Influence of vacuum annealing on the dispersion of thin double hafnium-copper films deposited onto oxide ceramic materials

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Introduction

Since ceramic materials, particularly oxide ones, are usually poorly wetted by molten metals, metal coatings are often used applied in various ways and adhesive-active metals such as titanium, chromium, niobium and others are the most commonly used to make such coatings. Then, thus metallized ceramic parts are brazed in vacuum or an inert medium (argon, helium etc.) by molten metallic solders on the basis of tin, silver, copper, nickel etc. In this case, the thickness of the solder seam is from 50 - 100 μm up to several millimeters. Sometimes, multilayer metal coatings are used, but the thickness of the layers and brazed seams remains high. At the same time, there is information that the reduction in the thickness of the brazed seam leads to a significant increase in the strength of the brazed joint. Obtaining brazed or welded joints of metallized ceramics is possible through reducing the thickness of both the metallization coating on the ceramics and the brazing layer by itself. This can be achieved if the soldering metal or alloy is also applied in the form of a rather thin film, the thickness of which does not exceed several μm. In addition, a thin soldering seam allows you to obtain precision welded or brazed ceramic and ceramic-metal units which can be used in microelectronics, radio engineering, microwave engineering etc.

This objective can be achieved by application onto the ceramic surfaces of double metal films, one of which is 100 - 200 nm thick and consists of an adhesion-active metal such as Ti, Cr, Hf, Nb etc., and the other is slightly thicker (2 - 3 μm) and serves as a solder, e.g. Cu, Ag etc., which will ensure joining of metallized ceramic materials during brazing or welding with fine (2 – 4 μm thick) solder seam.

The structure of such two- or multiphase coatings, determination of the optimal ratio of the thickness of each layer, processes of interaction at the phases interface, including the ceramic phase, is also an important area of research.

The study of two-layer hafnium-copper coatings (films) on oxide materials during annealing in vacuum and the creation of brazed and welded oxide ceramics joints based on them with super-thin brazed seam, the thickness of which does not exceed 5 μm, is the main task of the present work.

Materials and Experimental Procedure

In this paper an electron-beam method for sputtering of metal (Hf, Cu) films was used.

Solid non-metallic substrates were made of leucosapphire, alumina and zirconia ceramics as small thin plates 4 x 3 x 2 mm in size. One of the flat surfaces of each specimen was well polished to a roughness R_z=0.03 ÷ 0.05 μm. After polishing, all specimens were thoroughly defatted and burned in air at 1100 °C for one hour. As a metal deposited directly onto non-metallic surfaces, hafnium was used. Metallized samples were then coated by copper films serving as a solder when joining the samples. The quality of all applied films was controlled using a XJL-17 metallographic microscope.

The specimens with deposited onto them metal films were annealed in a vacuum chamber for various periods of time (from 5 up to 20 min) and at different temperatures (from 900 °C up to 1100 °C) in the vacuum not less than 2 x 10^{-3} Pa.

Annealed specimens were investigated using SEM and AFM microscopy with microphotographs storing. Using these microphotographs, the areas of metal islets on the surface of non-metallic samples were determined by the planimetric method. The experimental data obtained were processed in the form of graphs showing the dependence of the surface area of the samples covered with metal films on the annealing parameters (temperature, time).

Results and Discussion

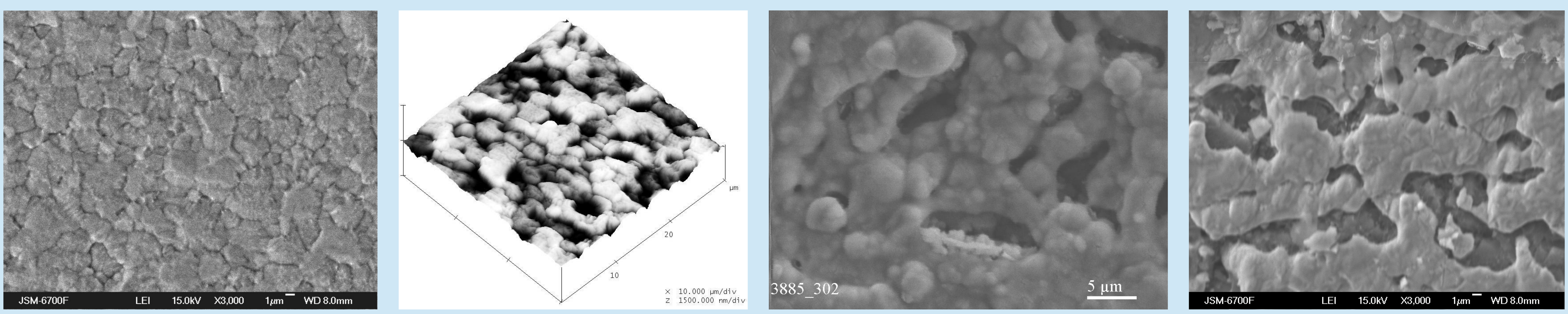
The hafnium metallization layer thickness at the leucosapphire, alumina, and zirconium ceramics substrates was 150 nm, whereas the copper layer thickness reached 1.5 μm. Copper film serving as a soldering metal for ceramic samples joining.

As a result of annealing up to 1000 °C, the films at all oxides' surfaces remained almost unchanged. The first noticeable changes in them appeared after 5 minutes of annealing at 1050 °C. With the annealing time increase up to 20 minutes, the films began to crack, although they still covered almost 85% of the oxide surface. The rise of the annealing temperature up to 1100 °C led to further swelling (Fig. 1. a, c, d) and cracking of the double films which now covered only 70–75% of the oxide surface; and the interaction of the molten copper layer with hafnium metallization of oxides becomes already noticeable after twenty-minute annealing.

With high magnification of an atomic force microscope, hafnium-copper double film deposited onto zirconia ceramics showed start of swelling and intense cracking. The height of the swellings reached almost 200 nm. Five-minute annealing at 1100 °C led not only to the significant films dispersion and cracking.

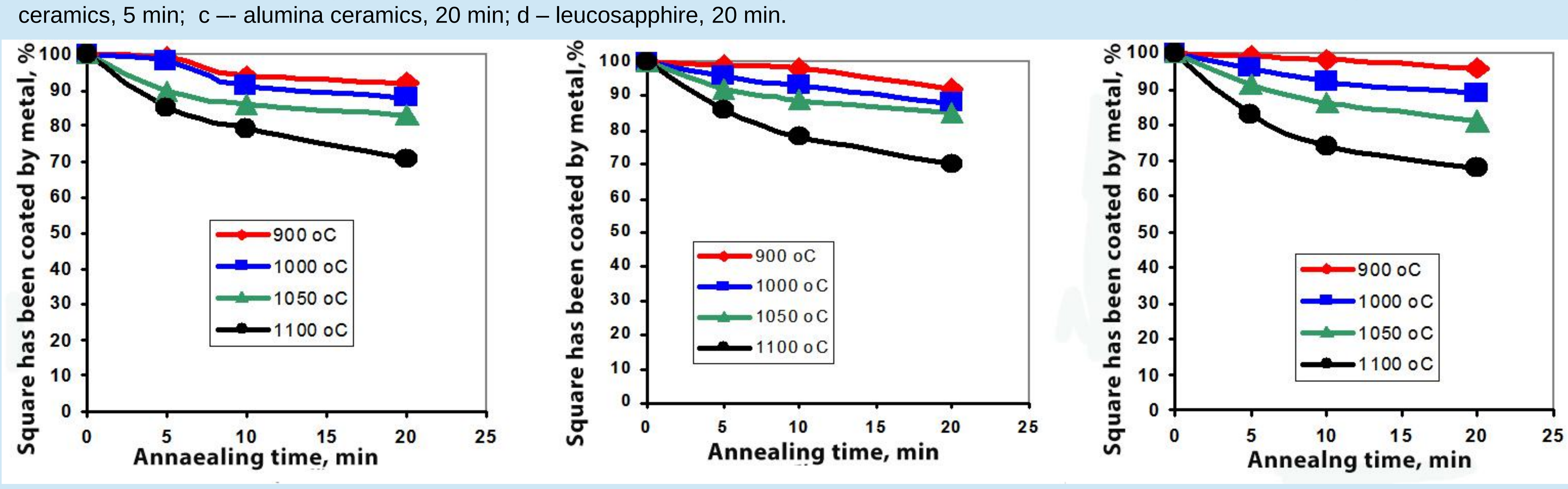
Figure 1, b, shows the image of the hafnium-copper double film at the dioxide-zirconium ceramics at high magnification of the atomic force microscope. This photo shows that the start of the interaction between hafnium and copper inside the film led to a significant change in the primary relief of the film, and the height of the swelling of the film reached 250 nm.

Figure 2 shows the kinetic curves of dispersion of double Hf-Cu films at the oxides surface depending on the annealing temperature and time. It follows from these dependences that these films can be used to join the oxides under investigation by pressure welding at these temperatures.



a b c d

Fig. 1. SEM (a, c, d) and AFM (b) images of double hafnium-copper film deposited onto oxide materials and further annealed at temperature 1100 °C during various time in vacuum: a, b – zirconia ceramics, 5 min; c –- alumina ceramics, 20 min; d – leucosapphire, 20 min.



a b c

Fig. 2. Dependence of oxide materials area covered by double hafnium-copper film on annealing time at various temperatures (900 – 1100 °C): a – alumina ceramics; b – leucosapphire; c – zirconia ceramics.

Conclusions

According to our study results kinetic curves of the investigated thin double hafnium-copper films decomposition have been built, using which one can determine the basic process parameters (temperature and exposition time at this temperature) for brazing or pressure welding of ceramic materials.

Using the data obtained, process regimes for joining by brazing and pressure welding were selected. According to these regimes, joints' prototypes with seams up to 2.5 μm thick were made, which strength reached 150 MPa.