The effect of grain boundaries on elastic and thermo-physical properties of metal-ceramics composites

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INTRODUCTION

Cermets (metal-ceramic composites) are modern construction materials used in different branches of industry. Their toughness and heat resistance are determined by their elastic and thermo-physical properties. In addition, these properties are significantly dependent on the grain boundaries in the material. These boundaries are formed in the sintering process. In this work, cermets based on corundum and stainless steel (sintered in a high vacuum at temperatures of 1500–1600 °C) are investigated. The volume of steel in the samples varies between 2 and 20 vol.%. The elastic moduli were measured by the ultrasonic method at room temperature, measurement of the thermal conductivity coefficient was carried out at temperatures of 100 and 200 °C, by a method of continued heating in an adiabatic calorimeter. We found two extremes for the dependence of the elastic moduli (E and G) on the stainless steel concentrations, the nature of which is unknown. The moduli values changed in the ranges of E = 110–310 and G = 60–130 GPa (for different temperatures of sintering). Similar dependence is observed for the thermal conductivity coefficient with values varying by 10 to 40 relative units. A discussion of the results based on the structure cermet model as multiphase micro heterogeneous media with isotropic physical properties is also presented.

AIME

The purpose of this work was searching of the formation of grain boundaries in metal-ceramics composites at various metal concentrations and sintering temperatures; influence these boundaries on elastic moduli and thermo conductivity to find the coupling of these properties, to estimate the optimal value of the metal concentration for achieve high quality of ready composites "corundum-stainless steel".

MATERIALS & METHODS

We investigated cermet samples based on α-Al_2O_3 in combination with commercial quality stainless steel (18 wt.% Cr, 9 wt.% Ni, 1 wt.% Ti and 72 wt.% Fe). To fabricate a cermet, an initial fine grained mixture was prepared by milling α-Al_2O_3 powder (2-5 μm) in a ball mill in the presence of balls of 1–2 cm in diameter made from stainless steel. The milling was terminated when the steel content in the α-Al_2O_3 powder became equal to 2.2, 4.0, 5.5, 11.0 and 21.0 vol.%. Then, the mixture obtained was doped with a plasticiser and subjected to dry compaction under a pressure of 100 MPa, followed by sintering in a high vacuum at either 1500 or 1600 °C. Finally, the samples were cooled in a furnace at an average rate of 100 °C/h and no further treatment was made. The prepared cermets ranged in volume porosity from 3 to 7% and had steel contents from 2.2 to 21.0 vol.%. The cermet samples (two series for two temperatures of sintering) were then cut into smaller parts of the required dimensions (10 mm in diameter and 8–15 mm in length), which were further ground and polished, depending on the measuring method. Toinvestigate the elastic properties of the cermets, we measured their density using the hydrostatic method and the velocity of longitudinal and transverse ultrasound waves with a frequency of 2 MHz. The measurement of mechanical stability requires special preparation of many samples to provide reliable results, whereas for the measurement of dynamic elastic moduli, only one sample is required. Using the pulsed phase-interferometer method [4] made it possible to determine the velocity of the ultrasound waves within an accuracy of 0.1–0.2% and 5% for the elastic moduli. Using the data obtained, we calculated Young's modulus, E, and the shear modulus, G, from the well-known formulas of the elasticity theory for an isotropic medium [4]. The thermal conductivity coefficient, λ, was measured using an adiabatic calorimeter, ИТ-λ-400 (Russia). The measuring of λ was carried out by a method of comparison with the standard sample. The measurement accuracy of λ was 2–3% for all samples. Examination of the surface structures (cleaved facet) of the cermet samples was made with a JSM-840 scanning electron microscope (JEOL Ltd.).

RESULTS & DISCUSSION

In Fig. **(1)**, a typical microstructure of the studied cermets, obtained by scanning electron microscopy (SEM), is presented. It can be seen there are three phases in the samples, corundum grains, metal drops and pores. The metal drops have sizes of 2–3 μm and are disposed usually on the joints of the corundum grains, smaller drops are disposed on the grain faces. It should be noted that inter phase grain boundaries are not observed and the size of the corundum grains did not change after sintering.

Fig. **(2)** shows the concentration dependences of the elastic moduli, E and G, for two series of samples (five pieces in each) sintered at 1500 and 1600 °C, respectively. We researched samples with concentrations of 2.2 to 21.0 vol.%. As can be seen from Fig. **(2)**, these curves show complicated behaviour for both series of samples, as moduli E and G decrease and increase with concentration changes with maxima generally at 11.0 vol.%. Minima are observed for curves 1, 1' and 2' at concentrations of 2.2 to 5.5 vol.%.

Fig. **(3)** shows concentration dependences of thermo-conductivity coefficient λ in arbitrary units for the same samples.

In a previous study [1], similar concentration dependences of the strength of metal-ceramic composites have been presented. Two maxima at ~15 and ~85 vol.% were reported. The authors suggested that the qualitative explanation of this effect was based on the influence of a new inter grain phase, which appeared in the sintering process. This phase, as a result of the thermal chemical reaction, possessed new elastic properties. In the estimation authors [5] the volume share of new phase can average tens percent's. The authors of Ref. [1, 2] consider formation of this phase as an important factor for the production of composites with optimal properties. Therefore at present the engineering and studying of this phase become actual [6]. If no component interactions exist, the composite will be an unusable "mechanical mixture". However, this mixture can be used as a simple model for estimating composite properties. In Ref. [7], this model allowed the authors to determine the elastic moduli of the inter grain phase for Cu powder with no porosity and ceramic MgO sintered in a vacuum. It should be noted that the SEM and XRES methods rarely determine the presence of inter grain phases (for example, it is absent in Fig. **(1)**. In the studied cermets, the above phase can exist as a kind of spinel [2], one of them we founded in boundary medium and identified as $FeAl_2O_4$ [8]. Therefore, it is of interest to compare the results for the elastic and thermo-physical properties, while observing the formation of the inter grain phase. This issue is the primary aim of this work.

Fig. **(3)** shows the concentration dependences of λ in arbitrary units for the same samples. We can see that the λ values for both series of samples decrease at 2.2–5.5 vol.% and increase for the second series at 5.5–21 vol.%, for the first series λ decreases in this range. Thus, the minimum elastic moduli (Fig. **(2)**) correspond with the minimum thermal conductivity coefficients (Fig. **(3)**). This effect is valid for both series samples sintered at various temperatures and in our view may be connected with the formation of the inter grain phase described in Refs. [1,2,6-9]. Indeed, at small metal concentrations (~1–2 vol.%), the boundaries of the inter grain phase cannot form, the layer is crumbly and therefore the composite has low elastic moduli and thermal conductivity coefficients (Figs.**(2)** and **(3)**). At concentrations of ~5.5 vol.%, the formation of the boundaries is complete, the inter grain layer possesses a perfect structure and as a result, the composite gains strong properties. If the metal concentration increases to 11 vol.%, the elastic moduli decrease because $E_{ceramics}$ **>** E_{steel}, therefore, the thermal conductivity coefficient increases because λ_{steel} **>** $\lambda_{ceramics}$. Further increasing the concentration to 21 vol.% leads to a noticeable decrease in E and G for all samples and λ in one of the samples (Fig. **(3)**). The increase in porosity of cermets from 3 to 7% may be the reason for the above effect. In our opinion, the gain in thermal conductivity coefficient for the second series will continue for further increases in the volume of steel because λ_{steel} **>** $\lambda_{ceramics}$. At steel concentrations of 20–30 vol.%, the composite structure approximates to the "mechanical mixture" model [2]. In addition the influence of other mechanism for heat transfer in high dispersion medium is possible [10].

The reason for the above considered model of inter grain phase formation may be phonon theory heat transmission in crystals. This theory has been used to explain experimental results of "heat pulses" in sintered composites [7,8]. This method studies the time dependence of propagation of no equilibrium phonons (~10^{12} Hz) at liquid-helium temperatures in ceramics. In a previous work [8], the "heat pulse" method was first used for cermets. It has been found that the appearance of the inter grain phase leads to a decrease in the phonon diffusion coefficient (~10^3 times), as compared with the value for the basic corundum ceramic, and a decrease in composite thermal conductivity at several metal concentrations. In addition, in Refs.[7,8], the phonon diffusion coefficient in nano-disperse corundum-iron composites was investigated at low temperatures. It was shown that a noticeable electron-phonon effect is observed if the size of metal particles is compared with the phonon wavelength, therefore "phonon capture" takes place. This effect decreases the thermal conductivity of the composite.

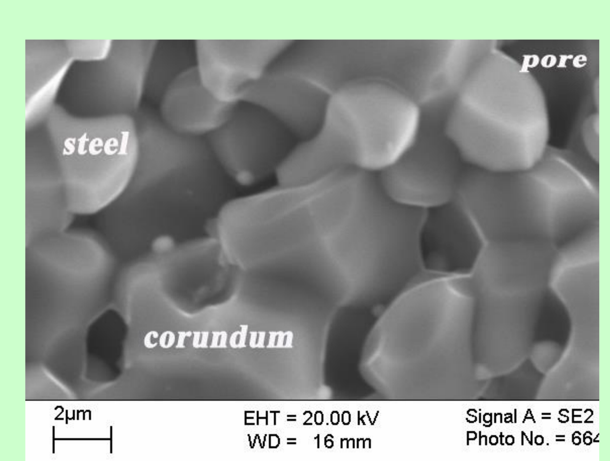

Fig. (1). SEM microstructure of the cermets samples sintered in a vacuum at 1500°C.

CONCLUSIONS

In the oxide cermets the concentration dependences of elastic moduli and the thermal conductivity coefficient have been obtained and discussed; relation between of elastic moduli and the thermal conductivity for metal concentrations 2-11 vol.% was established; the optimal value of metal concentration for investigated composites "corundum-stainless steel" were determined.

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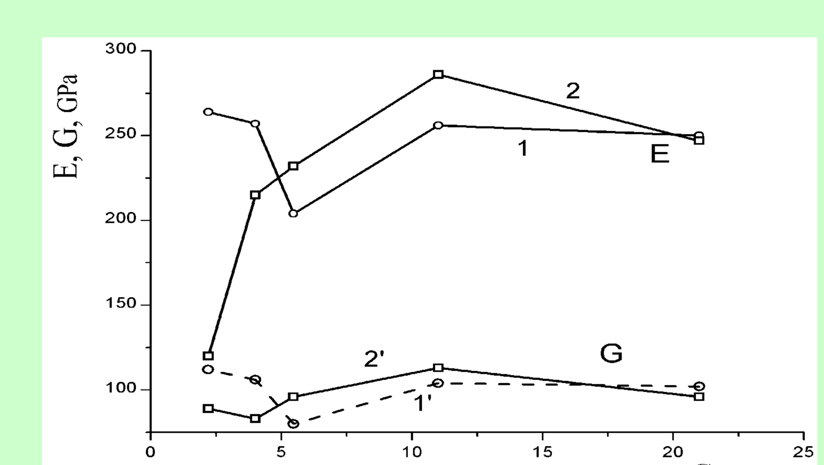

Fig. (2). Concentration dependences of elastic moduli, E and G, for cermets, sintered at various temperatures: 1500 °C – curves 1 and, 1' and; 1600 °C – curves 2 and, 2'.

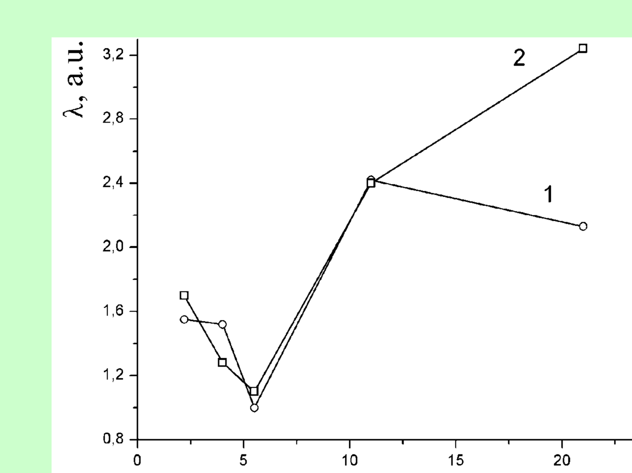

Fig. (3). Concentration dependences of the thermal conductivity coefficient (arbitrary units) in cermets sintered at temperatures of 1500 (1) and 1600 °C (2), λ = 1 corresponds to the standard sample value.