Materials Science and Engineering B 176 (2011) 32–40

Contents lists available at ScienceDirect

Materials Science and Engineering B

journal homepage: www.elsevier.com/locate/mseb

Ceramic matrix composites based on Mg-PSZ with Cr–Ni-steel-additions with improved thermo-mechanical properties

C. Wenzel*, C.G. Aneziris**

Institute of Ceramic, Glass and Construction Materials, Technische Universität Bergakademie Freiberg, Agricolastr. 17, D-09599 Freiberg, Germany

ARTICLE INFO

Article history:
Received 19 February 2010
Received in revised form 7 July 2010
Accepted 28 August 2010

Keywords:
Ceramic matrix composites
Zirconia
TRIP-steel
Thermal shock resistance

ABSTRACT

The application of ceramic materials is limited due to their inherent brittleness. In the past years attempts have been made to improve the fracture toughness of structural ceramics by adding a secondary phase. In the present paper the influence of metastable austenitic TRIP-steel powder on the thermo-mechanical properties of magnesia partially stabilised zirconia has been investigated. Ceramic matrix composites have been prepared using slip casting technology. The sintering was performed in different argon atmospheres. The incorporation of the metastable metallic phase led to the successful generation of composite materials with advanced mechanical properties, especially after thermal shock attack.

1. Introduction

Ceramic materials are known for their excellent chemical stability, wear resistance as well as hardness. A limitation to their application is the inherent brittleness. In the past years attempts have been made to improve the fracture toughness of structural ceramics due to the addition of a secondary phase. Among others, the addition of metallic inclusions has been subject in many investigations [1–4]. The enhanced toughness arises from the ductile metallic phase, which has the ability to deform plastically and to bridge the defects in the processing zone behind the crack tip. Different studies are focused on the reinforcement of alumina with Fe_3Al due to the great resistance to corrosion and oxidation of the intermetallic phase. An improvement in R-curve behavior attributed to crack bridging was identified [1,2]. Other studies concentrate on the reinforcement with zirconia and achieve toughening due to crack deflection or stress-induced martensitic transformation [5].

For engineering components zirconia is widely used because of its excellent mechanical and chemical properties. Zirconia appears in three modifications. The monoclinic phase (m-ZrO_2) is thermodynamically stable and exists below 1170 °C. Above this temperature the tetragonal modification (t-ZrO_2) occurs. At temperatures higher than 2370 °C up to melting the cubic phase (c-ZrO_2) is stable. The $t \rightarrow m$ transformation has a great importance for the mechanical properties of zirconia components. It appears with a volume increase of 3–5% and exceeds the critical fracture length in ceramics. Therefore unstabilised zirconia does not have relevant technical applications. Additions of Y_2O_3, CaO or MgO are used to stabilise t- and c-phases to room temperature. The high strength and fracture toughness of partially stabilised zirconia is based on the phase transformation $t \rightarrow m$ during crack growth. Thus during crack growth a processing zone that is under compressive strain is developed around the crack tip [6].

A promising material for application as secondary metallic phase is a metastable austenitic Cr–Ni steel. Mechanical loads on TRIP-steel materials (Transformation Induced Plasticity) lead to excellent mechanical properties due to the phase transformation from austenite to martensite. That is accompanied by a 1% volume expansion [7–11]. This phase transformation improves the ductility as well as the strength of the material.

In the present paper ceramic matrix composites based on magnesia partially stabilised zirconia with TRIP-steel additions have been investigated with focus on mechanical and thermo-mechanical properties. The reinforcement of partially stabilised zirconia with metastable austenitic Cr–Ni steel is a novelty.

2. Experimental

Composite specimen were prepared from 3.4 wt.% magnesia partially stabilised zirconia (Mg-PSZ, Saint Gobain, USA) and austenitic stainless steel powder AISI 304 (TLS, Germany). The Mg-PSZ powder had a mean particle size of 1.3 μm, its chemical

---

* Corresponding author. Tel.: +49 3731 394344.
** Corresponding author. Tel.: +49 3731 392505.
E-mail addresses: claudia.wenzel@ikgb.tu-freiberg.de (C. Wenzel), aneziris@ikgb.tu-freiberg.de (C.G. Aneziris).

0921-5107/$ – see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.mseb.2010.08.008

Table 1
Chemical composition of Mg-PSZ powder.

Oxide content in wt.%					
ZrO_2	MgO	HfO_2	SiO_2	Al_2O_3	TiO_2
Bal.	3.4	1.7	2.4	0.6	0.1

10% monoclinic, 36% tetragonal, 53% cubic.

Table 2
Chemical composition of AISI 304 stainless steel.

Alloying element in wt.%					
Fe	Cr	Ni	Mn	C	Si
Bal.	17.15	8.75	1.13	0.05	0.55

Table 4
Open porosity, bulk density and mean pore size of green bars.

Composition	Green samples		
	Open porosity (%)	Bulk density (g/cm^3)	Median pore size (nm)
100/0	35.4	3.57	353
90/10	36.2	3.84	282
80/20	36.5	3.87	418
70/30	35.7	4.13	438

composition is listed in Table 1. The chemical composition of the stainless steel powder is displayed in Table 2. The mean particle size was 18.8 μm.

The starting powders were mixed with deionised water with a ratio powder:water of 70:30. In preliminary test typical ceramic dispersants such as Dolapix CE 64 (Zschimmer & Schwarz) and Dolapix PC 75 (Zschimmer & Schwarz) were used to stabilise the suspension. The raw materials were mixed for 2 h and then filled in beaker glasses. The sedimentation behavior of the slurries was observed. In further tests a synthetic polyelectrolyte (KM 1001) and a hydrocolloid (KM 2000) provided by Zschimmer & Schwarz were used to disperse and stabilise the suspension (composition of the slurries is listed in Table 3). To improve the strength of the green bars Optapix PAF 35 (Zschimmer & Schwarz) was used. The raw materials were mixed for 2 h in a polypropylene chamber with zirconia milling media. Using slip casting technology, rectangular bars with 3.5 mm × 4.5 mm × 40 mm have been manufactured.

The debinding step took place at 400 °C in an oxidising atmosphere with a heating rate of 1 K/min and a holding time of 2 h. Afterwards the bars were sintered in an electrical furnace with Kanthal-Super 1800 heating elements type HT 1600 GT Vac (Linn, Germany) in argon atmosphere. Before sintering the furnace has been evacuated and then filled with protective gas (argon 5.0). Sintering was conducted with an excess pressure of 5 mbar. During sintering the furnace was flushed with argon with a flow rate of 2.5 l/min.

To study the influence of the furnace atmosphere on the properties of the ceramic matrix composites, two sets of experiments have been performed. In Series 1 the samples have been directly placed in the furnace. An oxygen concentration of 40 ppm was measured at the pressure relief valve with an oxygen sensor (Zirox SGM 4). The oxygen was introduced on the one hand with the protective gas (argon 5.0) and on the other hand by the furnace lining based on alumina. In Series 2 the samples have been set in graphite crucibles during sintering in argon atmosphere to prevent oxidation of steel particles. The heating rate was 5 K/min to 1550 °C for both sintering conditions. The holding time at sintering temperature was 2 h and the cooling rate 5 K/min to room temperature.

The influence of the TRIP-steel powder additions on the mechanical properties of the partially stabilised zirconia and the formation of new phases has been explored. After sintering the shrinkage was measured. Open porosity and bulk density were determined with the aid of mercury porosimetry (PASCAL series, Porotec, Germany). Flexural strength at room temperature was obtained by 3-point-bending tests following DIN EN 843-1 on as fired samples. The total energy absorption was determined according to Eq. (1):

$$W = \int_{0}^{S_b} P\,dS \tag{1}$$

where W is the total energy absorbed in crushing of the composite, P is the load, S the displacement and S_b the crush distance according to Jacob et al. [12]. Thermal shock resistance tests of the composite materials were performed according to DIN EN 820-3 after quenching from 600 °C in water at room temperature in oxidising atmosphere. Micro-structural characterisation was conducted using scanning electron microscopy (SEM) and electron backscatter diffraction analysis (EBSD). The formation of new phases has been investigated using X-ray diffraction (PANalytical X'Pert Pro MPD 3040/60, Netherlands). Using X'Pert Highscore Plus analysis software (PANalytical, Netherlands), phase identification has been done. The deformation induced phase transformation of the metastable steel from austenite to α-martensite has been determined using a ferromagnetic balance.

3. Results and discussion

Significant differences in particle size and densities of the starting powders zirconia and TRIP-Steel led to sedimentation of steel particles if Dolapix CE 64 or Dolapix PC 75 has been used as disper-

Table 3
Composition of the slurries.

Material	Type	Supplier	Composition		
			90/10 wt.%	80/20 wt.%	70/30 wt.%
ZrO_2 with 3.4 wt.% MgO		Saint Gobain, USA	61.09	52.7	44.79
Austenitic TRIP-steel powder	AISI 304	TLS, Germany	8.91	17.3	25.21
Sum			70	70	70
Water addition			30	30	30
Dispersant	KM 1001	Zschimmer & Schwarz, Germany	0.58		
Stabiliser	KM 2000		1.02		
Temporary binder	Optapix PAF 35		0.97		