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Feature article

An alternative composite approach to tailor the thermoelectric performance in SiAlON and SiC

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ABSTRACT

The thermoelectric properties of SiAlON and SiC based composites prepared by adding TiCN (5 and 10 vol.%) as a particulate or as a segregated three-dimensional network were investigated. Although the volume fraction of the TiCN phase was the same in both kinds of SiAlON-based composites, the one containing the segregated three-dimensional network exhibited larger power factor and higher figure of merit than the particle-reinforced composite. Such an enhancement was not observed in SiC. This outcome highlights the importance of the microstructure design and indicates that the segregated network approach may be an effective method to tailor the thermoelectric properties of composite systems.

1. Introduction

Thermoelectric (TE) materials and devices attract increasing attention because of their potential applications in the fields of energy conversion, thermal sensors, and cooling systems for electronic devices [1–3]. The performance of a TE device depends on the figure of merit of the TE materials ($ZT = \alpha^2\sigma T/\kappa$), where α is the Seebeck coefficient, σ is the electrical conductivity, κ is the thermal conductivity, and T is temperature. Therefore, in order to have high-performance TE materials, an ideal combination of high power factor ($\alpha^2\sigma$) and low thermal conductivity (κ) is required. In polycrystalline materials, the situation is more complex due to the presence of grain boundaries in which and in proximity of which the electrical and thermal properties can differ significantly from the bulk. In order to enhance the figure of merit, κ is required to be as small as possible, boundaries can be beneficial as they can selectively scatter phonons and charge carriers [4,5]. As for the electrical conductivity, it is known that the electrical transport along grain boundaries and interfaces can be improved or depressed, even by several orders of magnitudes, as it was shown for example for $LaAlO_3/SrTiO_3$ interfaces [6], for nanocrystalline ceria [7] and mesoscopic $SrTiO_3$ [8]. Therefore, microstructural design particularly of boundaries can be crucial for improving the desired functionality.

The materials used in thermoelectric generators (TEG) should be environmentally friendly, inexpensive, chemically and thermally stable, and scalable for mass production with high mechanical strength [9,10]. Skutterudites, half-Heusler compounds and silicon-based thermoelectric materials are current candidates for medium-high to high temperature applications. In addition, oxide thermoelectric materials seem promising due to their durability at high temperature in air, non-toxicity and low cost [11]. Also, carbides such as SiC are good candidates for high temperature applications, thanks to their thermal, mechanical and chemical stability although their electrical properties cannot compete with skutterudites and half-Heusler compounds [12–14]. In this context, it is worth mentioning that SiAlON-based composites are attractive for high-temperature applications for achieving high electrical conductivity without compromising their mechanical properties, as proven by their employment in glow plugs and heaters [15,16]. Nonetheless, the thermoelectric properties of SiAlON-based ceramics have not been investigated so far. One of the challenges related to the fabrication of components made of SiALON is due to its relatively poor densification during sintering. The most common compaction method is gas-pressure-sintering which enables reli-

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able reproducibility and improved properties by only moderate increase of the production costs compared to pressureless sintering [17].

In order to obtain high electrical conductivity in such systems, addition of a highly conductive secondary phase, e.g. Ti(C,N) [18–20] or TiB_2 [21], has been extensively studied. Not only a conventional composite approach (i.e. a mechanical mixture of the 2 phases) has been considered in the literature, but also the possibility of achieving a 'segregated network' consisting of a percolating highly conducting second phase (e.g. segregated at grain boundaries of the first phase) for optimizing the thermoelectric properties has been explored as well [22].

Note that according to the models [23–25] for usual multicomponent system, the effective figure of merit ($ZT_{effective}$) and the effective power factor ($PF_{effective}$) cannot be greater than those of its single constituents, unless interface/boundary effects come into play and become decisive. In a recent example, creation of the metallic 'nanoweb structure' achieved by partially coating grains of the target material with a metallic layer tens of nanometer thick, for example, before consolidation by spark-plasma-sintering delivered a nice example of overcoming the trade off between Seebeck coefficient and electrical conductivity [26].

Starting from these considerations, we investigated here whether obtaining a segregated 3D conductive network surrounding insulating (SiAlON) or semiconducting (SiC) particles may result in higher PF ($\alpha^2\sigma$) than a conventional particle reinforced composite consisting of the very same phases with the same volume fractions (see Fig. 1). With this in mind, the goal of this study is to compare the two different composite approaches and study the temperature dependence of the physicochemical quantities relevant for thermoelectricity between 300 and 1000 K of TiCN/SiAlON and TiCN/SiC composites having different microstructure designs.

2. Experimental procedure

In this study, three different sets of samples were prepared. Firstly, for the particle reinforced composites (PRC), 10 vol.% $TiC_{0.7}N_{0.3}$ (TiCN) with an average particle size <150 nm (Sigma–Aldrich) was mixed to SiAlON powder (MDA Advanced Ceramics Ltd. Eskisehir, Turkey). Secondly, in order to obtain a segregated three-dimensional network, spray-dried SiAlON granules supplied by MDA Advanced Ceramics Ltd. (Eskisehir, Turkey) were coated with $TiC_{0.7}N_{0.3}$ in order to obtain final compositions analogous to the previous ones (SNC) (i.e. 5 and 10 vol.% $TiC_{0.7}N_{0.3}$). Note that in this case, the spatial distribution of the second phase is different compared to the first composite. Lastly, commercially available SiC granules (SIKA Densitec-13, Saint Gobain, Norway) were coated with the same amount of $TiC_{0.7}N_{0.3}$. The resulting powders were then dry-pressed with a computer controlled automatic uniaxial press (Dorst, Germany) under 200 MPa. Two-stage sintering of the SiAlON-based pellets was carried out in a crucible of hexagonal boron nitride using a gas pressure sintering (GPS) furnace (FCT System GmbH, Germany). The first stage of sintering was achieved at 2213 K for 60 min under a nitrogen gas pressure of 0.2–0.5 MPa. In the second stage, both the peak temperature and gas pressure were raised to 2263 K and 10 MPa respectively, for the same dwell time while the compaction of the SiC-based pellets was carried out in a graphite mold using a spark-plasma-sintering (SPS) furnace (FCT Systems GmbH, Germany) at a maximum temperature of 2323 K (dwell time 10 min) in nitrogen atmosphere. Further details of the preparation route are given elsewhere [27]. The density of the sintered samples was measured by gas pycnometry (AccuPyc 1330). Phase identification was performed by x-ray diffraction (XRD) using a Rigaku Rint (2200-Japan) diffractometer with Ni-filtered Cu-Kα radiation (wavelength = 1.5418 Å).

For SEM investigations, the samples were polished by a conventional polishing method used for ceramic materials. Microstructural characterizations were conducted by using a Zeiss™ Supra 50 VP scanning electron microscope (SEM) attached with an EDX detector (Oxford).

The heat capacities of the samples were measured by DSC (NETZSCH STA 449F3), whereas the thermal diffusivities were determined by laser flash technique (Netzsch–LFA 457) using $10 \times 10 \times 2\ mm^3$ square samples between 300 K–1000 K. The thermal conductivity values of these samples were calculated according to the following equation

$$\kappa = C_p \cdot r \cdot D$$

in which κ is the heat capacity, C_p the specific heat, ρ the density and D is the thermal diffusivity.

The Seebeck coefficients and electrical resistivity of the samples were measured by using an ULVAC ZEM 3-M8 and an Alpha-A high-resolution dielectric analyzer (Novocontrol Technologies GmbH) (ac voltage 0.3 V, frequency range from 2 MHz to 1 Hz, under Ar atmosphere). The analysis of the impedance spectra was performed with the commercial software Z-View 2 by Scribner Associates Inc. The Seebeck measurements were carried out under He atmosphere without depositing any platinum contacts on the surface of the samples.

The relative uncertainties for the Seebeck coefficient (δ_α), electrical conductivity (δ_σ), and thermal conductivity (δ_κ) were evaluated to be 5%, 10%, and 6%, respectively. According to uncertainty propagation [28], the uncertainty for the power factor (δ_{PF}) was calculated as $\delta_{PF} = [(2\delta_\alpha)^2 + \delta_\sigma{}^2]^{1/2} \approx 14\%$, and the relative uncertainty for ZT (δ_{ZT}) was calculated as $\delta_{ZT} = [(2\delta_\alpha)^2 + \delta_\sigma{}^2 + \delta_\kappa{}^2]^{1/2} \approx 15\%$. The corresponding uncertainty bars are not visible for the quantities that are drawn in log scale.

3. Results and discussion

3.1. Phase and microstructural analyses

Back-scattered SEM (BSE) images taken from the polished surfaces of the SiAlON based composites and proposed schematic structure of the composites are displayed in Fig. 1. These micrographs, in which the contrast results from the different atomic number (Z) of the constituents, revealed that the elongated grains in dark gray correspond to β-SiAlON, while the small and equiaxed grains in light gray consist of α-SiAlON and the bright regions result from TiCN phase. This shows that both the preparation of (i) the composite and (ii) the TiCN segregated network were successfully achieved. The assignment of the different phases is in agreement with the analysis of the XRD patterns acquired from all samples (Fig. S1. in Supplementary Data). The main constituents are indeed α-SiALON, β-SiALON and TiCN, whereas little traces of SiC, C and TiO_2 could be detected in the segregated 3D network composite (SNC) and pure TiCN, respectively.

3.2. Thermoelectric and transport properties

The temperature dependence of the electrical conductivity (σ), Seebeck coefficient (α), power factor ($PF = \sigma \cdot \alpha^2$) and the resulting figure of merit ($ZT = PF \cdot T/\kappa$) between 300 and 1000 K for SiAlON-based composites are shown in Fig. 2.

As shown in Fig. 2(a), SiAlON is a pronounced electrical insulator and below 600 K it was difficult to obtain reliable electrical conductivity data (at this temperature, the total resistance of the sample was 8×10^7 Ohm, corresponding to the upper limit of the impedance spectrometer used here). Above this temperature the conductivity increases according to a thermally activated trans-