 2) and 1100 °C (3): (1) (Cu–10% Ga)/$Si_3N_4$; (2) (Cu–20% Ga)/$Si_3N_4$; (3) (Cu–17.5% Ga)/AlN.

The wettability dependencies on melt composition (Figs. 1–4) permit to design melts with required capillary characteristics.

Table 1
Wettability of cubic boron nitride by metal melts

| Melt (at.%) | Temperature (°C) | Contact angle (°) |
|---|---|---|
| Cu | 1100 | 137 |
| Ag | 1000 | 146 |
| Sn | 1100 | 137 |
| Cu + 10% Sn | 950 | 136 |
| Cu + 20% Sn | 950 | 135 |
| Cu + 10% Sn + 15% Ti | 950 | 28 |
| Cu + 20% Sn + 15% Ti | 950 | 21 |

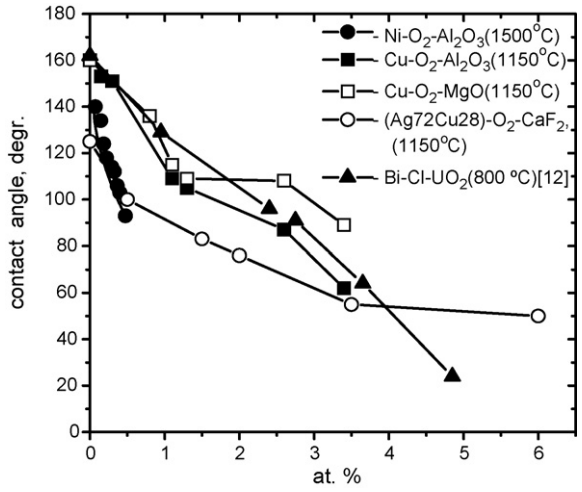


Fig. 4. Wettability of oxide ceramics with dominant ionic interatomic bond by melts containing electronegative elements (O2, Cl).

*3.1.2. Surface modification of solid phase by deposition of thin films of metals, which possess high adhesion to solid phase and are wetted easy by fillers (metallization)*

This process, which is also applied in our technologies, is considered below shortly for some particular cases. An example is shown in Fig. 5 of surface modification influence on the wettability.

*3.2. Results on brazing and pressure welding of different ceramic materials*

*3.2.1. High strength brazed joints of silicon nitride structural ceramic*

A lot of studies have been devoted to problems of high-strength $Si_3N_4$ brazing to ceramics or to metals. Traditionally Ag–Cu–Ti active fillers are used for $Si_3N_4$ brazing.[3,9] Bend strengths of $Si_3N_4$/Ag–Cu–Ti/$Si_3N_4$ joints was reported as ~500–800 MPa at room temperature.[10,11] Average bend strength was reported as $\sim 566 \pm 178$ MPa at room temperature for brazed assembly $Si_3N_4$/Au/Ni–Cr/Au/$Si_3N_4$ manufactured by so called "partial transient liquid phase bonding method".[13]

The goal of present research was to produce high-strength $Si_3N_4$/$Si_3N_4$ joint by filler alloys that do not contain such noble metals as Au or Ag.

Hot pressed $Si_3N_4$ ceramic was used with monolithic bend strength of 850 MPa. New Cu–Ga–Ti filler alloy was elaborated. The composition of the filler is defined by the following. Ti addition results in good wetting of $Si_3N_4$. Gallium promotes the wettability by Cu–Ti melts and reproducibility of results due to "effect of the third component". This effect was found out and described initially in ref.[14]. Sn addition (5–15 at.%) to Cu–Ti melt resulted in good stable wettability. Such three-component alloy appeared to be less sensitive to vacuum conditions and purity of components. Nature of the effect is not so clear. Sn decreases surface tension of Cu–Ti alloys, increases thermodynamic activity of Ti. So it promotes the wetting and spreading of the melt. Such three component alloys are more convenient in application. Nowadays Cu–Sn–Ti alloys are widely used for joining of graphite, diamond and ceramics. Cu–Ga–Ti alloys were elaborated taking into account above principles. Wettability data for Cu–Ga–Ti alloys are presented in Fig. 3 in contact with $Si_3N_4$.

The following was maintained to provide high strength for $Si_3N_4$/Cu–Ga–Ti/$Si_3N_4$ brazed joint:

- high degree of surface polishing of the ceramic up to $R_a \sim 0.04$ μm;
- low value of brazing gap (~10 μm);
- annealing of brazed samples to decrease stresses in the joint;
- brazing process was performed in high vacuum $2–3 \times 10^{-4}$ Pa at the brazing temperature 1000 °C.

Average bend strength was obtained as ~750 MPa for three-point tests. The maximum observed strength was 850 MPa. Weibull's plots for stress values are shown in Fig. 6. SEM photograph and EPMA lines are presented in Fig. 7. Temperature dependence of strength is shown in Fig. 8.

For $Si_3N_4$ brazing special attention should be paid to minimizing of a problem of thermal expansion coefficients (TEC)

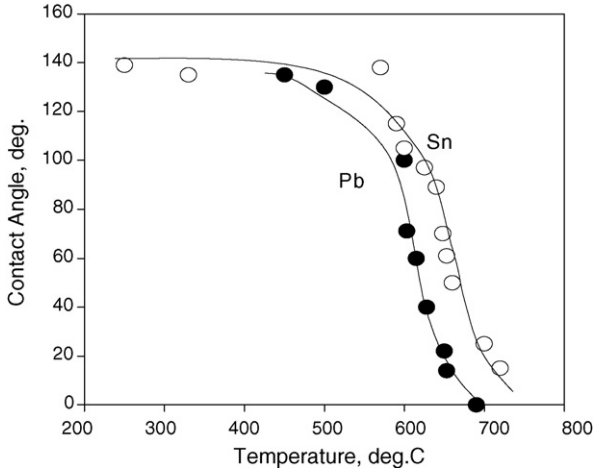


Fig. 5. Wettability of AlN with surface deposited Ti by Pb and Sn.

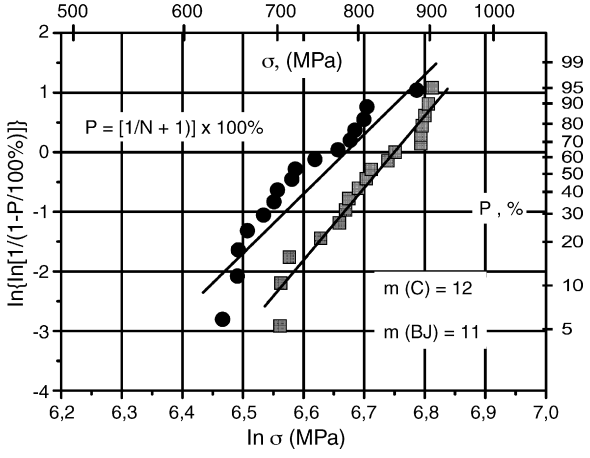


Fig. 6. Weibull's plot for strength of $Si_3N_4$ joints: circles—ceramic/ceramic assemblies; squares—monolithic ceramic.

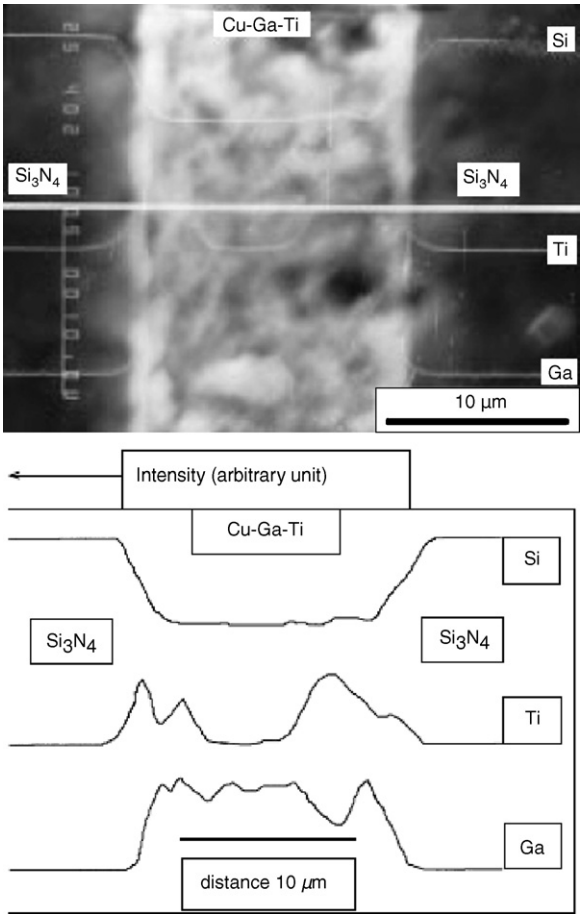


Fig. 7. SEM image of the brazing area (×4000) and EPMA line profiles for Si, Ti and Ga distribution through $Si_3N_4$/Cu–Ga–Ti/$Si_3N_4$ layers.

mismatch between ceramic and metals as $Si_3N_4$ possesses very low TEC value ($\sim 2 \times 10^{-6}\,^{\circ}C^{-1}$). TEC mismatch decreases strength of the brazed joint as mentioned above. Technique was developed to compensate the mismatch. The essence of the method is an application of intermediate gasket. Gasket is manufactured out of springs packed closely to each other. Diameter of the springs is ~0.8–1.2 mm. Springs are made of wire of diameter ~0.1–0.2 mm with step ~0.5 mm. The spring can be made of stainless steel, for example. Thickness of the gasket is equal to the external diameter of the spring. Springs are

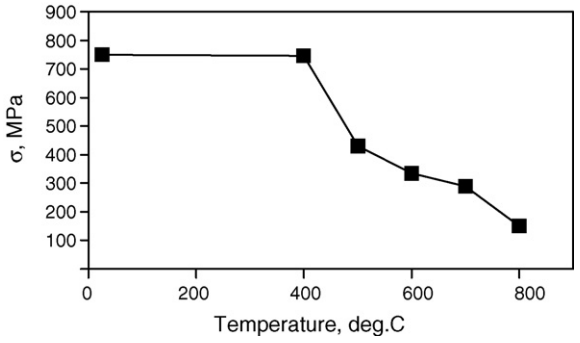


Fig. 8. Strength of $Si_3N_4$ brazed joints in dependence on test temperature.

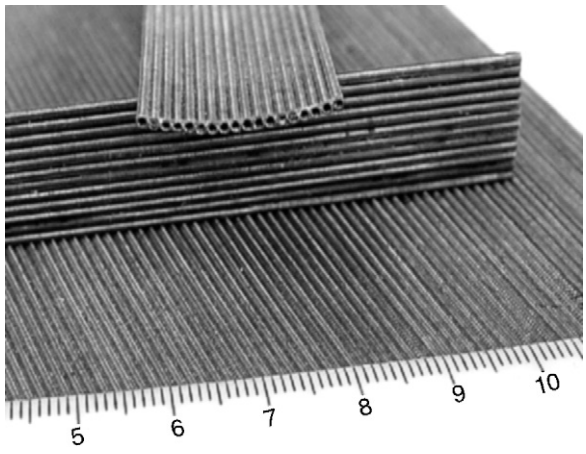


Fig. 9. Spring sheet gasket (top view and side views).

packed first together and glued by nitro-organic glue. The glue is evaporated out of the gasket during heating in form of gaseous substances: $CO_2$, $H_2O$ and nitrogen. Brazing is performed by Ti- or Zr-containing alloy. Quantity of the alloy is defined in the way that prevents penetration of the alloy through springs under action of capillary forces. The strength of such brazed joint cannot be very high. It is ~30–50 MPa. However, this strength is enough for a number of applications. It is an advantage that big details can be joint using the gasket (~100–200 $cm^2$). Pistons for internal-combustion engines were made by described method with ceramic plates of diameter ~100 mm. Photo of the spring gasket is presented in Fig. 9.

### 3.2.2. *Brazing of zirconium oxide ceramic by adhesion-active fillers*

Some methods were elaborated to join zirconia ceramic to forgeable iron, steel and titanium. Similar to $Si_3N_4$ brazing, Cu–Ga–Ti(Zr) alloys were tested as perspective fillers. Ga and Ti or Zr were added to Cu for the reasons described at the previous section.

$ZrO_2$–ceramic was used with bend strength of about 460 MPa. Cu–Ga alloys were prepared by co-melting of components and contained 80–85 at.% Cu. Metallic titanium and zirconium in metal and powder forms were used for the wettability experiments and main brazing procedure.

Data on the wettability of $ZrO_2$ by Cu–Ga–Ti(Zr) alloys are presented in Fig. 2. The lowest contact angle during experiments was about 30° for the Cu–Ga–Zr alloy. That is why Zr was chosen for brazing.

Several methods were tested to introduce Zr into the base metal melt. The best results were received by capillary infiltration of the zirconium powder with Cu–Ga melt. First, Zr powder has been mixed with organic liquid binder. A layer of obtained suspension was deposited onto ceramic and metal surfaces under brazing. The surfaces were dried in air. Then, the ceramic was placed on the metal. A ring of Cu–Ga alloy was placed near the brazing gap. In a process of heating Cu–Ga melt was spread over zirconium covered surfaces and filled the gap between the ceramic and metal. Zirconium was dissolved in liquid alloy and acted as an adhesive-active element promoting the adhesion

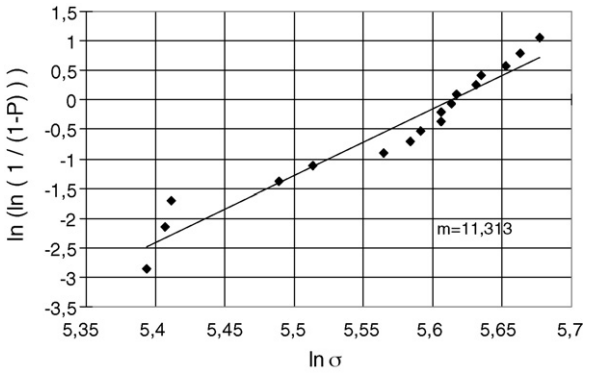


Fig. 10. Strength of $ZrO_2$/forgeable iron joints brazed by Cu–Ga–Zr filler.

between the filler and ceramic. The brazing was performed in vacuum at temperatures 1100–1150 °C.

Shear strengths was evaluated after the brazing of $ZrO_2$ to the forgeable iron. Average strength was 260 MPa; minimum strength was 220 MPa; maximum strength was 290 MPa. Weibull's plot for the samples is presented in Fig. 10. Fracture occurred partly through the filler, ceramic/filler and metal/filler interfaces.

Various details and assemblies were manufactured by the elaborated technology. Fig. 11 presents steel automobile valve with $ZrO_2$ plate.

### *3.2.3. Soldering and metallization of aluminium nitride ceramics*

Some processes are described in the literature for AlN brazing to metals (FeNi42 alloy, copper).[15,16] Ti-containing alloys of system AgCuInTi were used as a filler. Ti or Al were predeposited onto the ceramic surface for some samples. Strength of the brazed joints ranged from 90 MPa to 120–160 MPa depending on the metal part of the joint and filler. Joint strength was obtained as 40–60 MPa for diffusion welding of AlN.[15]

Mentioned above techniques provide work temperatures for brazed assemblies at the level starting from room temperature. Meanwhile, a number of AlN applications suppose cryogenic work temperatures (for example, as parts of thermosensors). It means that AlN/metal joint has to be hermetic and strong enough when temperature is lowered to cryogenic range. The purpose of our investigations was to obtain brazed AlN/metal joint for applications in temperature range from −200 °C to +200 °C. The joint had to retain vacuum tightness and strength at these temperatures and be resistant enough to thermocycling. The range of working temperatures excluded from consideration traditional fillers on the base of Cu–Ag alloys.

Pb and In were considered as prospective fillers taking into account that the filler had to be plastic at temperatures up to −200 °C. Pb was chosen as plastic low-temperature filler.

As it was mentioned above, the main problem for ceramic brazing is to overcome non-wettability of ceramic by metal filler. AlN brazing is not an exception. AlN is hardly wetted by majority of metal melts. Adhesion-active element has to be added to Pb to achieve melt spreading. On the base of the data,[17] Ti was chosen as an alloying additive to Pb.

Ti powder, mixed with the nitro-organic glue, was deposited onto the AlN surface. Wettability tests showed spreading of Pb over such AlN surface (Fig. 5) at temperatures ∼700 °C. Two methods of the filler location were tested prior to brazing. The filler was placed directly into the brazing gap or above the capillary brazing gap in a way that provides penetration of the filler into the gap. The last location was chosen to ensure proper positioning of parts to be brazed.

Brazing was performed in vacuum at temperatures 580–620 °C. Brazed assemblies passed control tests for vacuum tightness successfully, including the control after five thermocycles with cooling up to −200 °C and heating up to +200 °C. Rupture tests resulted in strength values of ∼40–50 MPa.

Independent on brazing task of AlN metallization arises for a number of AlN applications. That is to create surface metal layer with high electrical or thermal conductivity for different applications (electrode, capacitor plate, shield for electric field, etc.). For such purposes a technique was developed for AlN metallization. Ti-containing alloys on the base of plastic metals (particularly Sn) were used. Wettability of AlN by Sn–Ti melts is shown in Fig. 5. Metallization process was performed in the following way. Sn–Ti powder was mixed with nitro-organic glue. This suspension was deposited onto the AlN surface to be metallized. Detail was dried in air and heated up to ∼700–800 °C in vacuum $5 \times 10^{-3}$ Pa. Uniform metallic layer has been obtained with thickness of ∼0.5 mm. The layer thickness can be regulated by the amount of the deposited suspension. Control of metallized detail did not reveal delamination or surface defects of the metal layer. Picture of metallized AlN detail is shown in Fig. 12.

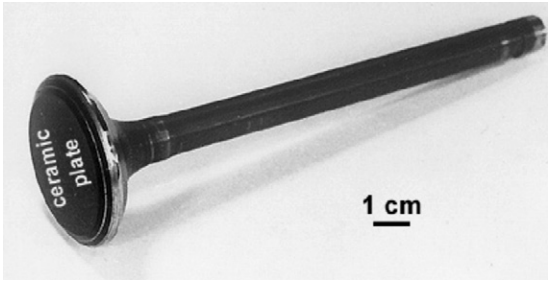


Fig. 11. Automobile valve with $ZrO_2$ ceramic plate.

Fig. 12. AlN ceramic detail metallized with Sn–Ti.

### 3.2.4. Brazed layered $B_4C$/metal macro-composites

$B_4C$ based materials are hard and wear resistant. They are prospective as parts for stone-grinding machines. However, application of $B_4C$ ceramic is limited due to its high brittleness. Reinforcement of the ceramic by metals permits to increase its resistance to shock loads and to get higher fracture toughness. Layered brazed $B_4C$/metal materials were designed as well as adhesion-active metallic fillers for their brazing.

Wettability of $B_4C$ materials was studied earlier.[8] As a whole, the wettability of these materials is better than that for oxide or nitride ceramics. Cr or Ti can be used as adhesion-active additives to base fillers in lower concentrations than for oxides. Alloys of Cu–Sn–Ti or Cu–Cr systems were used in present work for brazing. Brazing was performed in high vacuum at ~900–1100 °C.

Layered materials of different type and dimensions were obtained. Three-layer material $B_4C$/Me/$B_4C$ and multi-layer materials with 10–20 and more layers are among them. Materials were obtained in form of discs, pivots, and rectangular packages. Thickness of ceramic and metal layers varied. Typical dimensions were 3–4 mm for ceramic layer and 0.5 mm for metal layer (Fig. 13). Usually copper was used as a metal layer.

Shock load tests were performed for composite discs of 30 mm diameter made of three ceramic layers (~3 mm) and two metal layers (~0.5 mm). Procedure for the tests was as following. Steel ball with diameter of ~25 mm fell down from definite height striking plane horizontal surface of the ceramic/metal composite fixed on massive rigid metal base. Initially tests were performed for monolithic ceramic of thickness equal to the thickness of the composite. Minimal height was registered which brought about destruction of the ceramic into pieces. Then the procedure was repeated for the composite material. The height was defined when cracks appeared in the ceramic layer and brazed joint and metal layer remained undamaged. Shock energy was calculated from the height of the fall. Test results showed that shock energy for layered ceramic/metal composites is five to six times higher than for the ceramic material.

Results of the investigation were applied to design destruction elements for centrifugal stone mills. Namely, brazed reinforced details were manufactured and used as part of rotor for centrifugal stone mills (Fig. 14). Maximum stone pieces dimension was ~15 mm. Maximum velocity for impact of stones was ~200 m/s.

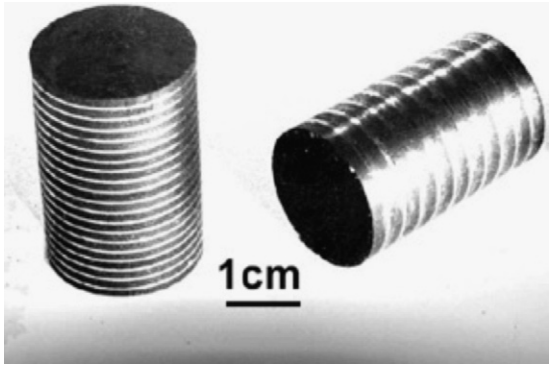


Fig. 13. $B_4C$/metal composite.

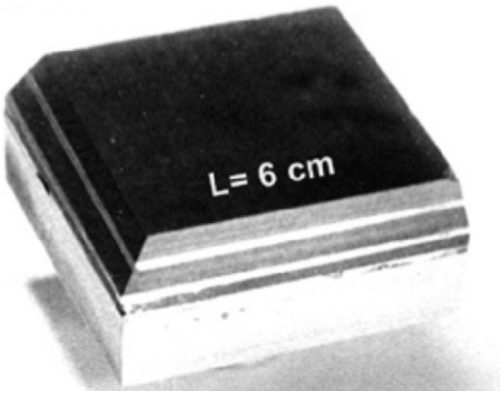


Fig. 14. $B_4C$/metal brazed part for centrifugal stone mill machine (dark layer—ceramic; light layer—metal).

General productivity of the mill was 1800 kg/h. The parts were heated up to 90–100 °C in a process of millwork. Ceramic/metal brazed details passed a set of industrial tests successfully, without significant destruction. They were declared as prospective details for parts of stone mills.

### 3.2.5. Brazing of $LaB_6$ to graphite

Unique complex of physical, mechanical and thermodynamic properties of lanthanum hexaboride allows using it widely as an emission material for the cathode in vacuum electronic devices. Term of exploitation of $LaB_6$ cathodes is about 1000 h at the temperatures of 1600–1800 °C. That exceeds by five to six times an operating time of tungsten cathodes in the same conditions. Reliable joining of $LaB_6$ to holders is required to provide stable work of the cathode unit with the emitter from lanthanum hexaboride. The joint has to retain working characteristics for ~1000 thermocycles with heating up to 1600–1800 °C in 2–3 min and subsequent fast cooling.

Metal fillers cannot be used for $LaB_6$ brazing for the cathodes when working temperatures are higher than 1600 °C, including fillers on the base of refractory metals. That follows from results on investigation of wettability and contact interaction of $LaB_6$ with metal melts.[18–22] Intensive chemical reaction proceeds at the metal melt/$LaB_6$ interface and metal reacts with boron of lanthanum hexaboride forming new borides. Also, dissolution of boron in the melt takes place. These processes result in boron diffusion from emitter, deterioration of emitting properties of $LaB_6$, lowering of mechanical strength for emitter/load-bearing detail joint and to cathode unit destruction in a short time.

Technology was developed in collaboration with laboratory of Dr. Y.B. Paderno for $LaB_6$ brazing to graphite by new refractory non-metal filler for a detail of the cathode units. Graphite was chosen as a material which does not interact with lanthanum hexaboride up to 2000–2200 °C.[19,20] The filler composition is $LaB_6$ with additions of 30 wt.% of carbon and 5 wt.% of boron. The filler does not deteriorate $LaB_6$ surface (Fig. 15). However, it wets well both $LaB_6$ and graphite, which is testified by a form of the meniscus (Fig. 16). The brazing was performed in high-frequency current furnace in Ar atmosphere of pressure $2–3 \times 10^5$ Pa, at 2000 °C.

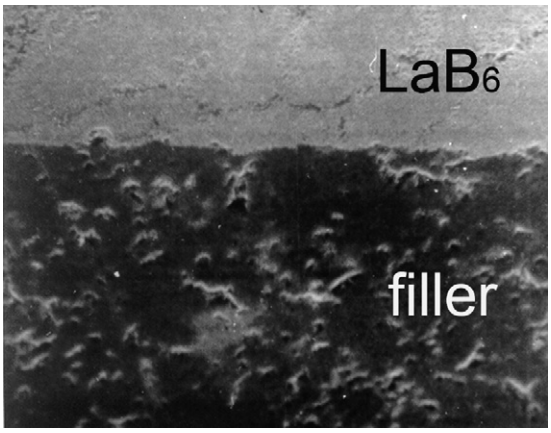


Fig. 15. Image (×300) of $LaB_6$/filler interface.

Obtained joints did not contain pores and cracks. Brazed samples were subjected to thermocycling tests. Thermocycle for the tests included heating up to 1600 °C in 2–3 min, holding at this temperature for 1–2 min and subsequent natural cooling with initial rate of 10–20 °C/s. Twenty-five brazed joints were subjected to the thermocycling. All of them remained intact and undamaged after 200 cycles. Bend tests for the brazed joints resulted in cohesion destruction within graphite part. Average strength value was $1 \pm 0.25\ kg/mm^2$. Image of the brazed detail is presented in Fig. 16. Thus, new refractory non-metallic filler on the base of $LaB_6$ and developed technology permit to obtain refractory brazed joint for $LaB_6$/graphite assemblies with working temperatures up to 1600–1800 °C.

### 3.2.6. *Brazing of superhard materials on the base of cubic boron nitride to steels for cutting tools*

Superhard materials on the base of dense modifications of boron nitride (SHM) take leading position for intensification of processes of hardened steel cutting. SHM cutting element can be attached to holder mechanically or by squeezing of heated holder or by brazing. First two methods do not provide strong positioning of the SHM element, do not allow use it up to complete SHM wear and to perform multiple re-sharpening of the instrument. Also, mentioned methods are inapplicable for manufacture of small-sized tools when size of SHM element is ∼3–5 mm in diameter and ∼4–5 mm in height. Thus brazing is the most reliable way to join SHM to holder.

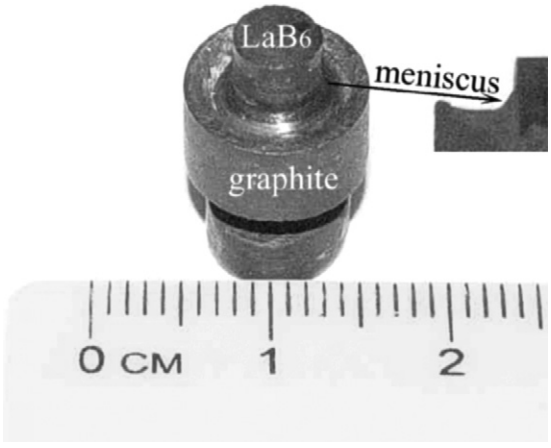


Fig. 16. $LaB_6$/graphite brazed detail.

Wettability data for boron nitride (Table 1) permitted to define Cu–Sn–Ti alloys as fillers for its brazing. The filler was used as a mix of powders of corresponding metals with addition of a small amount of more refractory metal. The powder was mixed with organic substance before the brazing. Also, the same mixture of powders was obtained and applied in form of ribbons with thickness of ∼0.10–0.20 mm. The brazing was performed in vacuum at the temperature 850–950 °C. Shear tests for SHM/steel joints resulted in strength values of about 142–147 MPa.

Obtained strength for SHM/steel joints is high enough to fix cutting element to half-closed or open slot of the holder. Also, described method allows to manufacture micro-cutters with cutting elements of diameter ∼1 mm and height 2–3 mm for precision processing of special units. In addition, application of adhesion-active filler promotes to increase the number for possible re-sharpening of tools during service from 2–3 up to 9–10.

Full cycle of the SHM cutting tool production was developed. It includes brazing by above filler, hardening of the steel holder (if it is necessary) and sharpening of a cutting element. Optimum brazing gap value for SHM/steel is about 0.1 mm. Some of brazed and brazed/sharpened SHM cutting tools are presented in Fig. 17.

### 3.2.7. *New technique to activate metal fillers with Ti*

Preparation of Ti, Zr-containing active alloys is complicated process. Experimental research on active alloys shows that the best results on their spreading are achieved when non-active base metal (Cu, Cu–Sn, Cu–Ag, Cu–Ga, etc.) interacts with an active additive (Ti, Zr, etc.) in situ on the ceramic surface. In this case the best wettability can be obtained as well as lower sensitivity of adhesion characteristics to alloy oxidation, pollution, etc.

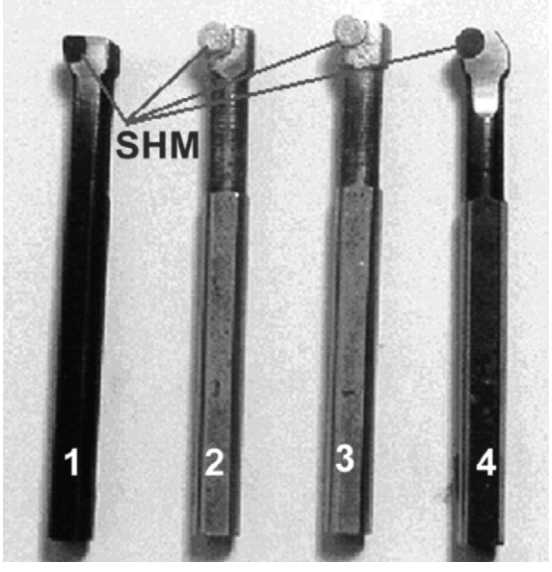


Fig. 17. SHM/steel brazed cutting tools (2 and 3) and brazed/sharpened cutting tools (1 and 4) (×1).

Usually, preliminarily melted Ti alloys (Cu–Sn–Ti, Cu–Ag–Ti, etc.) wet ceramic not as good as alloys formed in situ, especially for oxide ceramics. That is why two- or three-layer ribbons tend to be made nowadays: base metal/active metal/base metal, etc. Also, base metal wires are produced with active metal core (Ti). At the same time, a number of companies produce preliminarily co-melted active filler alloys. WESGO Metals and BrazeTec Gmbh are among those companies.

New technology was developed for preparation of active filler with low Ti content (∼5 wt.%) in form of layered foils. Such fillers are composed of two layers. First layer is inactive foil of base alloy with thickness of 60–100 μm. The second layer is thin porous semitransparent foil of Ti with effective thickness of 15–30 μm. Such fillers can be used as two independent layers or they can be glued together with special organic glue. Content of Ti in the filler can be regulated by control of thickness of either foils or the porosity of Ti foil. Thin porous Ti foil provides uniform distribution of Ti in the brazed joint.

Active Ti foils were obtained of dimensions ∼30 mm × 300 mm (Fig. 18a). Fig. 18b illustrates porosity level of the foil: letters of text can be seen through the foil. Fig. 18c shows Ti foil that is glued to the base filler (Cu–9% Sn). A number of ceramic/ceramic joints were obtained using layered foil at brazing temperature 980 ± 20 °C.

Preliminary melted alloys with high Ti or Zr content are used for brazing of metals. Normally they are made by electro-arc melting when it is hard to homogenize the alloy properly. New refractory crucibles were elaborated which are inert in contact with Ti, Zr, Hf alloys and are not wetted by these alloys.

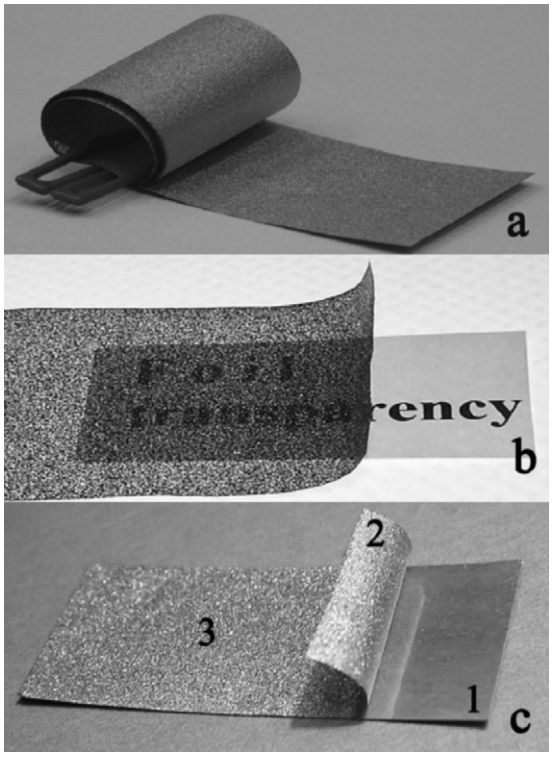


Fig. 18. Thin porous Ti brazing foil: (a) active Ti foil; (b) porosity level of the foil; (c) Ti foil that is glued to the base filler (Cu–9% Sn).

This holds true for active element concentration up to 50–80% (contact angles 120–130°). Thus, there is new possibility for active alloys melting. Such alloys can be isothermally melted and homogenized at high temperatures for long time in new inert refractory crucibles.

### 3.2.8. *Pressure welding (diffusion bonding) of structural $ZrO_2$ ceramic and functional $Al_2O_3$ ceramics in air*

Some works are reported on brazing of $ZrO_2$ and $Al_2O_3$ ceramics to itself by different fillers in vacuum or in argon.[23–25] Strength values were obtained as ∼400–420 MPa. It is also reported in literature that high pressure welding of these materials results in significantly lower strength. For example, 175 MPa strength was obtained in ref.[26] in the vacuum when Ni gasket was used. Strength of the joints reached ∼250 MPa when pressure welding was performed in air and Pt gasket was used.[27,28]

Our investigations were aimed to increase the strength of $ZrO_2/ZrO_2$ and $Al_2O_3/Al_2O_3$ joints when process is carrying out in air through Pd or Pt gasket. The bonding process was optimized and higher values for the bond strength were obtained.

Samples' assembling for joint manufacture was carried out by inserting the platinum gaskets between ceramic parts to be joined in specific ceramic equipment made of zirconia. Samples' joining by pressure was carried out in a SVK 8163 furnace with heaters able to heat samples up to 1700 °C in air. This furnace was equipped with a special device allowing transferring the pressure (25 MPa) to the samples. Joining temperature was varied from 1200 °C up to 1550 °C. Exposure time was varied from 30 min up to 240 min.

Strength can be increased by increase of bond formation temperature to 1450–1550 °C or by increase of pressure holding time to 200–240 min. Samples obtained by the optimized brazing regime were tested by three-point bend test. Values for $ZrO_2/ZrO_2$ bend joint strength were ∼500 MPa, which is 80% of bulk ceramic strength (Fig. 19). Bend joint strength was ∼350–360 MPa for $Al_2O_3$ ceramic (Fig. 20). Strength was defined as average from five to seven measurements for each particular set of materials and technological regimes. An example is presented in Table 2 for full set of measurements data

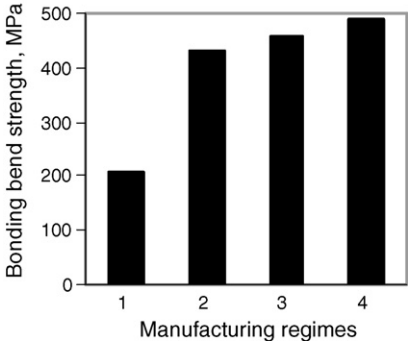


Fig. 19. Bend strength of diffusion welded $ZrO_2/Pt/ZrO_2$ joints in dependence on welding regimes: (1) $T = 1300$ °C, $p = 25$ MPa, $\tau = 30$ min; (2) $T = 1300$ °C, $p = 25$ MPa, $\tau = 120$ min; (3) $T = 1300$ °C, $p = 25$ MPa, $\tau = 240$ min; (4) $T = 1550$ °C, $p = 15$ MPa, $\tau = 30$ min.

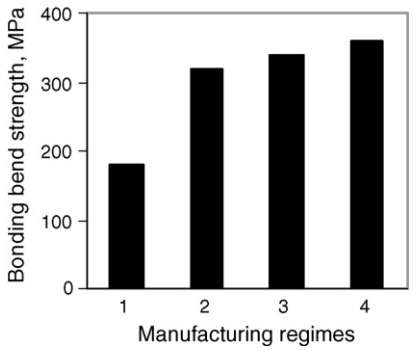


Fig. 20. Bend strength of diffusion welded $Al_2O_3$/Pt/$Al_2O_3$ joints in dependence on welding regimes: (1) $T = 1300\,^{\circ}C$, $p = 25$ MPa, $\tau = 30$ min; (2) $T = 1300\,^{\circ}C$, $p = 25$ MPa, $\tau = 120$ min; (3) $T = 1300\,^{\circ}C$, $p = 25$ MPa, $\tau = 240$ min; (4) $T = 1450\,^{\circ}C$, $p = 15$ MPa, $\tau = 30$ min.

Table 2
Bend strength data for $ZrO_2$/Pt/$ZrO_2$ joints welded at 1550 °C for 30 min under the pressure of 15 MPa

| Sample number | Bend strength (MPa) | Average value (MPa) |
|---|---|---|
| 1 | 505 | 490 |
| 2 | 495 | |
| 3 | 480 | |
| 4 | 510 | |
| 5 | 460 | |

for $ZrO_2$/Pt/$ZrO_2$ joint. The pressure welding was performed at 1550 °C for 30 min under the pressure of 15 MPa.

Refractory view portholes were manufactured by mentioned above technique in air through Pt gasket for pyrometers and observation of high temperature physical processes. The porthole is an optical disc made of sapphire with thickness of 3–4 mm and diameter of up to 30 mm. The disc is welded to $Al_2O_3$ ceramic tube by high pressure welding in air using Pt gasket. Such window is reliable to work in oxidizing medium up to 1600–1700 °C and perspective for many technical applications.

### *3.2.9. Pressure welding of sapphire/metal details through Al gasket in a vacuum*

Design and technology were developed for manufacture of metal/sapphire portholes which are able to work for a long time under simultaneous influence of temperatures (up to 600 °C) and high gas pressures (up to 10 MPa) (Fig. 21). The porthole is sapphire disk of diameter up to 100 mm and thickness of 10–12 mm. The disk is joined to Ti flange in the vacuum $1 \times 10^{-2}$ Pa at

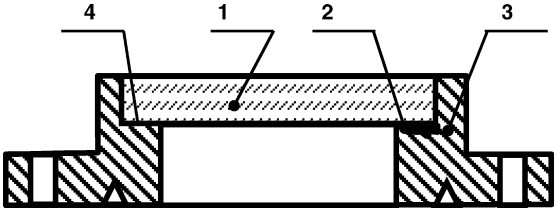


Fig. 21. Scheme of welded sapphire/titanium porthole: (1) sapphire disk; (2) ledge of the flange; (3) titanium flange; (4) aluminium gasket.

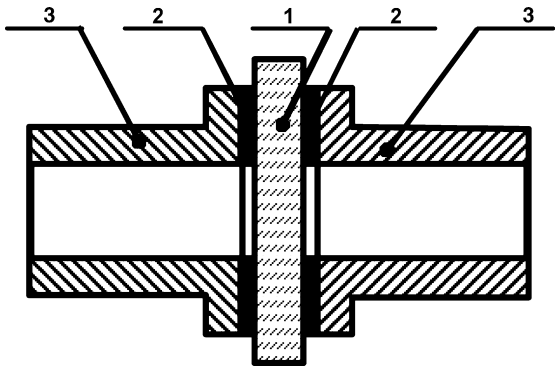


Fig. 22. Scheme of sapphire/metal welded porthole for gyrotron: (1) sapphire disk; (2) aluminium gasket; (3) titanium parts.

600 °C through plastic aluminium gasket. Gasket material was chosen on the base of wettability data. They showed that Al possesses high adhesion to oxide ceramics.[29] Some difficulties take place at the Al wettability tests due to presence of oxide film on the Al surface. The film hampers melt spreading unless test temperature is above ~1000 °C. Pressure welding promotes oxide film destruction at lower temperatures resulting from plastic deformation of the metal at pressure loading.

Welding was performed in vacuum furnace equipped with hydraulic pressure system. The pressure system allowed loading details up to the necessary level. Pressure applied to the detail under welding was 8–10 MPa. Advantages of the porthole design are the following. Corresponding ledge of the flange accepts loads applied to the sapphire disk. Plastic metal gasket, deformed during welding process, provides strength and tightness of the detail.

Exit porthole of gyrotron is another type of metal/sapphire detail obtained by pressure welding through Al gasket (Figs. 22 and 23). This porthole is an exit for powerful stream of super high frequency energy (power of 0.5 MW and frequency of 150 GHz). The porthole is highly polished sapphire disk of thickness 4–5 mm and diameter 80–100 mm, which is welded by both sides to Ti alloy parts. Pressure welding was carried out in vacuum furnace equipped with mechanical pressure system. Welding was performed in vacuum $1 \times 10^{-2}$ Pa at 600 °C under pressure 10 MPa.

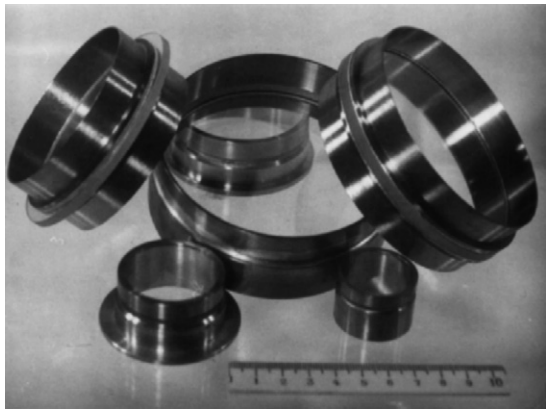

Fig. 23. Sapphire/titanium welded portholes of different designs.

Gyrotron porthole provides vacuum tightness at working temperatures ranging from −196 °C to +550 °C. Portholes were subjected to several hundreds of thermocycles with regime +20 °C–−196 °C–+20 °C without breaking of vacuum tightness.

#### *3.2.10. Cold welding by pressure for metal/non-metal details*

Cold pressure welding through plastic metal gasket was developed for vacuum tight details for laser technique, electronics, radio-details, optics, etc.[30] Metal parts of such details can be made of Al, Ti, Ni and other metals and alloys. Non-metal parts can be made of quartz, sapphire and ceramics. Low melting point metals are used for gaskets, for example, indium, lead, etc.

Technology composes two stages:

(1) preliminarily metallization of both metal and non-metal parts by low melting point plastic alloy, such as In–Ti, Pb–Ti, etc.;
(2) pressure welding of metallized parts.

The following description of cold welding of silica glass ceramic/aluminium detail illustrates the technology. Metallization of silica glass parts was performed by low melting point active filler in a vacuum at 600–700 °C. The metallization technology is similar to those described in Section 3.2.3. Aluminium parts were metallized with low melting point inert filler (indium) by ultrasound using standard ultrasound brazing equipment. Vacuum apparatus was employed for joining equipped with hydraulic pressure system. Joining was performed in the vacuum $1 \times 10^{-2}$ Pa under pressure 0.5–0.7 MPa at room temperature. The joint was hermetic and almost free from internal stresses.

This technology is applied for final assembly of different complex units when heating of their parts is not acceptable.

## 4. Conclusions

Systematic investigations were performed on the wettability by metal melts of different types of solid bodies and materials (mainly ceramic materials on the base of oxides, carbides, nitrides, etc.).

Generalisation of obtained results and their physico-chemical interpretation permit to develop principles for control of melts capillary properties. The control of the melt capillary properties allows to design fillers for ceramic brazing.

Several adhesion-active filler alloys were developed as well as brazing technologies for application in different branches of techniques. It includes high strength brazed joints of silicon nitride ceramics, brazing and diffusion welding of zirconium oxide ceramics, brazing and metallization of aluminium nitride ceramics, brazing of lanthanum hexaboride to graphite, brazing of layered macro-composites of boron carbide ceramic, pressure welding for aluminium oxide ceramics, brazing for SHM cutting tools, new technique to activate inactive fillers.

Technological data are illustrated with examples of brazed details manufactured for practical applications.

## Acknowledgements

Authors thank G.A. Kolesnichenko, N. Zyukin, A. Prokopenko, A. Durov, T. Stetsyuk and D. Kurkova for their participation in experimental work.

## References

1. Naidich, Yu. V., High strength ceramic brazed joints. Scientific and technological bases. *Ind. Ceram.*, 1999, **19**, 162–167.
2. Nicholas, M. G., *Joining of Ceramics*. Chapman and Hall, London/New York, 1990, pp. 3–70.
3. Lugscheider, E., Boretius, M. and Tillmann, W., The development of high-strength. Active-brazed silicon nitride and silicon carbide joints. *Cfi/Ber. DKG*, 1991, **68**, 14–22.
4. Peteves, S. D. and Nicholas, M. G., Evaluation of brazed silicon nitride joints: microstructure and mechanical properties. *J. Am. Ceram. Soc.*, 1996, **79**, 1553–1562.
5. Pask, J. A., From technology to the science of glass/metal and ceramic/metal sealing. *Am. Ceram. Soc. Bull.*, 1987, **66**, 1587–1592.
6. Naidich, Yu. V., The wettability of solids by liquid metals. In *Progress in Surface and Membrane Science*, ed. P. Vincenzini. Academic Press, New York, 1981, pp. 353–487.
7. Naidich, Yu. V., Payka Nemetallicheskih Tugoplavkih Materialov. Dostizheniya i Perspektivy. In *Suchasne Materialoznavstvo XXI Storichya*, ed. I. K. Pohodnya. Naukova Dumka, Kyiv, 1998, pp. 529–562 (in Russian).
8. Naidich, Yu. V., *Kontaktnie Yavleniya v Metallicheskih Rasplavah*. Naukova Dumka, Kiev, 1972, pp. 1–196 (in Russian).
9. Tomsia, A. P., Pask, J. A. and Loehman, R. E., Joining nitride ceramics. *Ceram. Eng. Sci. Proc.*, 1989, **10**, 1631–1654.
10. Johnson, S. M., Mechanical behaviour of brazed silicon nitride. *Ceram. Eng. Sci. Proc.*, 1989, **10**, 1846–1853.
11. Peteves, S. D., Nitride ceramic joining. In *Proceedings of the 8th CIMTEC World Ceramic Congress*, 1994, pp. 164–169.
12. Bredhurst, O. and Buchanan, A., *Aust. J. Chem.*, 1961, **14**, 409–414.
13. Ceccone, G., Paulasto, M., Nicholas, M. G., Peteves, S. D. and Glaeser, A. M., Application of the partial transient liquid phase bonding method for joining silicon nitride ceramic. In *Proceedings of the 4th Euro Ceramics Conference on Coating and Joining*, 1995, pp. 101–108.
14. Naidich, Yu. V. and Kolesnichenko, G. A., Study of the wetting of diamond and graphite by liquid metals. *Powder Metall. Met. Ceram.*, 1963, **2**, 35–38.
15. Wlosinski, W. K., Joining AlN to copper by using functionally graded materials. *Trans. JWRI*, 2001, **30**(SI), 413–418.
16. Wlosinski, W. and Zhu, S., Joining AlN ceramic to metals with R.F. sputtering film. In *Proceedings of the 9th CIMTEC World Ceramic Congress*, 1998, pp. 987–994.
17. Taranets, N. Yu. and Naidich, Yu. V., Wettability of aluminium nitride by molten metals. *Powder Metall. Met. Ceram.*, 1996, **35**, 282–285.
18. Naidich, Yu. V., Zhuravlev, V. S., Frumina, N. I., Paderno, Yu. B., Krasovskii, V. P. and Filippov, V. B., Contact interaction of lanthanum hexaboride with metallic melts. *Powder Metall. Met. Ceram.*, 1992, **31**, 345–348.
19. Kresanov, V. S., Malahov, N. P., Morozov, V. V., Semashko, N. N. and Shlyuko, V. Y., *High Effective Emitter of Electrons of Lanthanum Hexaboride*. Energoatomizdat, Moskva, 1987, pp. 1–156 (in Russian).
20. Gert, L. N., Babad-Zazryapin, A. A. and Minatkin, V. I., Interaction of lanthanum hexaboride with molybdenum, tantalum and graphite. Izvescheniye AN SSSR. *Ser. Neorganicheskie Materialy*, 1969, **5**(12), 2198–2201 (in Russian).
21. Kondrashov, L. N., Paderno, V. N., Martynenko, A. N. and Smirnov, V. P., Electron-microscopical investigation of the character of the reaction of lanthanium hexaboride with nickel. *Powder Metall. Met. Ceram.*, 1983, **22**, 506–512.
22. Ordanian, S. S., Paderno, Y. B., Nikolaenko, E. E. and Horoshilova, I. K., Interaction in $LaB_6$–$TiB_2$ system. *Neorganicheskiye Materialy*, 1984, **20**(5), 851–858 (in Russian).

23. Santella, M. L., Pak, J. J. and Frueran, R. J., Analysis of microstructures formed by brazing $Al_2O_3$ and $ZrO_2$ with Cu–Ag–Ti. In *Abstract Paper Presented at 70th AWS Meeting*, 1989, pp. 225–227.
24. Rathner, R. C. and Green, D. J., Joining of yttria–tetragonal zirconia polycrystal with an aluminium–zirconium alloy. *J. Am. Ceram. Soc.*, 1990, **73**, 1103–1105.
25. Moorhead, A. J., Henson, H. M. and Henson, T. J., *The role of interfacial reactions on the mechanical properties of ceramic brazements. In Ceramic Microstructures 86: Role of Interfaces*, ed. J. Pask and A. Evans. Plenum Press, New York, 1987, pp. 949–958.
26. Esposito, L. and Bellosi, A., Features affecting the joining process of ceramic materials. In *Proceedings of the 3rd International Conference on High Temperature Capillarity*, ed. N. Eustathopoulos, K. Nogi and N. Sobczak, 2000, pp. 401–412.
27. Allen, R. V. and Borbidge, W. E., Solid state metal–ceramic bonding of platinum to alumina. *J. Mater. Sci.*, 1983, **18**, 2835–2840.
28. Christensen, J. and Gotthjaeip, K., Diffusion bonded joints in alumina and ps-zirconias with excellent thermo-shock and mechanical properties. *DVS-Ber.*, 1992, 187–189.
29. Naidich, Yu. V., Chubashov, Yu. N., Ishchuk, I. N. and Krasovskii, V. P., Wetting of some nonmetallic materials by aluminum. *Powder Metall. Met. Ceram.*, 1983, **22**, 481–483.
30. Naidich, Yu. V., Gab, I. I., Kurkova, D. I., Stetsyuk, T. V. and Abramov, Ye. V., *Ukrainian Patent No. 60637 A*.