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Ceramic matrix composites with gradient concentration of metal particles

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Abstract

The design of ceramic–metal composites with a gradient concentration of the metal particles fabricated by the slip casting method is presented. The gradient concentration of the metal particles was achieved through their sedimentation under the action of the gravitational force and a magnetic field. The paper describes the method of calculating the distance between the ceramic particles and indicates the correlation between this distance and the size of the metal particles. Preliminary experimental results of fabricated Al_2O_3–Fe composites confirmed the calculations.

The metal particles, whose density is higher than that of ceramic particles, can undergo gravity-induced sedimentation only when the distance between the ceramic particles is greater than the diameter of these metal particles. With a slip casting containing 50 vol.% of solid phase, no concentration gradient of metal particles occurred. The Fe gradient concentration was achieved when the sedimentation was aided by a magnetic field.

Keywords: Gradient ceramic–metal composites; Slip casting

1. Introduction

The principal advantage of ceramic–metal composites is an increase of the resistance to brittle fracture compared to that of the ceramic matrix.[1,2] The increase of the fracture toughness depends on the amount, size and shape of the metal phase and on the uniformity of their distribution.[3–5] The metallic phase distributed throughout the ceramic matrix can in addition modify its electric, thermal and magnetic properties.

By modifying the uniformity of distribution of the metal particles within the ceramic matrix, we can design gradient-type composites.[6–9] The variation of the percent content of the metallic phase as a function of the distance from the surface of the material can be tailored to the gradients of the thermal and mechanical loads that act upon a given product. For example, it is often required that the metallic phase content should be increased in the near-surface zone of the product. Several applications demand that not only the percent content of the metallic phase in the volume of the component should be varied, but also the particle size of this phase should vary in a gradient way. By modifying the particle size of the metal in a composite, we can precisely control its properties. The literature data and our own experiments indicate that, in composites, the particle size of the metallic phase affects essentially crack propagation.[3–5,10,11] Fig. 1(A) shows a schematic representation of a composite with a gradient of the metallic particle concentration in the ceramic matrix, and Fig. 1(B)—a representation of a composite with a gradient of the metal particle size.

The major problem in designing gradient composites lies in controlling the gradient of the concentration or size of the metal particles within the ceramic matrix. This gradient strongly depends on the technique of fabrication of the composites, which must also take into account their specificity.

The main aim of the present work is to present the possibility to fabricate ceramic–metal gradient composite by slip casting. The concentration gradient achieving through the sedimentation process of the metal particles (whose density greatly exceeds the density of the ceramic powder) due to gravitation and also to the action of a magnetic field was considered. The calculation of the sedimentation of the metal particles in ceramic matrix presented in the first part of paper are completed by the preliminary results of fabricated composites. In this part of work the gradient of metal particles concentration was determined by qualitative analysis—observations of microstructure of composites in optical microscope.

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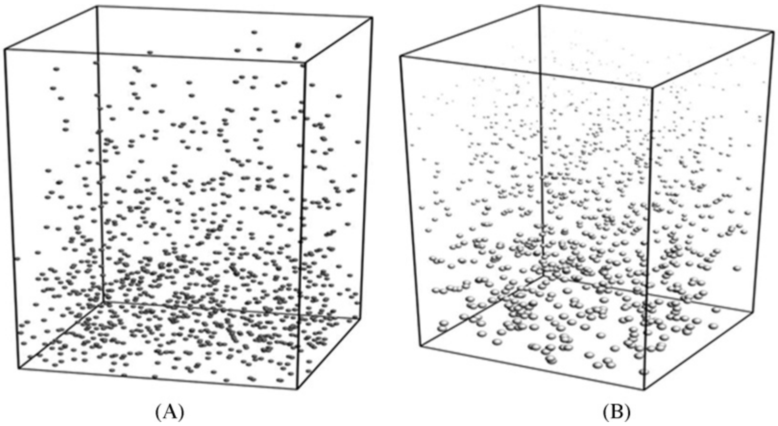

Fig. 1. Schematic representation of a gradient composite: (A) gradient distribution of the metal particles within the ceramic matrix and (B) gradient distribution of the metal particle sizes; metal particles indicated by the black dots.

2. Theoretical aspect of experiment

In order to produce gradient-type ceramic–metal composites with the use of a ceramic casting slip, it is necessary that the concentration of the solid phase and the size of the ceramic powder particles should be properly selected. For the occurrence of sedimentation of particles of a higher density (metal particles), the average distance between the ceramic powder particles of a lower density should be greater than that of the particles of the greater density. This is illustrated schematically in Fig. 2.

The distance between the ceramic powder particles depends on the solid phase concentration and on the size of these particles. In the calculation of this distance, let us assume that the powder particles have a spherical shape. If the volume of the casting mass is denoted by V and the volume of the solid phase in casting mass by V_s it is obvious that $(V - V_s)$ represents the volume of the place which is not occupied by the solid phase (volume of area between particles). If we assume that the number of inter-particle distances is equal the number of the particles which is correct for a large number of particles and which is fulfilled for ceramic casting mass because in this case, the average size of powder particles is on the colloidal level, the average distance between the powder particles is given by the equation:

$$D_{av} = \sqrt[3]{\frac{V}{n}} - 2r \tag{1}$$

In introducing above formula the volume of casting mass and the volume of ceramic powder and the radius of ceramic powder were used.

Where n is the number of the ceramic powder particles with the radius r, given by

$$n = \frac{V_s}{4/3\pi r^3} \tag{2}$$

In these calculations, the assumption that only gravitational and magnetic field forces was made. For simplicity of calculation the capillary forces associated with the filtration of the liquid through the gypsum die, the Brownian movements and the electrostatic forces due to the electric dipole layer formed around the ceramic powder particles were omitted. Introducing Eq. (2) into

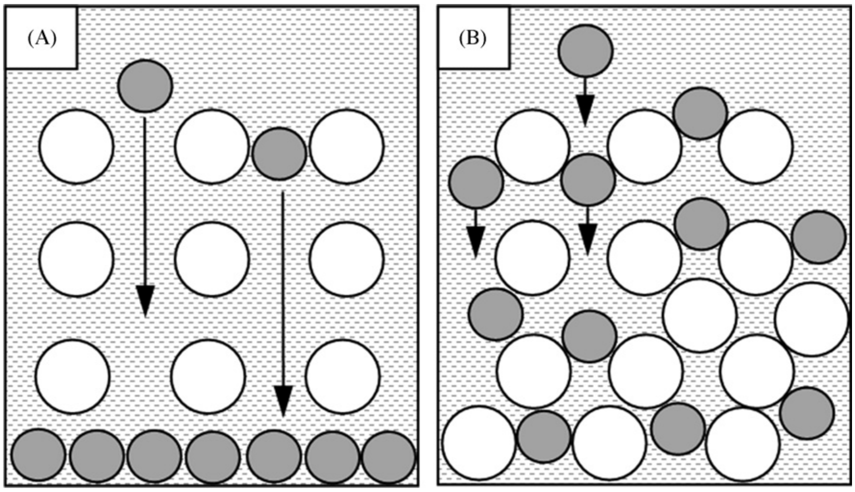

Fig. 2. Schematic of the sedimentation process: (A) size of the Fe particle is smaller than the distance between the ceramic particles, Fe particles flow down and (B) size of the Fe particle is equal or bigger than the distance between the ceramic particles, Fe particles is trapped between the ceramic particles; (ceramic particles, white dots; Fe particles, grey dots).

Eq. (1) (for a constant particle radius) we obtain a relationship that links the average inter-particle distance with the particle size and concentration of the solid phase. This relationship is shown in Fig. 3. We can see from these calculations that for the gradient of the metal concentration to be achieved through the sedimentation of the metal, it is necessary that the concentration of the solid phase contained in the ceramic slurry as well as the size of the ceramic powder and metal particles be properly selected. Sedimentation can only be effective in forming a gradient of the concentration of the metal particles, if the size of these particles does not exceed the distance between the ceramic powder particles (Fig. 2(A))—otherwise the sedimentation of the metal particles is practically impossible, since they are blocked in-between the powder particles (Fig. 2(B)). It should be noted that the distance between the ceramic powder particles decreases with decreasing particle size and in addition is dependent on the volumetric content of the solid phase in the ceramic slurry (Eqs. (1) and (2)). This means that the gradient of the metal particle

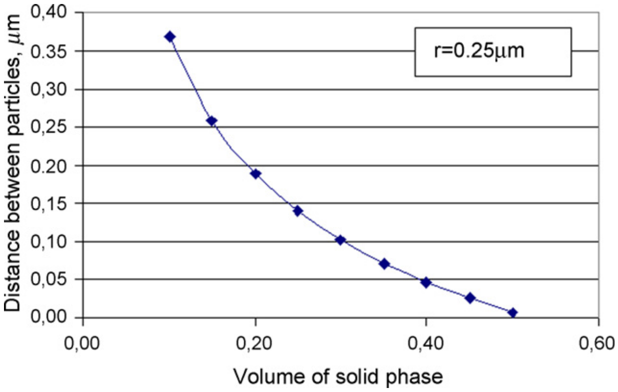

Fig. 3. Relationship of distance between particles and volume of solid phase for the fixed size of particles.

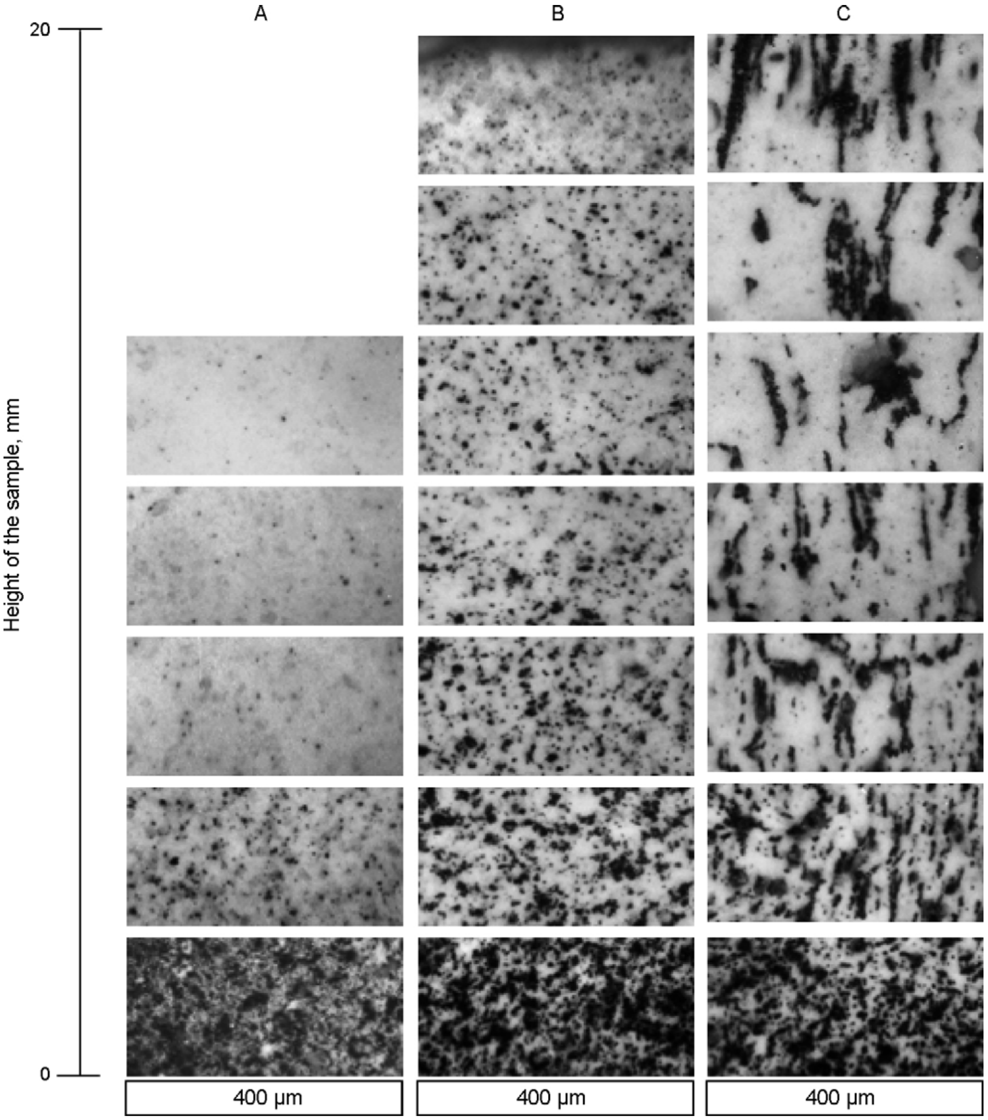

Fig. 4. The microstructures of Al_2O_3–Fe composite obtained by sedimentation method (optical microscope): (A) solid phase concentration 30 vol.%, (B) solid phase concentration 40 vol.% and (C) solid phase concentration 50 vol.% with magnetic field.

concentration depends on the particle size of the ceramics and metal. If the metal particles are equal or greater in size than the ceramic particles, the desired gradient must be forced by, e.g. a magnetic field.

3. Experimental example

This theoretical reasoning has been confirmed by our experiments, in which we examined the Al_2O_3–Fe composites produced by the slip casting technique. The materials used were Al6SG aluminum oxide (α-Al_2O_3) delivered by the Alcoa Co., with an average particle diameter of 0.5 μm and density of 3.92 g/cm^3, and an iron powder delivered by BASF GmbH, Germany, with a particle diameter of 4 μm and density of 7.81 g/cm^3. The casting slip also contained deflocculants (Despex A-40, Allied Colloids Ltd.), surface active substances (*n*-octanol, Aldrich Co. Ltd.) and a binder (poly(vinyl alcohol)—molecular weight 31,000, hydrolysis rate 88%). Poly(vinyl alcohol) was introduced in the form of a 10% aqueous solution. Distilled water was the solvent. The influence of these substances on the reological properties of ceramic slip mass is well known.[12,13] The solid content of alumina and iron powder varied from 10 to 50 vol.%. The constituents of the casting slip were mixed for 0.5 h, and added with the alumina and iron powders. Then the mass was mixed again for 1 h, and poured into a porous die. The microstructure of Al_2O_3–Fe composite obtained by the sedimentation method also with magnetic field are presented in Fig. 4.

For the composite with 30 vol.% of solid phase (vol.% of Fe equal to 5), the gradient concentration of the Fe particles is visible (Fig. 4(A)). In the case of the composite with 40 vol.% of solid phase (vol.% of Fe equal to 5) a slight gradient concentration of the Fe particles is observed (Fig. 4(B)). On the contrary, in the composite with 50 vol.% of solid phase (vol.% of Fe equal to 5) the gradient of the Fe particles concentration was obtained only when the casting process was carried out in the field of a strong magnet placed directly beneath the gypsum die. The magnetic field forced the iron particles to move towards the magnet. Moreover, the iron particles were arranged according to the lines of the magnetic field (Fig. 4(C)).

4. Conclusions

Results presented in the work allowed to formulate the following conclusions:

1. Composites with a gradient concentration of the metal particles distributed within the ceramic matrix can be fabricated by sedimentation due to the gravity forces. With the metal particles of a higher density than the density of the ceramic powder particles, the sedimentation method is only effective if the distance between the ceramic particles or agglomerates of particles is greater than the size of the metal particles.
2. When the gravity-induced sedimentation fails, i.e. the size of the metal particles is equal to, or greater than the distance between the ceramic particles, the gradient concentration of the metal particles can be forced by a magnetic field used to enhance the sedimentation. With the use of a magnetic field, the metal particles arrange themselves along the magnetic lines. The use of a magnetic field in the casting slip process is a new method of fabrication of gradient-type materials. The studies of fabrication by this method the ceramic–metal composites with gradient concentration of metal particles and analyses of their microstructure and properties are being carried out at the Faculty of Materials Engineering and the Faculty of Chemistry, Warsaw University of Technology.

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References

1. Wachtman, J. B., *Mechanical properties of ceramics*. John Wiley and Sons, New York, 1996.
2. Shackelford, J. F., *Introduction to materials science for engineers* (*4th ed.*). Prentice-Hall Inc., 1996.
3. Sbaizero, O. and Pezzoti, G., Influence of the metal particle size on toughness of Al_2O_3/Mo composite. *Acta Mater.*, 2000, **48**, 985–992.
4. Su, X. and Yeomans, J., Microstructure and fracture toughness of nickel particle toughened alumina matrix composites. *J. Mater. Sci.*, 1996, **31**, 875–880.
5. Sigl, L. S., Mataga, P. A., Dalgleish, B. J., Mc Meeking, R. M. and Evans, A. G., On the toughness of brittle materials reinforced with a ductile phase. *Acta Metall.*, 1988, **36**(4), 945–953.
6. Kawasaki, A. and Watanabe, R., Effect of gradient microstructure on thermal shock crack extension in metal/ceramic functionally graded materials. In *Proceedings of the conference 4th international symposium on functionally graded materials*, 1996, pp. 143–148.
7. Parameswaran, V. and Shukla, A., Processing and characterization of a model functionally gradient material. *J. Mater. Sci.*, 2000, **35**, 21–29.
8. Tomsia, A. P., Saiz, E., Ishibashi, H., Diaz, M., Requena, J. and Moya, J. S., Powder processing of mullite/Mo functionally graded materials. *J. Eur. Ceram. Soc.*, 1998, **18**, 1365–1371.
9. Shiono, T. and Noda, K., Fabrication of ceramic composites consisting of powders with different specific gravity by the slip-casting technique. *J. Mater. Sci.*, 1997, **32**, 2665–2669.
10. Konopka, K. and Oziębło, A., Microstructure and the fracture toughness of Al_2O_3–Fe composites. *Mater. Charact.*, 2001, **46**, 125.
11. Konopka, K., Matysiak, H. and Olszyna, A., Homogeneity of the microstructure of the Al_2O_3–Mo composite depending on the mixing time of the powders. In *Proceedings of the 6th international conference on stereology and image analysis in materials science*, 2000, pp. 203–208.
12. Szafran, M. and Rokicki, G., Effect of acrylic–styrene copolymer chemical structure on the properties of ceramic tapes obtained by tape casting. *J. Am. Ceram. Soc.*, 2001, **84**(6), 1231–1235.
13. Szafran, M., Wiśniewski, P. and Rokicki, G., Effect of glass transition temperature of polymeric binders on properties ceramic materials. *J. Therm. Anal. Calorim.*, 2004, **77**, 319.