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Brazing and Metallization of Zirconia Ceramics with Ni–Cr–Ti Filler to Fabricate Products Operating at High Temperatures

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Ni–Cr–Ti system is considered as filler for ZrO_2-ceramics brazing and metallization because of its high melting temperature. The contact angle near 40° is reached for (Ni–56Cr)–15Ti composition; the adhesion is provided by the formation of an oxidized titanium transition layer on the interface. A method of spreading the nickel–chromium melt on titanium plate is elaborated for metallization and brazing. A mix of metal powders and an infiltration of nickel–chromium melt through titanium powder on ceramics surface or in brazing gap are also used. The method of spreading shows the better results because high-disperse titanium oxidizes with oxygen from zirconia.

Key words: brazing, metallization, zirconia, wetting, infiltration, spreading.

Систему Ni–Cr–Ti було розглянуто як прилюток для лютування та металізації ZrO_2-кераміки, зважаючи на її високу температуру топлення. Для композиції (Ni–56Cr)–15Ti досягнуто крайовий кут близько 40°; адгезія забезпечується утворенням перехідного шару окисненого титану на межі поділу. Розроблено спосіб металізації та лютування розтіканням нікель-хромового розтопу по титановій пластині. Також використано суміш металевих порошків і просочування нікель-хромового розтопу через титановий порошок на поверхні кераміки або в лютівному зазорі. Метод розтікання показав ліпші результати, оскільки високодисперсний титан окиснюється Оксиґеном з діоксиду Цирконію.

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Ключові слова: лютування, металізація, діоксид Цирконію, змочування, просочування, розтікання.

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1. INTRODUCTION

At the moment, the methods of brazing of ceramic materials, including zirconia based, have been developed, which provide quite high characteristics of brazed joints [1, 2]. Titanium is used as an adhesive-active component of such solders. The disadvantage of these technologies is a relatively low melting point of fillers. The operating temperatures of such joints do not exceed 600–700°C. However, currently there is an increasing need to produce solder joints operating in extreme conditions with operating temperatures of 900–1000°C, while parts containing these joints are required in many high-temperature use (turbines, internal combustion engines, electron beam equipment, fuel cells, electrolysers, *etc.*). Therefore, it is important to develop methods for obtaining ceramics compounds with high operation temperature. Basically, such technologies are developed for oxygen-free ceramic materials [3–7]. Zirconium is by a solder in many applications, but is little used for oxide ceramic materials. Therefore, it is important to test high-temperature active metal melts as fillers for ZrO_2-ceramics brazing or metallization.

2. MATERIALS AND METHODS

Dense ceramics based on zirconia, partially stabilized 3.5 at.% of yttria, high purity nickel, chromium (not lower than 99.997%), iodide titanium, high-pure powders of nickel, chromium, and titanium were used in the experiments. The composition of nickel–chromium (54 at.% Cr) alloy corresponding to eutectic one [8], with the melting point of 1618 K, was chosen as a solvent of active metal, to which various amounts of titanium were added. This composition has relatively low melting temperature and high enough concentration of chromium providing the heat resistance. This alloy was prepared by remelting appropriate amounts of components in vacuum in alumina crucibles. For brazing experiments, titanium foil 0.2 mm thick was also used.

Surfaces of ceramic samples for wetting experiments were polished with a diamond paste of 0.7–0.3 μm. In the brazing operations, ceramic disks of 10-mm diameter were joined to disks of 15-mm diameter.

Wetting was studied by the sessile drop method at 1350°C. The experiments were performed in vacuum no worse than 10^{-3} Pa; images of the drops were obtained using a high-resolution digital camera.

Three methods for metallization or brazing were used.

For the first method, a mix of chromium, nickel and titanium powders was prepared and was painted on the surface of the ceramic for metallization or in the brazing gap. Then, samples were dried and annealed in vacuum.

For the second technique, titanium powder was applied to the surface of the ceramic disk or in the brazing gap between the joined discs. After drying, the samples were weighed, and a piece of Ni–54Cr alloy was situated on the layer of Ti powder; samples were annealed in vacuum. Titanium powder is easily impregnated with metal melts, then, dissolves in them and acts as an active addition that provides metal adhesion to solid oxide.

According to the third technique, on the surface of ZrO_2-ceramics or between the brazed details, a titanium plate of 0.2-mm thickness was situated, on it placed a piece of Ni–54Cr alloy; the samples were annealed in vacuum. After melting, the nickel–chrome-liquid filler spreads on the titanium plate, covering the surface intended for metallization or penetrating into the brazing gap, and dissolves the titanium, thus, formed a melt with high adhesion to ZrO_2.

3. RESULTS AND DISCUSSION

The results of experiments on wetting of the ZrO_2-ceramics by Ni–Cr–Ti melts are presented on Fig. 1 as the dependence of the contact angle on the atomic concentration of titanium in melt.

The addition of titanium improves significantly wetting of ceramics; at 15% of titanium, the contact angle is of about 40°. This is enough for brazing [9]. In addition, it needs to note that the equilibrium contact angles were reached during not more than 5 min; it is fast

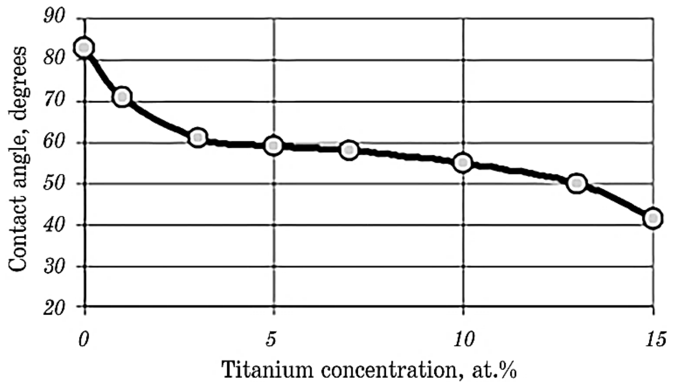


Fig. 1. The dependence of contact angle on titanium concentration in Ni–54Cr melt for wetting of ZrO_2-ceramics.

enough. The darkening of ceramics was observed, apparently due to the loss of oxygen with the formation of a non-stoichiometric phase, which is characteristic for contact of zirconia and metal melts containing titanium [10]. Unlike [10], where dark areas with a strict boundary were formed in the volume of ceramics, in these experiments, ceramic samples darkened within all volume. Since the spread of the dark area is a diffusion process [10], its acceleration in these experiments is explained by the increase in temperature that intensifies diffusion.

From the sample, where the drop of the (Ni–54Cr)–10Ti melt solidified on the ceramic surface, the cross-section was fabricated; the microphotography of the ceramics–-metal interface after etching with nitric acid is represented in Fig. 2.

The alloy of the solidified drop has a eutectic structure (dark areas correspond to a phase rich in nickel) consisting of a matrix enriched with nickel, where grains of a phase enriched with chromium are distributed. There are no noticeable differences in the distribution of nickel or chromium near interface and in the depths of the drop. A thin transition layer presents in the interface; probably, it consists of oxidized titanium, providing adhesion of the metal to the solid oxide, as in other systems [9]. The thickness of the layer is uneven; obviously, it has an island structure.

Since sufficient wetting was reached and the adhesion of the drop to the substrates was high, the (Ni–56Cr)–15Ti composition was tested as filler for brazing and metallization of the ZrO_2-ceramics by the methods described above. The temperature was of 1350°C; holding time—5 min. Photographs of some samples are represented in Fig. 3.

In all metallization methods, satisfactory results were obtained: the metal layer was kept on the surface of the ceramics firmly enough. When using the method of the nickel–chrome on the titanium plate

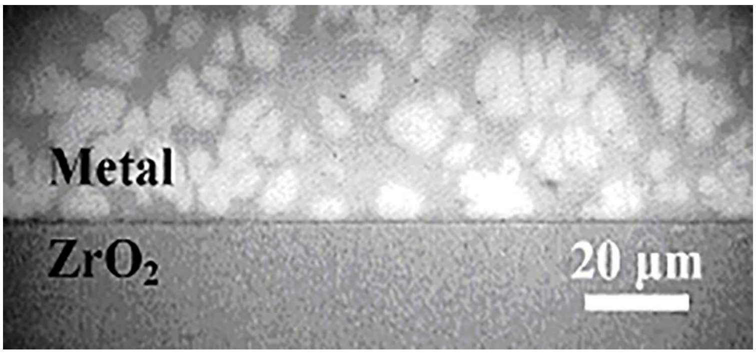
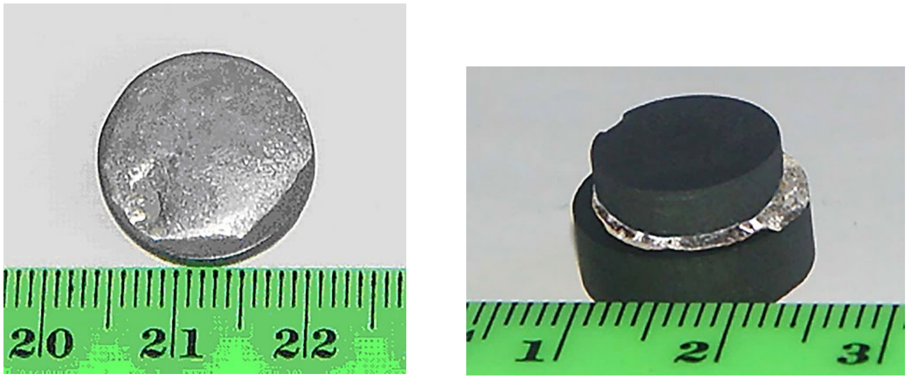


Fig. 2. Microphotography of the ceramics–metal interface for the (Ni–54Cr)–10Ti drop solidified on the surface of ZrO_2-ceramics after the etching.



a *b*

Fig. 3. Samples of ZrO_2-ceramics metallized (*a*) and brazed (*b*) by nickel–chromium melt spreading on titanium plate.

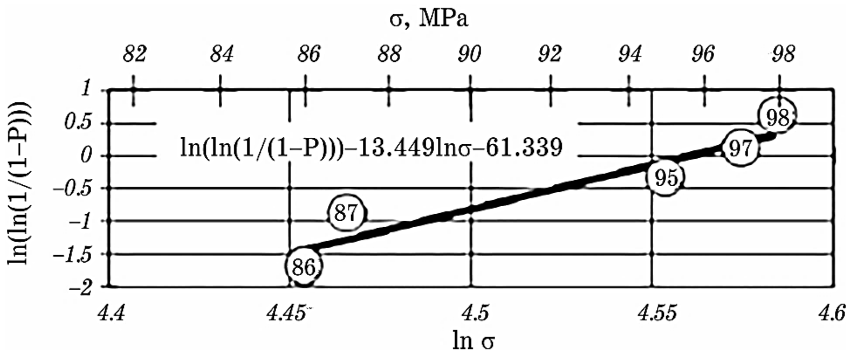


Fig. 4. The Weibull plot for shear strength of ZrO_2-ceramics to itself joints brazed by spreading of nickel–chromium melt on titanium plate.

spreading, the metal surface was the cleanest and homogeneous (Fig. 3, *a*); for methods using a mixture of powders and the infiltration of the nickel–chromium melt through the layer of titanium powder, signs of coating oxidation are noticeable.

The shear strength of the joints brazed using the mixture of powders or infiltration was no more than 40 MPa. However, the strength of the joints obtained by spreading of the solder on the titanium plate was of 86–98 MPa; the Weibull plot for these strength values is presented in Fig. 4.

Low strength for the method using a mixture of powders can be explained by the presence of contaminations adsorbed from air in the powders. In the case of infiltration, annealed titanium powder was used, so the influence of contamination is excluded.

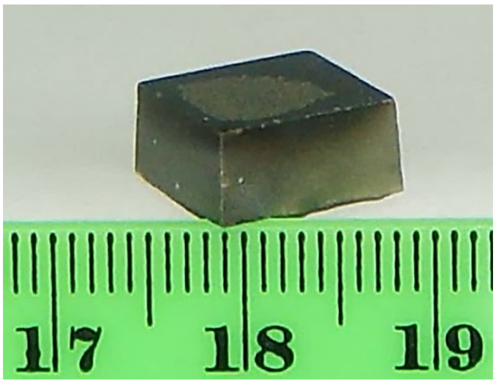


Fig. 5. Darkening of ZrO_2-ceramics with applied Ti powder on its surface after annealing in vacuum; 1350°C; 15 min.

Therefore, the following explanation can be suggested: the high-pure high-active titanium powder is in a closed contact with ceramics, and the mobility of anions in the structure of zirconia at brazing or metallization temperature is also sufficient [11], so, oxygen from ZrO_2 interacts with the titanium powder oxidizing it. As result, the quality of metal coatings and brazing joints degrades. To check this assumption, a sample of ceramics with titanium powder applied to its surface was annealed in vacuum at 1350°C 15 min. The ceramic has darkened and more intensively near the covered with titanium surface (Fig. 5). Therefore, titanium powder on the surface of the zirconia can indeed be oxidized by oxygen from the substrate at the experimental temperatures.

4. CONCLUSION

The Ni–Cr–Ti system may be used for metallization and brazing of ZrO_2-ceramics. The method of spreading of nickel–chromium melt on titanium plate was elaborated and shown the better results in comparison to methods with using of powders, because high-disperse titanium oxidizes by oxygen from zirconia.

The results obtained open up the possibility of producing brazed and metallized products for high-temperature applications.

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