

OBTAINING OF GAS-TIGHT GLASS-CERAMIC JOINTS OF MULLITE ARTICLES THROUGH THE NANOCRYSTALLIZATION OF $Y_2O_3-Al_2O_3-SiO_2$ GLASS

ИЗГОТОВЛЕНИЕ ГАЗОПЛОТНЫХ СТЕКЛО-КЕРАМИЧЕСКИХ СОЕДИНЕНИЙ ДЕТАЛЕЙ ИЗ МУЛЛИТА ПУТЕМ НАНОКРИСТАЛЛИЗАЦИИ $Y_2O_3-Al_2O_3-SiO_2$ СТЕКЛА

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Abstract: Obtaining gas-tight joints between mullite articles was made by crystallization of yttrium aluminosilicate glass. The glass joint layer softens at joining temperature (1450-1470°C) to bond the mullite samples without additional pressure and then crystallized during cooling. The good adhesion of crystallized glass to mullite surfaces ensure the gas-tight joints with permittivity $2.5 \cdot 10^{-4}$ sccm/cm. The eutectic like crystallization of initial yttrium aluminosilicate glass into yttrium silicate and mullite lead to formation the nanocomposite structure which ensure the 4 point bending strength value near 105 MPa.

Keywords: GAS-TIGHT JOINTS, MULLITE, GLASS, CRYSTALLIZATION

1. Introduction

Mullite $3Al_2O_3 \cdot 2SiO_2$ is a good and cheap oxide material for high temperature structural and refractory applications because of high enough mechanical properties at high temperatures and acceptable thermal conductivity value (6-15 W/m·K). However, fabrications of complex form details from ceramic materials are limited by ceramic brittleness, increasing of machining cost and material losses from cutting procedure. So, the assembling of complex shapes from simple parts by joining can be acceptable procedure. For some applications, for example SOFC, the joining procedure is a basic problem in the stack fabrication procedure. The high temperature strength, creep and gas impermeability of joints are the key factors in case of devices, which works under gas flows and mechanical loads.

It is well known the several methods of the joining of ceramic materials: i) joining by brazing technique (Ag, Au, etc.) [1]; ii) joining by mechanical load – sealing [2, 3]; iii) joining by glass-ceramic intermediate layer [4, 5, 8]. The brazing technique is often used in electronic industry and vacuum technique and its application limited of 400-500°C working temperatures. The sealing technique involves the use of an external load for seam sealing. The glass-ceramic interlayer joins can work at high temperatures (800-1000°C) and maintains their properties for a long time.

The good joining with glass-ceramic interlayer is ensuring by the good wettability and low mismatch of thermal expansion coefficients between the interlayer and the mullite. Besides, the low level of viscosity (near 10^5 dPa*s) should be in glass state for ensure the wetting of ceramic material and high level of viscosity (near 10^9 dPa*s) should be in glass-ceramic state for prevention of outflow of joint material from seam. In view of these requirements, $Y_2O_3 - Al_2O_3 - SiO_2$ glasses (YAS) seem to be the suitable joint material for the joining of mullite material.

In this research, we study the structure formation, strength and gas permittivity of joint between the mullite material (bars and pipes) with yttria–aluminia–silicate (SiO_2 54 wt%, Al_2O_3 18 wt%, Y_2O_3 28 wt%) glass powder. The optimal joining conditions, microstructures and strengths of the joint, as well as gas permittivity, were characterized.

2. Experimental

2.1. Material preparation

Mullite samples were fabricated by sintering of mullite powder, which was synthesized by calcination of the mix of the aluminum hydroxide with silica hydroxide in stoichiometric composition. The $Si(OH)_4$ or hydrous silica gel and aluminum hydroxide were precipitated in ammonia water solution separately. The wet silica gel and aluminum hydroxide were mixed in water, filtered, dried in

a microwave furnace with an output power of 700 W at a frequency of 2.45 GHz and calcined in a resistive furnace at 1200°C for obtaining maximal value of mullite phase [6, 7].

For determination of mechanical properties of sintered mullite materials and joined samples the rectangular shape samples (40*5*20 mm and 25*25*1 mm) and tube with diameter 20 mm, height 30 mm and wall 3 mm thick were prepared firstly by means of uniaxial cold pressing at 60 MPa, then isostatic pressing at 200 MPa and finally pressureless sintering at 1600 °C for 1h.

The composition of YAS glass was SiO_2 54 wt%, Al_2O_3 18 wt%, Y_2O_3 28 wt%. This composition has very high melting temperature (near 1650°C) and we melted the oxide mix at 1800°C 30 min in inductive furnace. After that the glass was quenched in water and ball milled in planetary mill MSK-SFM-1 (MTI Corp., USA) at 400 rpm for 4 h using YSZ milling media.

2.2. Materials characterization

The powders, sintered specimens and crystallized YAS glass-ceramic were characterized by means of XRD (Dron-3) with Cu-K α radiation for crystallite sizes and quantitative phase analyses. Particle sizes of different calcined powders were estimated by means of transmission electron microscopy (JEM 200, Jeol, Japan). The microstructures of the mullite ceramics and its joints were studied by scanning electron microscopy (JSM 6490LV Jeol). The density of sintered mullite material was determined by Archimedes method.

The shrinkage data of the pressed pellet from this glass powder was obtained using a dilatometer (DIL 402 PC, Netzsch) during heating sample till melting process begun. The dilatometer was calibrated using a standard sample of Al_2O_3 . The detected control points during heating the glass sample T_d – 958.5°C, T_c – 1368°C and T_m – 1420°C (Fig. 1) were in a good agreement with literature data.

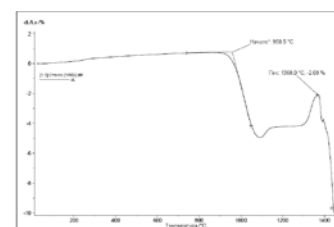


Fig.1 The shrinkage curves for YAS glass powder

The joints between two (40*20*5mm) mullite bars were carried out on 40*5 mm side by YAS glass powder slurry (Fig. 2). The glass powder slurry was prepared by mixing glass powder in 3wt% polyvinilbutiral ethyl alcohol solution. The joined samples were cut perpendicular the joint seam for obtaining rectangular samples

5*5*40 mm for testing on 4 point bending. The flexural strength was measured using a four-point bending test on polished samples with a cross-head speed of 0.5 mm/min (Tinius Olsen H50kT, USA).

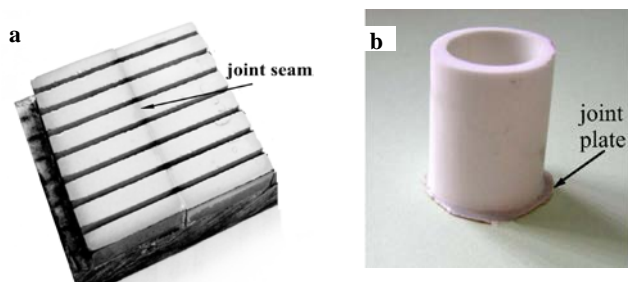


Fig.2 The joined mullite samples for bending strength (a) and gas permittivity (b) testing

For gas tight test the joints between sintered mullite tube and plate, which were cut from bar (25*25*1 mm) were prepared. The joint regime was: heating to 1470°C with 180°C/h, dwelling time 2h and heating to 1200 with 120°C/h and final cooling to room temperature with a furnace. Measuring of joints gas permittivity was carried out on monitoring of pressure in the joined tube samples by DDR-1200 - pressure monitor (J-KEM Scientific, USA), which can support and measure pressure in the set volume. The measuring provided at next regime: heating to 100, 200, ...900°C at 150°C/h, exposure on temperature and measure pressure decay, heating at next temperature and so on. The measurement system of pipes, valves and other (without sample), has leak $1.5-2.2 \cdot 10^{-6}$ Pa*m³/c at pressure in the system of 40-50 kPa. The measurement of test-tube sample or closed sample (with identical volume) shows that leak of test-tube sample and system was $2.2-2.7 \cdot 10^{-5}$ Pa*m³/c.

3. Results and discussion

The XRD data shown that after calcinations at 1200°C the formation of mullite powder is almost completed (92% mullite and 6% cristobalite). After sintering of this powder at 1600°C the phase composition was represent only mullite phase. The chemical composition of powders and sintered samples were analyzed by SEM with EDS analysis. The chemical composition of mullite was practically corresponding to stoichiometric composition Al₂O₃:SiO₂ as 72.5:27.5. The density value of sintered mullite material was 3.11 g/cm³, porosity – 0.35%. The SEM investigations (Fig. 3) of fractured surface represent a uniform distribution of micron size of mullite grains (average diameter 2.8 μm). The coefficient of thermal expansion (CTE) of mullite material was $6.28 \cdot 10^{-6}$ /K. At the sintered and cooled YAS sample the CTE was also measured. In temperature region 200 – 900°C the CTE value was $6.7 \cdot 10^{-6}$ /K.

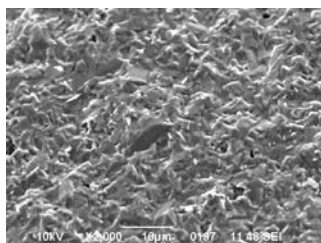


Fig. 3 SEM image of fracture surface of sintered at 1600°C mullite material

The 4 point bending strength value of mullite material was 184 ± 22 MPa and for joined samples - 104 ± 16 MPa. This value in several times higher in comparison with strength value which can be obtained under joining by noncrystallized glasses.

The testing of joined sample on gas tightness shows that in the temperature range from RT to 900°C the leak rate through the joining made from YAS glass between tube and plate from mullite material does not exceed $2.5 \pm 0.5 \cdot 10^{-4}$ sccm/cm (Fig. 4). This is high enough values, which can be compared with tightness of SOFC components [8].

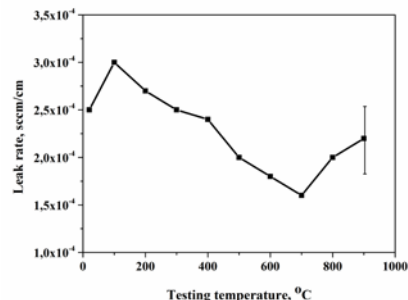


Fig. 4 Leak rate versus testing temperature through joints between two mullite samples joined by YAS glass

As is well known the strength values of glass materials is very low and can not ensure the strength of joints. Increasing of strength value of glass material achieves by addition in glass material ceramic or metallic particles or carried out the partial crystallization lead to formation oxide inclusions in a glass matrix. The crystallization of YAS glass is typical example of such strengthening. The advantage of YAS glass in mullite joining process is the formation of mullite phase during crystallization.

The YAS glass was investigated after joining process (heating and cooling) for determination of crystallization behavior and changing of chemical composition. The joint layer thickness was near 70 μm. The joint layer and border between ceramic mullite material and joint material do not contained the porosity. This is evidence that joint regime is correct. After crystallization the joint material consists basically from yttrium silicate and mullite phase. At SEM image we can see the character needle like crystals of mullite (Fig. 5). The small amount of third phase (white crystals) was not identified. The concentration of alumina in these inclusions is slightly decreased (3-5%) (spectra 5, 6, 7 in Table 1) and yttrium oxide increased in comparison with average values (spectrum 3 in Table 1).

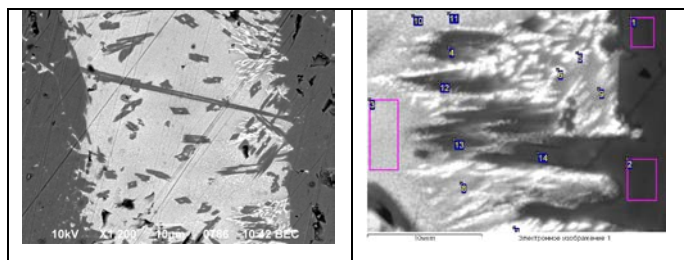


Fig. 5 The SEM image of mullite - mullite joints by YAS glass-ceramics. The cross section of joint seam with low – a) and high magnification – b). On fig. 5b the EDS analyses zone are marked.

Table 1. The EDS analysis data of crystallized YAS glass. The number of spectrum corresponds to analyzed zones on fig. 5b.

Spectrum	Concentration, wt%		
	Al ₂ O ₃	SiO ₂	Y ₂ O ₃
1	72.40	27.60	0
2	72.79	27.21	0
3	18.03	51.61	30.37
4	30.28	58.05	11.67
5	13.75	49.56	36.68
6	15.83	51.02	33.15
7	14.59	48.83	36.58

At bigger magnification we see that crystallization in YAS glass at cooling pass by eutectic like mechanism (Fig. 6). The small points of darker phase – the mullite crystals in yttrium silicate glass-ceramics. A typical inclusions mullite size less than 20 nm.

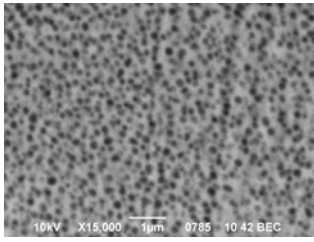


Fig. 6 SEM image of joint layer from crystallized YAS glass

So, the formation of composite or nanocomposite structure during crystallization YAS glass lead to increasing the strength value of joint seam between two mullite samples. The good adhesion of YAS glass to mullite material and low CTE mismatch between mullite and YAS glass-ceramic allow producing the gas-tight joints. In addition, this method of the joining by YAS glass-ceramic can be used to join for other materials with close CTE values, for example SiC.

Conclusion

Yttrium aluminosilicate glass powder was used as the joint material for joining two mullite samples of different forms. The glass joint layer softens at joining temperature (1450-1470°C) to bond the mullite samples without additional pressure and then crystallized during cooling. The good adhesion of crystallized glass to mullite surfaces ensue the gas-tight joints with permittivity $2.5 \cdot 10^{-4}$ sccm/cm. The eutectic like crystallization of YAS glass into yttrium silicate and mullite lead to formation the nanocomposite structure which ensure the 4 point bending strength value near 105 MPa. The YAS glass can be used as joint material for bonding materials with CTE value near $6 \cdot 10^{-6}/K$.

Acknowledgments

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