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Glass–ceramic functionally graded materials produced with different methods

V. Cannillo, L. Lusvarghi, T. Manfredini, M. Montorsi, C. Siligardi, A. Sola *

Dipartimento di Ingegneria dei Materiali e dell'Ambiente, University of Modena and Reggio Emilia, Via Vignolese 905, 41100 Modena, Italy

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Abstract

Functionally graded materials (FGMs) are innovative composite materials characterized by a gradual spatial change in composition, microstructure and related properties. This work was focused on glass–alumina functionally graded materials, produced via percolation of molten glass into a sintered polycrystalline alumina substrate and via plasma spraying. The glass composition, belonging to the $CaO–ZrO_2–SiO_2$ system, was purposely designed in order to minimize the difference between the coefficients of thermal expansion of the constituent phases, which may induce thermal residual stresses in service or during fabrication. The ingredient materials as well as the resultant FGMs were carefully characterized. In particular, a great attention was devoted to the microstructural investigation of the penetration profile.

Keywords: Microstructure-final; Mechanical properties; Al_2O_3; Glass; Functionally graded materials

1. Introduction

Functionally graded materials (FGMs) are an innovative and attractive class of composite materials. Their distinguishing characteristic is that the constituent phases are not uniformly distributed, but the composition and microstructure vary in space, following a determined law.[1] As a consequence, a spatial change in properties arises from the compositional and microstructural gradient and it may be tailored to the assigned thermo-mechanical loading conditions. Therefore, FGMs allow to exploit the peculiarities of the ingredient materials but the gradual change in composition and microstructure minimizes the residual stresses which may be caused by the heterogeneity of the constituent phases.[2]

If the functional gradient is properly designed, FGMs may show unexpected properties, which differ from those of the single ingredient materials and also from those of the traditional (not graded) composite materials having the same mean composition. For example, Jitcharoen et al.[3] attentively considered a glass–alumina functionally graded material, obtained by melting a $CaO–Al_2O_3–SiO_2$ glass and inducing its percolation into a polycrystalline alumina substrate via a thermal treatment. The resulting system displayed a gradual change of composition associated with a smooth increase of the elastic modulus as a function of depth. This, in turn, made better the superficial hardness, improved the contact-damage resistance and substantially suppressed the Hertzian cone cracking phenomenon. Moreover, Suresh et al.[4] proved that, if the gradient in elastic modulus is optimised, the superficial resistance to frictional sliding contact of the glass–alumina FGM may be significantly enhanced with respect to the alumina alone.

The present contribution was focused on similar FGMs, made up of a $CaO–ZrO_2–SiO_2$ glass and a polycrystalline alumina substrate. The graded systems were obtained via different routes, i.e. (I) molten glass percolation (starting from glass powder and from glass bulks) and (II) plasma spraying. Glass percolation is an example of a natural transport based process,[5] since it exploits the glass attitude to penetrate into a polycrystalline alumina by moving along its grain boundaries. Plasma spraying, instead, is a constructive technique,[5] since the graded profile is built up layer by layer. Besides characterizing the ingredient materials, the final graded systems were accurately investigated and compared. In order to analyze the resulting profile, particular attention was paid to the SEM inspection. Moreover, as regards the FGMs

* Corresponding author. Tel.: +39 059 2056240; fax: +39 059 2056243.
E-mail address: sola.antonella@unimore.it (A. Sola).

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obtained via percolation, the SEM images were used to evaluate the compositional profile, quantifying the glass volume fraction as a function of depth.

2. Materials and methods

2.1. Ingredient materials

As already mentioned, a $CaO–ZrO_2–SiO_2$ glass and a polycrystalline sintered alumina were used to produce the FGMs.

2.1.1. Alumina

As far as the substrate is concerned, a commercial sintered alumina was used.[6] The alumina, which is characterized by a polycrystalline microstructure, is a high purity product (purity: 99.7%), supplied in the form of square tiles (around 50 mm × 50 mm × 8 mm). The mineralogical nature of the alumina was tested by means of a X-ray diffraction (XRD) (Philips PW 3710). The alumina morphology was investigated via SEM observation; in particular, the microstructural features of the cross-section were made more clearly visible by performing a thermal etching (30 min at 1500 °C). The coefficient of thermal expansion was evaluated with a NETSCH-DIL 404 dilatometer. The Young's modulus as well as the Poisson's ratio were measured by subjecting an alumina bar to a resonance-based technique (EMOD, Lemmens Grindosonic® MK5).

2.1.2. Glass

As regards the glass, a formulation belonging to the $CaO–ZrO_2–SiO_2$ (CZS) ternary system was chosen, since a previous research had proved that the glasses belonging to such system usually show relevant chemical, physical and mechanical attributes.[7,8] In particular, CZS glasses are often characterized by high values of the Young's modulus and toughness (with respect to other glasses). Moreover, while designing the glass formulation, an attempt can be made to minimize the discrepancy between the glass and the alumina coefficients of thermal expansion. To conclude, it is worth noting that the absence of Al_2O_3 in the glass composition may simplify the characterization of the final FGM, since the constituents of the substrate (i.e. alumina) are not present in the glass and vice versa.

The glass was produced by mixing, milling and melting commercial raw materials in powder form (quartz, calcium carbonate and zirconium silicate). Some glass was directly plunged into cold water and the resulting frit was wet ball-milled and dried off in a kiln. The glass powder was used to produce both the percolated and the thermal sprayed FGMs. The remaining glass was poured thus obtaining a 70 mm × 10 mm × 10 mm bar, which was subsequently annealed at 800 °C for 60 min. Then the glass bar was cut into 1 mm thick slices, which were needed for the FGM fabrication via percolation starting from the glass in bulk form. In the same way (purposely pouring and annealing the glass) two more specimens were obtained: a bar, appropriate for the evaluation of the coefficient of thermal expansion (45 mm × 5 mm × 5 mm), and a disk, suitable for the resonance-based measurement of the mechanical properties (diameter of 50 mm; thickness of 6 mm). To conclude, a glass fragment (not annealed) was ground and subjected to a differential thermal analysis (NETZSCH-DSC 404) which, coupled with a proper crystallization study, gave further information about the glass thermal behaviour.

2.2. Functionally graded materials

In order to fabricate the glass–alumina FGMs, two different methods were employed: molten glass percolation and plasma spraying. Moreover, the percolation method was developed in two alternative versions: starting from glass powder and starting from glass bulk slices. Therefore, three different FGMs were obtained: percolated starting from the glass in powder form (later on named "powder percolated FGMs"), percolated starting from the glass in bulk form ("bulk percolated FGMs") and plasma sprayed ("thermal sprayed FGMs").

In order to produce the "powder percolated FGMs", the glass powder, previously sieved through a 32 μm-meshed sieve, was applied on to the alumina substrate in the form of an aqueous suspension. The powder weight fraction was set to 66.5% in order to optimise the rheological properties of the suspension and a 2 wt.% vynilic binder was added in order to improve the handiness of the green system.[9] A 1 mm thick layer of suspension was uniformly spread on the alumina substrate and then the water was dried off in a kiln. To conclude, the alumina–glass system was purposely heat treated, thus, inducing the glass melting and subsequent penetration into the polycrystalline alumina. The system was heated from room temperature to 500 °C at 5 °C/min and from 500 to 1600 °C at 10 °C/min; it was left at 1600 °C for 4 h and then it was cooled from 1600 to 1000 °C at 20 °C/min; after that, the specimen was completely cooled down in air.

The "bulk percolated FGMs" were obtained by placing a 1 mm thick glass slice onto the top surface of the alumina substrate and performing the same heat-treatment described above.

As regards the "thermal sprayed FGMs", a graded multilayered glass–alumina coating was deposited on an alumina substrate via a plasma torch. In fact, the graded coating was constructed by depositing several layers, each of which was created by spraying a mixture of fixed composition of commercial alumina powder[10] and CZS glass powder. The mean composition of the strata progressively changed from a 80 vol.% alumina–20 vol.% glass layer at the interface with the substrate to a 100 vol.% glass top layer. The substrate surface was previously grit-blasted with SiC powder in order to enhance the coating adhesion and the glass powder was atomized in order to optimise the spraying process. To conclude, a "thermal sprayed" FGM was subjected to a properly designed thermal treatment in order to induce the sintering and controlled crystallization of the glass.

All the resulting FGM specimens were cut along a vertical plane, thus, making visible the cross-section and in particular the graded profile. In order to check the possible formation of new crystal phases, an XRD was performed on the FGM cross-section. Since an accurate microstructural investigation was required, the FGM cross-sections were carefully observed by SEM.

In particular, with regard to the "percolated FGMs", for the purpose of estimating the depth reached by the glass, during the SEM observation the FGM cross-section underwent a local chemical analysis by X-ray energy dispersion spectroscopy (X-EDS). Moreover, the cross-section of a "bulk percolated FGM" sample was carefully polished and chemically etched for 10 s with a 5 vol.% aqueous solution of hydrofluoric acid; the chemical etching, which removed the glass but did not affect the alumina grains, made more evident the microstructural features of the FGM section. Several partially overlapped SEM images were taken and then joined like a jigsaw puzzle, thus, obtaining a wide picture of the cross-section. This column-like image, representing a 120 μm wide, 1600 μm deep area, was purposely elaborated and used to evaluate the glass volume fraction as a function of depth.

3. Results and discussion

3.1. Ingredient materials

The alumina XRD pattern revealed the presence of only one crystal phase, which was identified with corundum syn. (α form of the alumina). The microstructure, observed after the thermal etching, appeared substantially homogeneous, with small pores, evenly dispersed throughout the alumina cross-section. It is worth noting that the porosity was made more evident by the thermal treatment and that the alumina density, however, is really high, around 3.9 g/cm^3.[6] The coefficient of thermal expansion resulted to be 8.28×10^{-6} K^{-1}; the Young's modulus and the Poisson's ratio were 379.2 GPa and 0.21, respectively.

The alumina thermo-mechanical properties are to be compared with those of the glass.[8] First of all, the glass coefficient of thermal expansion was 8.65×10^{-6} K^{-1}, a value really close to that of the alumina. Moreover, the Young's modulus, which resulted to be 96.2 GPa, was very high for a glass; the Poisson's ratio was evaluated to be 0.27. It is really important to know the properties of the ingredient materials, since they may deeply influence the FGM final behaviour. Moreover, it would be desirable to achieve a good correspondence between the thermo-mechanical properties of the ingredient materials – especially the coefficients of thermal expansion – thus reducing the residual stresses which may be caused by the system heterogeneity.

The differential thermal analysis showed that the glass transition occurred at about 790 °C. The glass crystallized at about 1050 °C, promoting the growth of wollastonite and $Ca_2ZrSi_4O_{12}$ as main phases.

3.2. Functionally graded materials

3.2.1. Powder percolated FGMs

The XRD patterns which were collected on the "powder percolated FGM" cross-section (Fig. 1) and the alumina cross-section substantially showed the same peaks. This means that neither the heat treatment nor the glass infiltration induced a relevant formation of new crystalline substances.

As regards the X-EDS analysis of the FGM cross-section, the SiO_2 was assumed as a "marker" of the glass, since it was not initially present in the substrate. The X-EDS confirmed that in the "powder percolated FGMs" the glass penetrated into the alumina substrate, reaching a maximum depth of around 5000 μm (Fig. 2a).

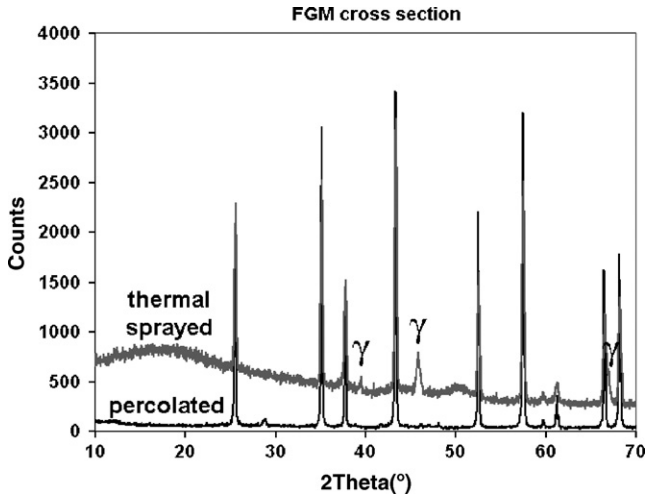

Fig. 1. XRD patterns of the "percolated" and "thermal sprayed FGM" cross-section.

The SEM observation immediately revealed a diffused crystallization of microscopic zirconia particles dispersed in a glass matrix (Fig. 3). It is likely that the zirconia amount was not enough to be detected by the XRD, however its development was evident. The formation of a new crystal phase may be beneficial to the FGM performances, since the crystal particles may act as reinforcements in the glass phase. Nevertheless the crystallization results in a modification of the composition of glass, whose properties are altered as well. Since it is not possible to define reliably the new glass composition and quantify the zirconia crystallization, it is hard to predict the actual thermo-mechanical behaviour of the final graded system. As a consequence, the "powder percolated FGMs" will be discarded in the following.

3.2.2. Bulk percolated FGMs

The XRD was substantially analogous to that of the "powder percolated FGM": again, the only crystallographic phase detected was the α-alumina of the substrate. The X-EDS analysis proved that the glass percolated into the alumina substrate up to 1600 μm of depth (Fig. 2b). Therefore, if the glass is employed in bulk instead of in powder form, the maximum depth of penetration is smaller. In fact, it is likely that the powder glass is more reactive than the bulk, thus, enhancing the kinetics of infiltration. The SEM observation of the cross-section confirmed that the "bulk percolation" method did not induce a significant crystallization of new phases and, in particular, zirconia particles. This is consistent with the fact that the CZS glasses in bulk usually have a reduced attitude to crystallize with respect to the powder.[7]

Since the "bulk percolated FGMs" could be successfully produced, a more detailed microstructural investigation was performed by chemically etching the FGM cross-section. The selective chemical etching, in fact, removed the glass without affecting the alumina grains, thus, making more visible the

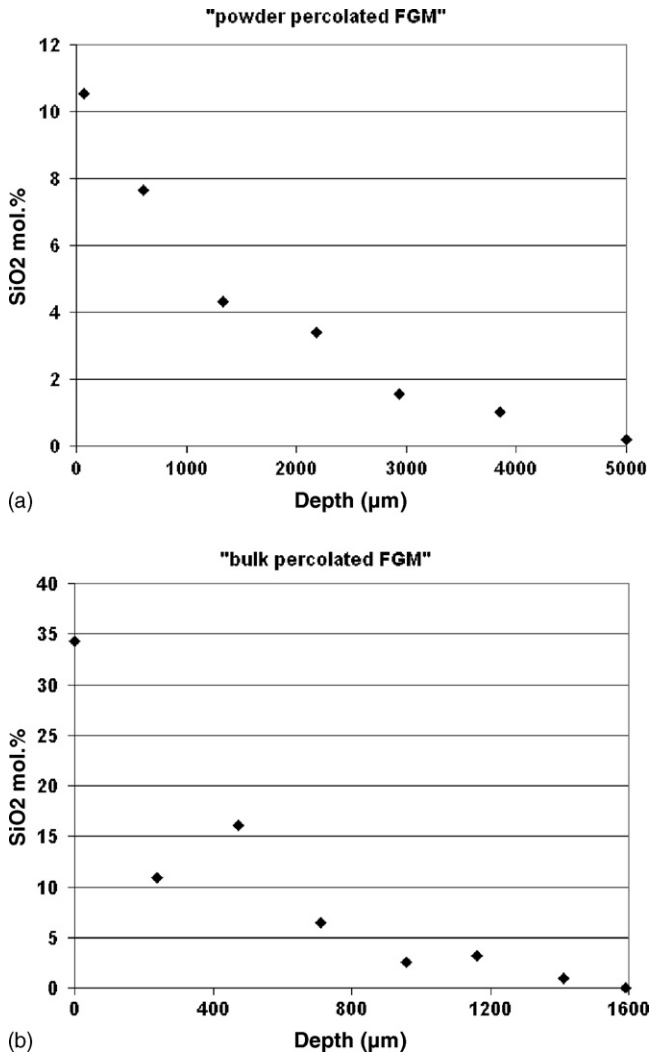

Fig. 2. SiO_2 content as a function of depth in the "powder percolated FGM" (a) and the "bulk percolated FGM" (b).

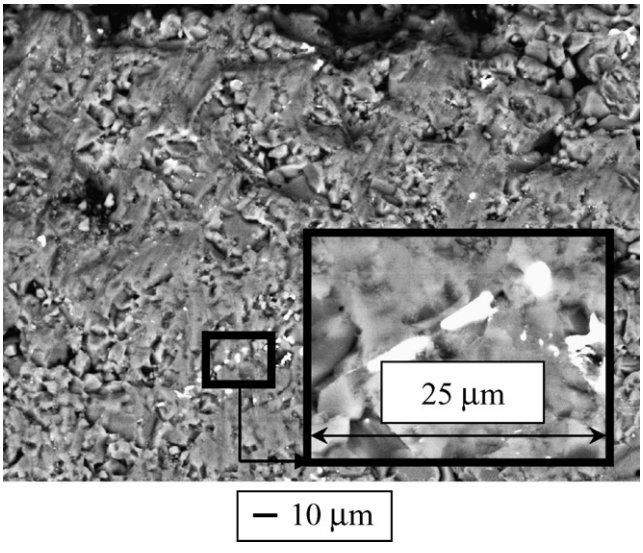

Fig. 3. The "powder percolated FGM" underwent a crystallization of zirconia, as shown in the detail.

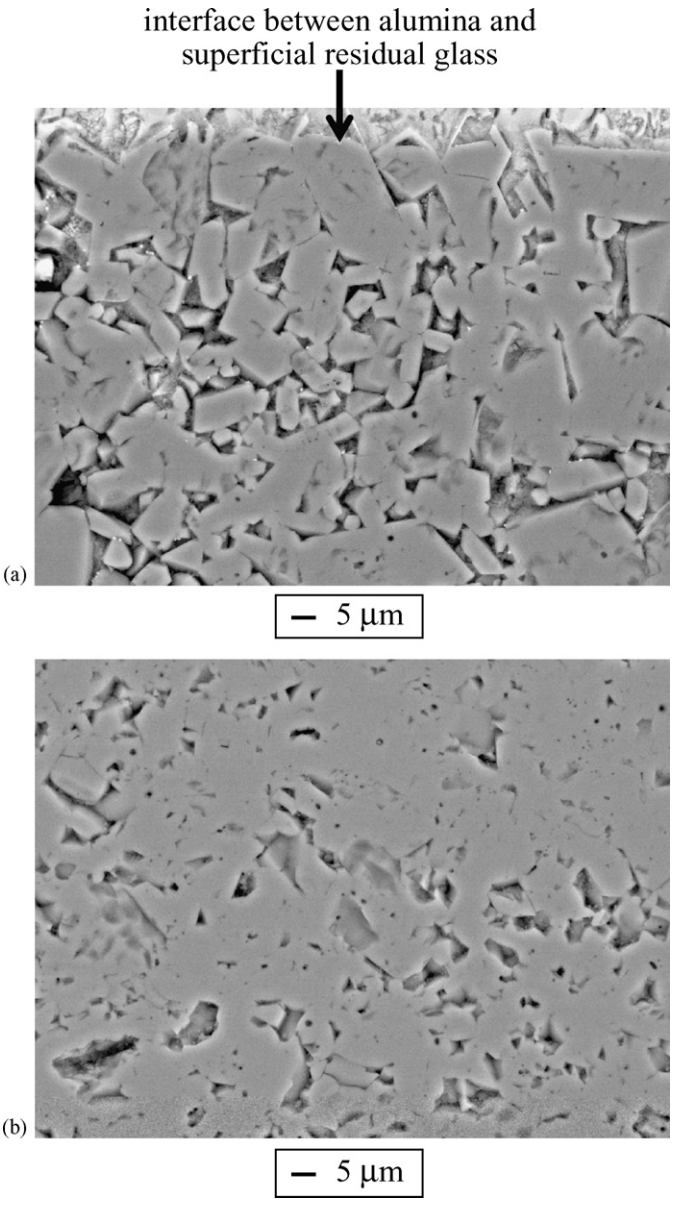

Fig. 4. Microstructural details of the "bulk percolated" FGM cross-section taken at about 50 μm of depth (a) and 1600 μm of depth (b).

microstructural features. The SEM observation of the chemically etched specimen clearly proved that the microstructure progressively changed along the glass penetration direction, as shown in Fig. 4a and b. The SEM images suggested that the glass penetrated into the alumina substrate by moving along its grain boundaries and partially filling the pores possibly present in the substrate.[11] This means that, even if the compositional and microstructural gradient is continuous at the macroscale, the resulting system is discrete and stochastic at the microscale, since distinct domains of alumina (i.e. alumina grains) and glass can be identified. Therefore, if the microscale is considered, thermal residual stresses may arise at the alumina–glass interface[12] and these local stress concentrations may result in local damages and, in the end, large-scale failures. Since the reliability of FGMs may be affected by the microscale thermal stresses, it is of the utmost importance to select the ingredient materials

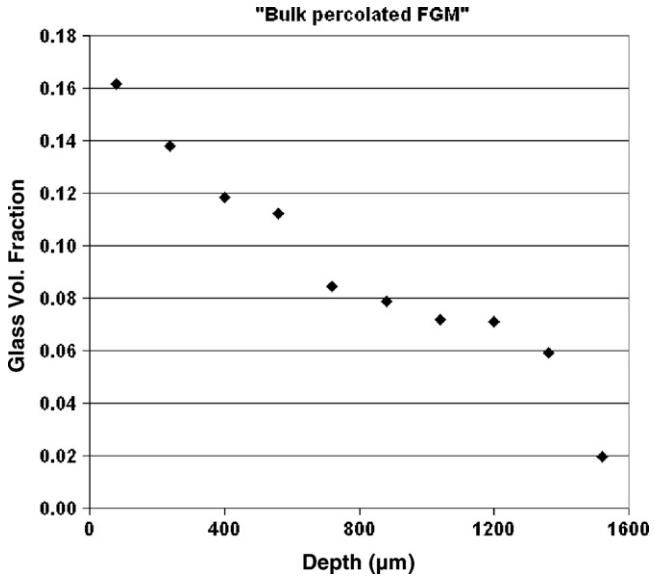

Fig. 5. Glass volume fraction of the "bulk percolated FGM" as a function of depth.

thus minimizing the mismatch in thermo-elastic properties, as mentioned above.

Moreover, several SEM photographs of the chemically etched specimen were taken (in file format) and then joined like a jig-saw puzzle in order to obtain a 120 μm wide, 1600 μm deep picture of the graded cross-section. Such column-like overall image of the graded profile was elaborated and the glass volume fraction was evaluated as a function of depth (Fig. 5). For this purpose, it was assumed that the glass volume fraction could be considered equivalent to the volume remained empty after the chemical etching. It is possible to see that the glass volume fraction diminishes at increasing depths, following a trend which is substantially linear. The trend, however, is not strictly monotonic, due to the microstructural heterogeneity mentioned above.

3.2.3. *Thermal sprayed FGMs*

Unlike the previously described ones, the XRD pattern of the "thermal sprayed FGM" (Fig. 1) showed two different sets of peaks: one set was related to the α-alumina of the substrate, the other one was due to the partial transformation of the sprayed alumina powder from the α polymorph to the γ one, which was caused by the really high temperatures reached in the plasma flux and the subsequent quick cooling down of the splats.

The SEM examination showed that the resultant deposited coating was about 500 μm thick (Fig. 6a). The alumina splats and the glass ones could be easily distinguished but the inter-splat connection was really good. Some residual pores were dispersed throughout the coating thickness, but the major problem with the as-sprayed system was the relatively poor adhesion at the substrate–coating interface. Therefore the "thermal sprayed FGMs" were heat-treated performing a double isotherm: a first isothermal step at 850 °C for 30 min enabled sintering to start and a second isothermal step at 1050 °C for 30 min led to a fine and controlled crystallization of wollastonite and $Ca_2ZrSi_4O_{12}$

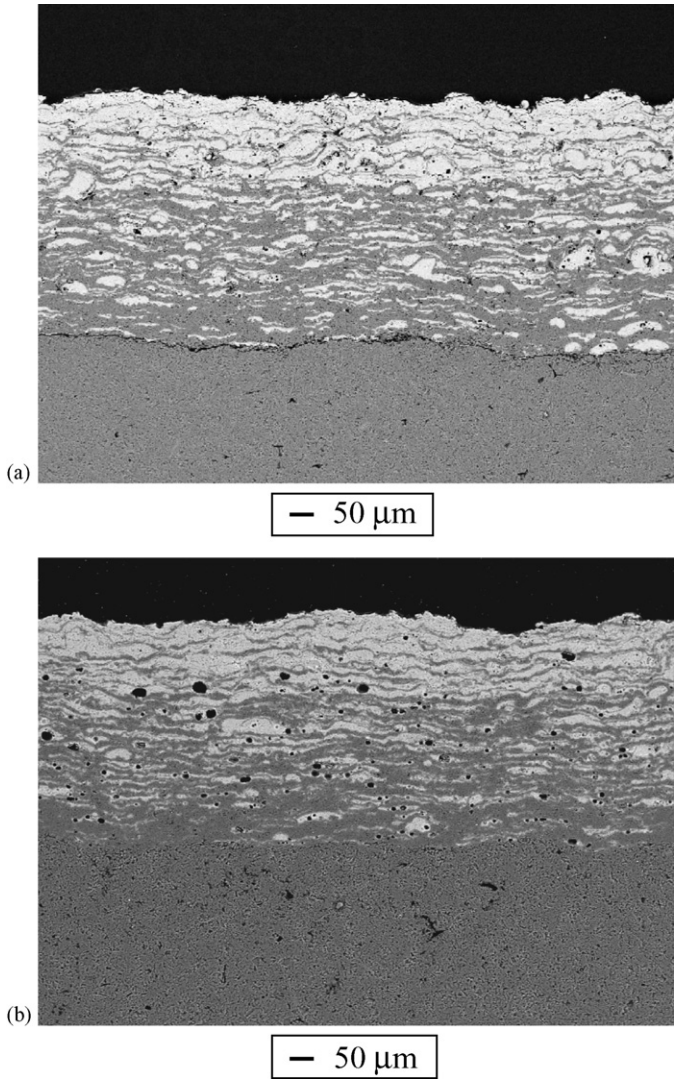

Fig. 6. Cross-section of the "thermal sprayed FGM" as sprayed (a) and after heat treatment (b).

(in traces), as proved by the XRD. The pores, though not completely eliminated, assumed a round shape and, most of all, the coating–substrate adhesion significantly improved (Fig. 6b). It is worth noting that the heat treatment caused a wide crystallization of the glass phase, but did not significantly altered the spatial distribution of the alumina and the newly crystallized glass. As a consequence, the final system may be considered a new FGM, made up an alumina phase and a glass–ceramic phase. The thermo-mechanical characterization of the new system is still in progress.

4. Conclusions

Many fabrication methods were proposed to obtain glass–alumina FGMs. Some specimens were produced via a natural transport based method, which employs the capability of molten glass to percolate into a polycrystalline alumina substrate. The glass was used in powder form and in bulk form (thin slices). In the former case, the glass could penetrate very deeply into the

substrate, up to 5000 μm, but a not-controlled crystallization of zirconia was observed. In the latter case, since the glass in bulk form possessed a smaller penetration kinetics but also a lower attitude to crystallize with respect to the powder, the maximum depth of penetration was reduced to 1600 μm, but no significant crystallization occurred. The overall trend of the graded profile was linear but not strictly monotonic, since the FGM microstructure resulted to be discrete and heterogeneous. Furthermore, a constructive method was attempted to produce glass–alumina FGMs, since a thick graded coating was built layer by layer via a plasma spraying route. This approach is more expensive than percolation, but it seems to be extremely attractive, since it enables to built arbitrarily the compositional gradient; moreover, the process is more controlled and reproducible than percolation. However, since the as sprayed FGMs showed some residual porosity and a weak coating–substrate interface, a proper thermal treatment was performed to improve the FGM performance. The thermal treatment facilitated the sintering of the glass and promoted a wide but controlled crystallization; the resulting system, therefore, may be considered as a new glass ceramics-alumina FGM, whose properties are still under study.

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