BRAZING OF FERROELECTRIC CERAMICS IN AIR ENVIRONMENT AND PURE OXYGEN ATMOSPHERE

Yu.V. NAJDICH, T.V. SIDORENKO and **A.V. DUROV**
I.M. Frantsevich Institute of Problems of Materials Science, NASU, Kiev, Ukraine

The technology for brazing in air environment and commercially pure oxygen atmosphere as well as method for deposition of coatings using metal melts with high degree of wettability of ceramics have been developed for the $BaTiO_3$-base ferroelectric ceramics. The technology developed makes it possible to substantially increase adhesion strength of coatings and brazed joints, widen existing and open new possibilities for manufacture of different instruments and devices.

Keywords: *brazing, metallization, ferroelectric ceramics, barium titanate, metal-oxygen technology*

Functional ceramic materials, composition of which includes compounds with structure of perovskite similar to barium titanate $BaTiO_3$ (such structure is based on ratio of three atoms of oxygen to each two atoms of the metal), occupy special position in state-of-the-art electrical engineering and electronics. These materials have rather wide range of applications, for example, development of multilayer capacitors with high capacity, electric field sensors, and great number of piezoelectric and ferroelectric instruments (sensors, drives) and thermistors.

Metal coatings on surface of the ceramics may act as electrodes for capacitors and an intermediate layer for joining the ceramics with a metal using brazing [1].

Perovskite titanium-base ceramics exists in two states: ferroelectric (stoichiometric $BaTiO_3$ compound) and a semiconductor (the $BaTiO_{3-x}$ structure with oxygen-related defects, which is formed, in particular, at annealing of the $BaTiO_3$ ceramics in high vacuum) [2]. Semiconductor ceramics is used in electronics and electrical engineering. We have developed technology for vacuum brazing of the $BaTiO_{3-x}$ perovskite semiconductor ceramics with application of braze alloys which contain adhesively active component, for example, titanium [3]. The brazing is performed in high vacuum at temperature 700–1000 °C, that's why it can not be used for joining the $BaTiO_3$ ferroelectric ceramics.

Barium titanate of stoichiometric composition, which has high ferro- and piezoelectric properties, may be heated without changes only in the environment containing oxygen (air). For joining such materials special braze alloys and technological processes are used. A favorable factor consists in the fact that oxygen, dissolved in certain metals, enables significant increase of wettability and adhesion of these metals to ceramics. Influence of oxygen on wettability and surface and interphase tension of the metal melts was investigated in [4–6]. It was established that oxygen effectively increases adhesion of copper, silver, nickel and some other metals to ion compounds, for example, oxides. The following systems were investigated in detail: Cu–O–Al_2O_3, Cu–O–MgO, Ni–O–Al_2O_3, Ag–O–Al_2O_3, Ag–Cu–O–Al_2O_3. Of special interest in this respect is the Ag–Cu–O system. We made assumption that metal-oxygen technology is also applicable for joining ferroelectric barium titanate.

According to [7], adhesively active action of oxygen is explained by the fact that addition into a molten metal of some metalloid, which has sufficient affinity to electrons, pulls back the latter from atoms of the metal. They transform into positive ions which are bound with the solid phase anions, that causes wetting of the ion crystal with a metal melt.

At present only one work [8] is known, which is devoted to brazing of the $Pb(Mg_{0.33}Nb_{0.67})O_3$ perovskite compound using alloys of the Ag–CuO system. Scientific basis of this process is not yet developed, and reasons of wetting action of oxygen are not explained. Unfortunately, the authors of [8] are not, evidently, aware of our works of 1960–1970s [4–6] which concern oxide materials.

Purpose of this work is investigation of wettability of the $BaTiO_3$-base ceramic ferroelectric materials with a metal melt, development of compositions of braze alloys and technological conditions for producing brazed joints of the $BaTiO_3$ ceramics for joining with each other parts of the ceramics and the ceramics with metals, and deposition of the adhesively strong metal coating on surface of the ferroelectric perovskite ceramics. As basis of the braze alloys the Ag–Cu–O system alloys were used.

Specimens of barium titanate-base ceramics were specially produced using solid phase synthesis in laboratory of M.D. Glinchuk (the I.M. Frantsevich IPMS, NAS of Ukraine). Used in the experiments disks from the $BaTiO_3$ ceramics had diameter 20 m and thickness 3 mm. Porosity of the specimens was not more than 3.5 %. Substrates from the $BaTiO_3$ ceramics were ground and polished. Roughness of the surface equaled 0.02. Degree of the $BaTiO_3$ ceramics wetting was investigated using the sitting-drop method.

Experiments and technological processes were performed in air environment (such investigations were never carried out yet). A special installation was designed, in which experiments were carried out in flowing oxygen at insignificant back pressure. Temperature of the experiment was 980, 1050, 1100 °C. Commercially pure oxygen was used. It was assumed that insignificant impurities of nitrogen and some other elements would not exert significant influence on results of the experiments.

Change of the $BaTiO_3$ ceramics contact angle θ depending upon content of copper in the melt is presented in Figure 1. At temperature 980 °C under vacuum conditions contact wetting angle for pure silver equaled about 130°, in air — 96°, and in pure oxygen — 75°. Addition of about 10 at.% Cu into silver caused reduction of the contact wetting angle down to 45–47° (in air environment) and almost full spreading of the alloy ($\theta \approx 5$–10°) in pure oxygen.

Temperature increase intensifies wetting process — contact angle reduces up to 25–30° in air environment (at 10 at.% Cu in silver melt) [9]. In case of using pure oxygen full spreading may be achieved as soon as at 6–7 at.% Cu.

Reasons of high capillary activity of the alloys in pure oxygen consist in significant equilibrium concentration of oxygen in the melt at its high partial pressure in the environment (partial pressure of oxygen in air equals 21 kPa, pure oxygen — 100 kPa). According to Siverts law, concentration of oxygen, dissolved in solution of silver in air, equals

$$[O]^{Ag}_{air} = k\sqrt{0.21},$$

and in pure oxygen

$$[O]^{Ag}_{pure\ ox} = k\sqrt{1}.$$

As far as solubility of oxygen in silver in air at 980 °C equals 10.5 cm^3/g, one may calculate that in pure oxygen it will be 2.2 times higher, i.e. about 22.9 cm^3/g.

So, brazing of the $BaTiO_3$ ferroelectric ceramics may be performed in air environment, but it is better to perform it in pure oxygen.

In the ceramics/ceramics combination braze alloy of the Ag + 10–15 at.% Cu (in air environment) and Ag + 3–5 at.% Cu (in pure oxygen) compositions was used.

In joining of ferroelectric ceramics with a metal one has to use as the latter, as showed the practice, platinum which ensures strong similar brazed seams.

An option for applying a silver-copper coating was developed with subsequent brazing to it of a platinum conducting electrode, the function of which successfully fulfilled a silver wire.

Tear and shear strength of the brazed joints was determined. It is known that it depends upon strength of the ceramics itself. Strength of the specimens of produced by us brazed joints equaled from 20 to 50 MPa. It is possible to increase these values if one uses pore-free well sintered ceramics (strength of dense ceramics from aluminium oxide may constitute about 100 MPa). It should be noted that strength of

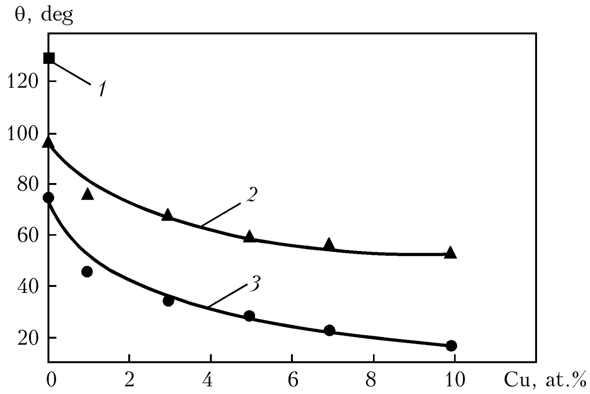

Figure 1. Dependence of contact wetting angle θ of $BaTiO_3$ ceramics by Ag–Cu–O system melts upon content of copper in them at 980 °C: *1* — melt of pure silver in vacuum; *2, 3* — melt of Ag–Cu system in air environment and pure oxygen, respectively

brazed joints often is not a critical characteristic of the perovskite ceramics/metal melt contact, because in practical use of devices on basis of ferroelectric materials mechanical loads are not very significant.

An important task is application of a thin metal coating on the ferroelectric ceramics (for example, interlayers of a capacitor). This requires ensuring of high wetting with a metal of the ceramics surface. Theoretically for producing a continuous film from a molten metal it is necessary that spreading factor had a positive value:

$$K = W_a - W_c,$$

where W_a and W_c, are the works of adhesion and cohesion, respectively.

This may be implemented if pure oxygen is used as the atmosphere. In case of the air environment special methods were used: the CuO copper oxides were applied on the ceramics in the form of a powder and annealed in air for formation of a continuous layer, and then a mixture of silver and platinum powders was applied and annealed at 970 °C, whereby in the system were present a metal melt and a solid metal (platinum) in a highly dispersed state, due to which

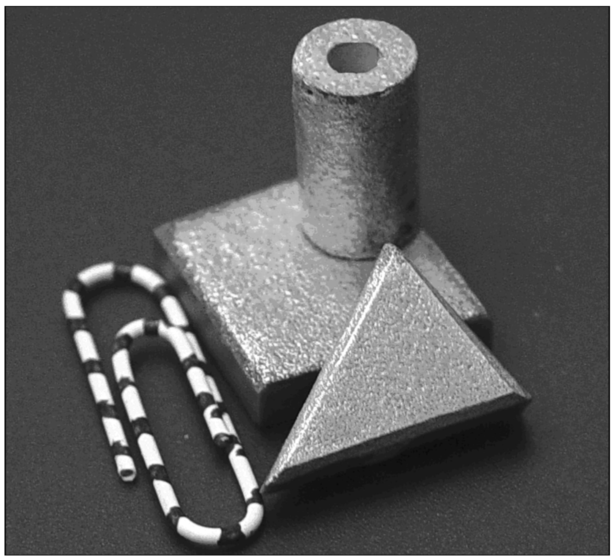

Figure 2. Specimens of $BaTiO_3$ ferroelectric ceramics metallized using metal-oxygen technology