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Ceramics International 40 (2014) 821–826

CERAMICS INTERNATIONAL

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Spark plasma sintering of ZrB_2–SiC composites with in-situ reaction bonded silicon carbide

Alberto Ortona[a,*], Miguel A. Lagos[b], Giulio Scocchi[a], Jorge Barcena[b]

[a]ICIMSI-SUPSI, Strada Cantonale, CH-6928 Manno, Switzerland
[b]TECNALIA, Industry and Transport Division, Mikeletegi Pasealekua 2, E-20009 Donostia-San Sebastian, Spain

Received 1 June 2013; received in revised form 20 June 2013; accepted 20 June 2013
Available online 6 July 2013

Abstract

This work presents a new hybrid manufacturing process to produce ZrB_2–SiC ceramics with the SiC phase synthesized in situ by reaction bonding. Since ZrB_2–SiC composites properties strongly depend on their grain size, finer and thus more expensive powders are usually employed. In the first part of the process, silicon carbide with a fine microstructure was produced by the reaction bonding between silicon powders and carbon derived from powders and pyrolysed phenolic resin The latter, being fluid before polymerization, filled the interstices between the powders thanks to the high pressure applied. Because of this behavior, after spark plasma sintering, the resulting microstructure presents the SiC phase dispersed between the ZrB_2 grains in a different ways when compared with the standard ceramic powders consolidation methods.

Keywords: Ultra-high temperature ceramics; Reaction bonding; Spark plasma sintering

1. Introduction

SiC has been added to transition metal diborides (ZrB_2 and HfB_2) for aerospace applications in view of increasing the oxidation resistance of pure ZrB_2 and HfB_2 at temperatures above 1600 °C [1–4]. In these oxidative conditions, researchers reported the formation of an oxide scale of borosilicate glass layer (BSZ) containing SiO_2, ZrO_2 and B_2O_3 [1–3,5–7] and the formation of an intermediate region, between the oxides and the un-reacted material, characterized by SiC depletion [8–10]. Generally SiC–ZrB_2 composites show, as SiC amount increases, a higher bending strength [11], small grain size [12] and, above the SiC 50 vol%, when oxidized, the restrain of SiC depletion [13] underneath the oxide layer. There are several manufacturing techniques to produce dense ZrB_2–SiC ceramics [11]: hot pressing[14], spark plasma sintering [15], reactive hot pressing [16,17], pressureless sintering [18,19].

Before their consolidation, the constituent materials preparation play a role into the final composite microstructure. In non-reactive pressing techniques, powders are dispersed, e.g. ball milled, attrition milled, ultrasonicated, in a liquid which is then evaporated. In this case, for small volume fractions (<20 vol%), the final composite microstructure is characterized by dispersed SiC grains placed between ZrB_2 particles [19]. For higher volume fractions, SiC grains can gather in larger clusters upon sintering [9,20], forming a percolation network.

For reactive consolidations and pressureless sintering a polymer is commonly added. It can work after pyrolysis as a sintering aid [18,19] or as a reactant of the final constituent material [16,17]. Zhu et al., for example, used preceramic polymers, e.g. polycarbosylane (PCS), to coat ZrB_2 powders and remove oxide impurities [21], while Guo et al. used PCS as SiC precursor and employed Silicon to remove Carbon impurities from PCS pyrolysis [22].

SPS for the production of ZrB_2–SiC composites via reaction bonding (RB) has been investigated by Zhao et al., using Zr, Si and B_4C as constituent powders [15]. Nonetheless, the literature does not report on ZrB_2–SiC composites in which SiC is formed

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*Corresponding author. Tel.: +41 586666647.
E-mail address: alberto.ortona@supsi.ch (A. Ortona).

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http://dx.doi.org/10.1016/j.ceramint.2013.06.074

in-situ via RB of Silicon and Carbon (see reaction R1), the latter derived from the pyrolysis of a common polymeric precursor like a phenolic resin.

$$Si_{liquid}+C_{solid} = SiC_{solid}[\Delta H = -73 \text{ kj mol}^{-1}] \quad (R1)$$

A similar approach was employed to manufacture C_{fibre}/SiC_{matrix} composites [23], leading to a porous composite since consolidation pressure was not applied.

This new approach brings to a different composite microstructure which might further improve its oxidation behavior.

2. Experimental

2.1. Materials

Composites were produced mixing ceramic and graphite powders with a plastic binder. Materials employed in the present work were: Silicon (grade AX20 Stark Ag, Goslar, D) average particle size *d*50 of 7.5 µm; micronized (~64 µm diameter) phenolic novolac powder (Momentive, Columbus, OH, USA); zirconium diboride (grade A, Starck Ag, Goslar, Germany) average particle size *d*50 of 0.3–5.0 µm; graphite (TIMREX® KS4 by TIMCAL SA, Bodio, Switzerland) average particle size *d*50 of 2.4 µm.

Three composites were produced mixing the above mentioned materials in different ratios (Table 1).

In the sample B, the silicon amount was added in order to produce SiC by the reaction bonding of the carbon from the graphite and from the pyrolysis of the phenolic resin. Carbon yield (55 wt%) was measured with a TGA analysis, (Mettler Toldedo Inc., Im Langacher Greifensee CH) in conditions similar to the pyrolysis thermal cycle (Fig. 1).

In order to study the influence of the amount of metallic silicon on the final samples composition, three composites were prepared. Considering as 100% the amount of silicon necessary for the stoichiometric reaction with the pyrolyzed carbon in sample B, less silicon (95%) was added in sample A and more (105%) in sample C.

2.2. Preforms preparation

The sample's production was performed following a procedure developed to produce Si–SiC–ZrB_2 composites by reactive silicon infiltration [24]. Powders were mixed with distilled water (80 wt% with respect to the solid charge) for 60 min by ball milling in a sealed container, then the phenolic powder was added and milling continued for further 60 min. The compound was dried into a vacuum furnace at 60 °C for 24 h. Uniaxial compression was then performed with the following parameters: holding time 200 s, pressure 56 MPa and temperature 150 °C. The volume of powder put into the die was calculated in order to produce, after pressing, a 4–5 mm thick green preform.

Green samples were pyrolysed at 1500 °C under inert atmosphere with a heat ramp of 60 °C/h from room temperature to 500 °C and of 500 °C/h up to 1500 °C followed by natural cooling.

2.3. Spark plasma sintering

The consolidation experiments were performed in a spark plasma sintering furnace model S8451 (FCT, Frankenblick, Germany). This equipment can supply a direct current of 10000 A of intensity under a maximum tension of 10 V. The DC current was applied with pulse time of 10 ms and a pause time of 5 ms.

The preforms were introduced in a graphite die between two graphite punches. The diameter of the samples was 20 mm. During the tests, the chamber was maintained in vacuum

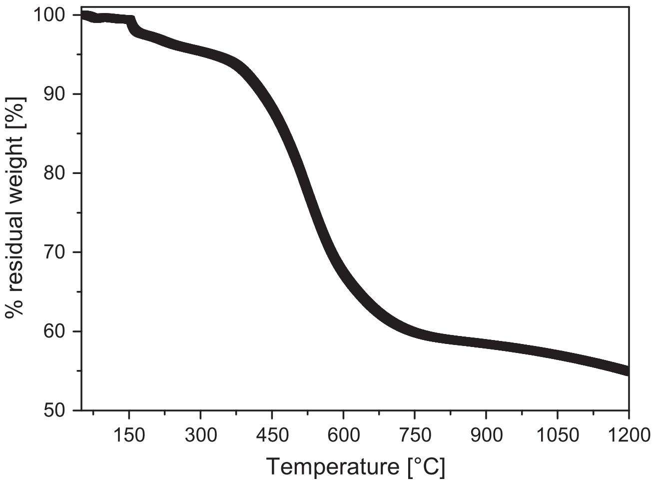

Fig. 1. Thermo gravimetric analysis of the phenolic resin from room temperature to 1200 °C with a heat ramp of 10 °C/min in nitrogen.

Table 1
This table present in the first columns V_f of constituent materials within the green samples after uniaxial pressing. The last four columns present the calculated the V_f of the constituent materials after pyrolysis (with the 0.55 wt% C yield and the reaction bonding between Si and C) and after an "ideal SPS" giving a fully dense material.

Sample	V_f after consolidation				Theoretical V_f			
	ZrB_2	C	Si	Phen. Resin	ZrB_2	SiC teor	C residual	Si residual
A	0.447	0.137	0.235	0.181	0.602	0.324	0.074	
B	0.425	0.130	0.273	0.172	0.582	0.389	0.029	
C	0.405	0.124	0.308	0.164	0.559	0.418		0.023

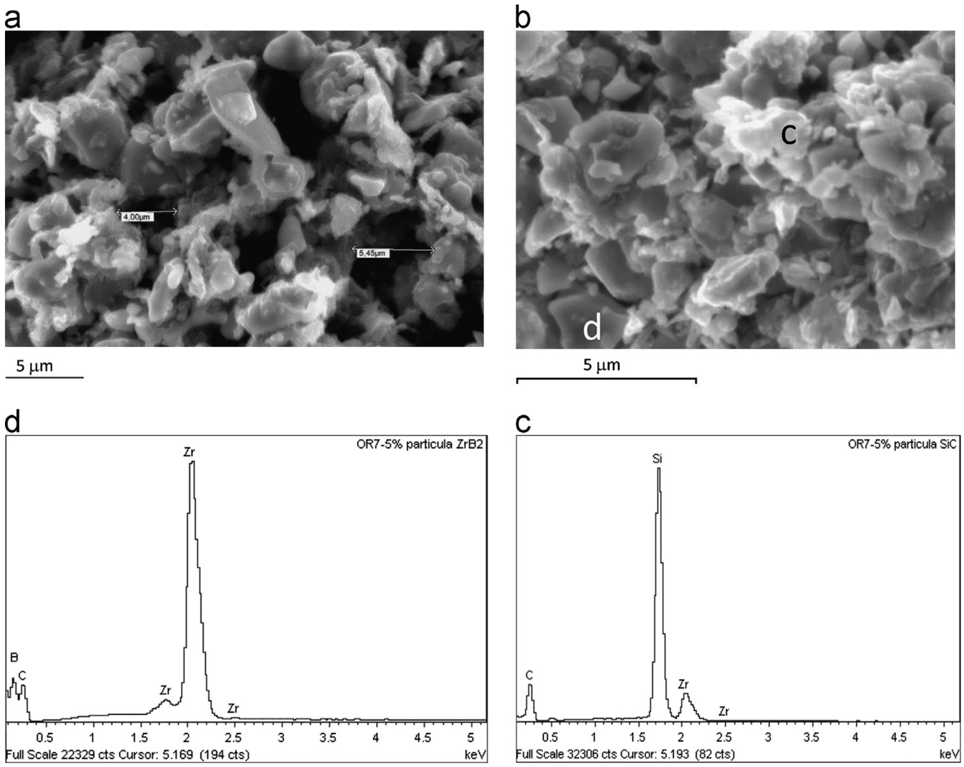

Fig. 2. Fracture surface of sample C after pyrolysis: (a) low magnification showing typical pore size and distribution, (b) higher magnification showing ZrB_2 large grains (d) bound by a continuous phase, mostly βSiC (c).

(10^{-2} Pa). Temperature was controlled by a pyrometer that measured the temperature into the graphite upper punch. A hole, drilled into the punch till a distance of 5 mm from the surface of the sample, was used to point the pyrometer.

The maximum temperature of the cycle was 1850 °C with a holding time of 1 min. The heating rate was 80 °C/min and the compression load was 50 MPa

2.4. Characterization

XRD analysis was carried out using a D500 apparatus (Cu_Kα radiation, $\lambda=0.154$ nm, $2\theta=20$–100°, 40 kV–30 mA, scan step 0.1°) from Siemens Germany. Microstructure and semi-quantitative chemical composition were analyzed by optical and SEM microscopy (5910 LV microscope Jeol JP with an Inca 300 EDS device by Oxford Instruments, UK).

Electrolytic etching was performed in NaOH (20 vol%) for 5 min with 15 V at room temperature. Sample's density was measured according to the standard UNE-EN-993-1 (the Archimedes method).

3. Results and discussion

The apparent density of the preforms after pyroloysis was ~48% of their theoretical density. Fig. 2 presents the fracture surface of the pyrolysed preform C. It is possible to observe the pores distribution and size as well as the ceramic powders partially bound with a finer phase of in situ reaction bonded SiC. The picture gives also an idea of the open porosity distribution.

The EDS analysis shows that there are some particles with a composition rich in Zr and B (most problably ZrB_2) and other smaller particles with a composition rich in Si and C (most problably SiC).

After SPS sintering, density was around 98% of the theoretical value in all the samples (98.1 for sample A, 98.2 for sample B and 98.1 for sample C). The microstructure obtained in the sample A is displayed in Fig. 3. Material microstructure is different from that of composites obtained by reactive synthesis of Zr, B_4C and Si powders by SPS or by dispersed ZrB_2 and SiC powders further compacted by SPS because, thanks to the speed of this process, they tend to keep their pristine powder shape [14]. The microstructure of the composites produced in this work is much more similar to the one of ceramics obtained by hot pressing of ZrB_2 and SiC powders [4,7]. ZrB_2 grains are generally equiaxed, while SiC ones are slightly elongated; the main difference with hot pressed composites consists in the small grain size of both phases typical of other works where fine and thus expensive powders were employed [25–27]; this characteristic is due to the manufacturing route and in particular to the short cycle time of SPS, which hinders the evolution of the grain coarsening processes.

A proposed mechanism for the microstructure evolution during the three process steps is depicted in Fig. 4. During preform consolidation and before curing, the molten phenolic novolac powders fill the empty spaces between the powders.

During the last ramp of the pyrolysis cycle, polymer-derived Carbon is in intimate contact with the solid charge and temperature is high enough to allow the diffusion of C into Si and hence the formation of SiC; because of the mass losses and shrinking, a typical crack pattern is present in the material. In samples A and B, during this step of the process, Silicon and Carbon fully react and convert into βSiC [28], the evidence being the absence of a Si peak in the XRD patterns (see Fig. 5a and b). For sample C, instead, excess Silicon is still present after pyrolysis (Fig. 5c). Finally, after SPS, porosity is reduced to 2%. Interestingly, after this last step, no residual Silicon is present in sample C; this might mean that the Silicon that is left after pyrolysis has either reacted with the Carbon from the graphite die or has evaporated as SiO due to small quantities of Oxygen that were probably present in the original Silicon powder [29]. Finally, during the process ZrB_2 did not react with Silicon [24] and remained crystalline as shown in Fig. 5 which displays the XRD patterns of the composites before and after their SPS consolidation.

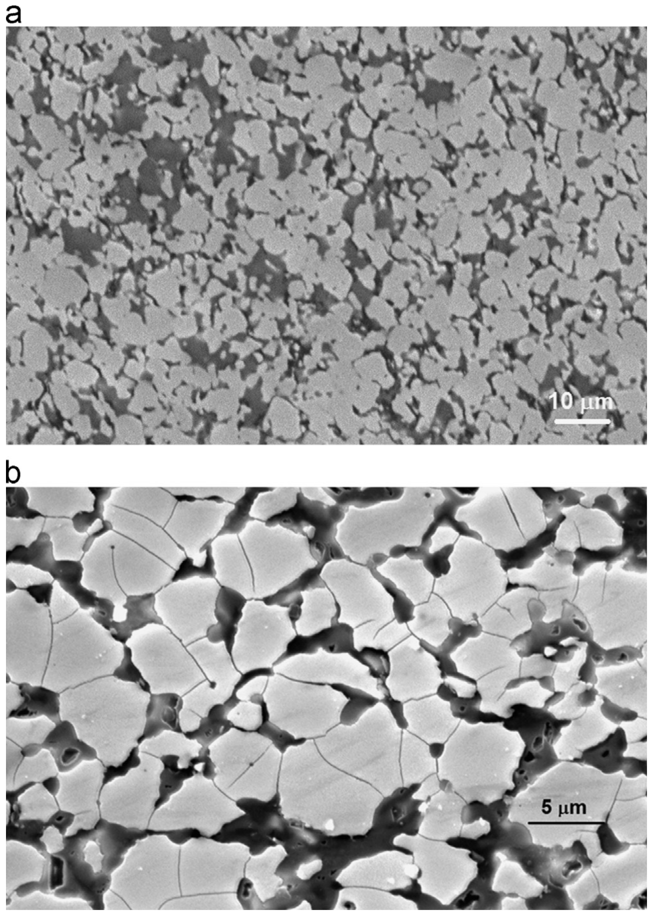

Fig. 3. Micrographs of sample A after cutting and polishing (a) and after etching (b). ZrB_2 grains (light gray) are surrounded by SiC (dark gray).

4. Conclusions

This paper presents a new hybrid manufacturing process in which ZrB_2–SiC composites were produced by spark plasma sintering preforms in which SiC was obtained by in-situ reaction bonding between Carbon and Silicon. The resulting materials have a density ~98% of their theoretical value and present an interesting microstructure in which SiC is dispersed within ZrB_2 differently from composites obtained by other reactive processing. The amount of Silicon powder, within a range of 5% around the quantity needed for the stoichiometric reaction with C, seems not to affect the final composition of the material. Because of the amount of the phenolic resin used to consolidate the powders, the produced samples contain rather high amounts of carbon and thus of silicon carbide (see Table 1), further work is ongoing to produce samples with less phenolic resin in order to increase

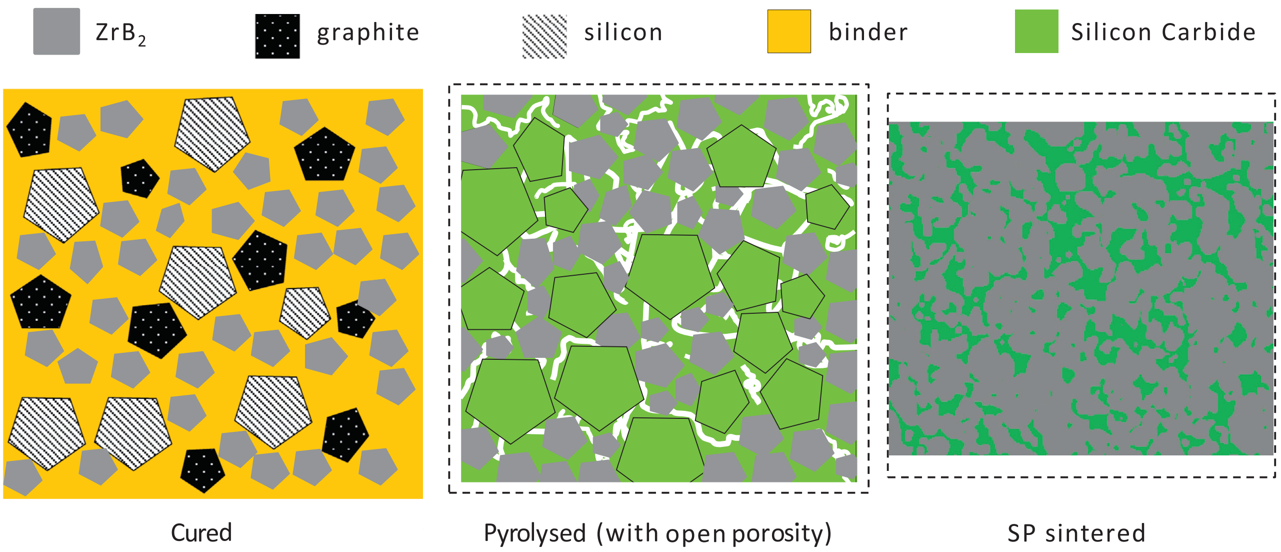

Fig. 4. Formation mechanism of the ZrB_2–SiC composite after consolidation and curing, pyrolysis (accompanied by sample isotropic shrinking ~4%) and SPS (segmented SEM image of sample A). Dashed lines correspond to the volume before each phase.

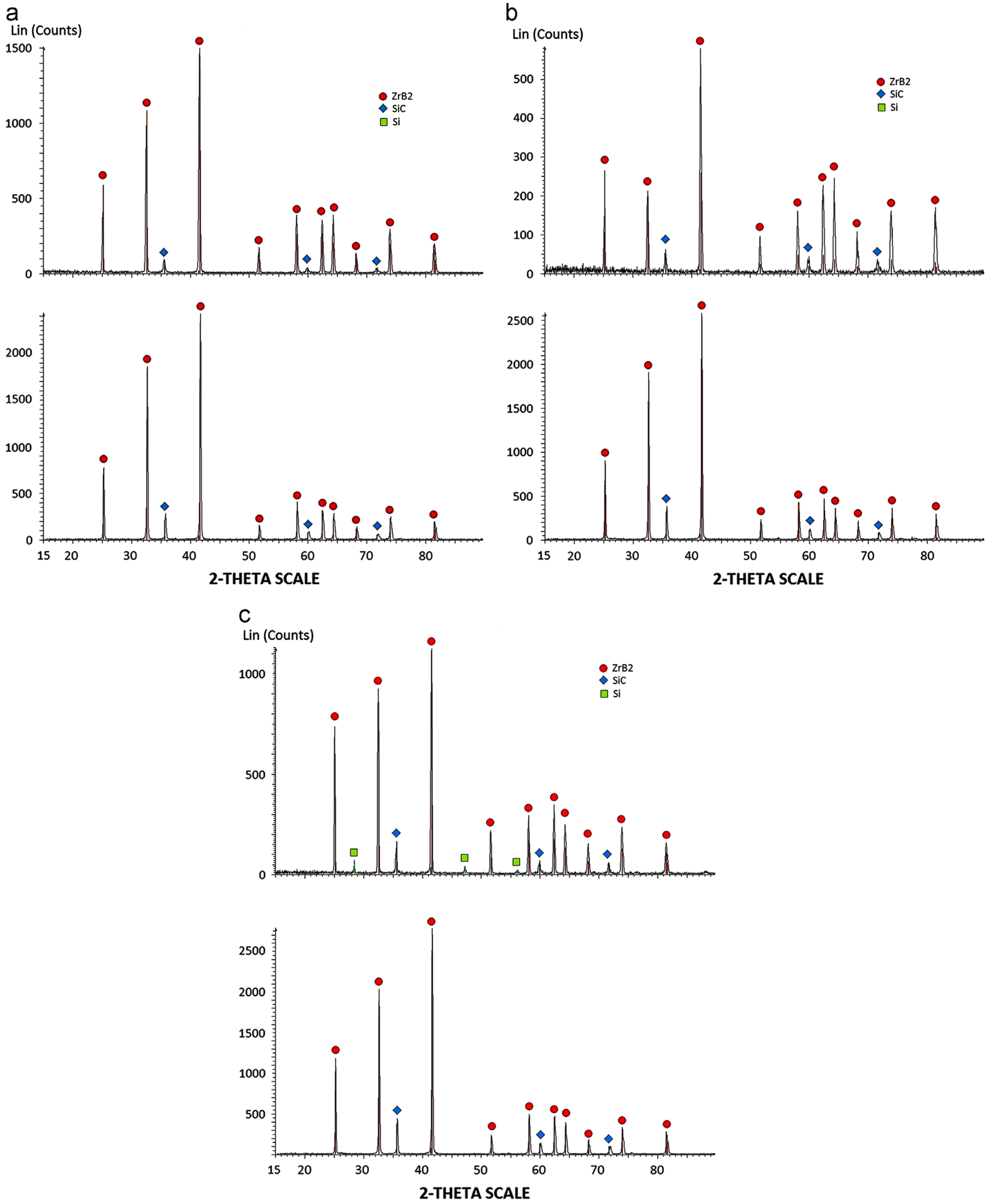

Fig. 5. XRD patterns, before SPS (top), after SPS (bottom). Samples A (a), B (b) and C (c).

the amount of ZrB_2 into the final product (90–70 vol%) and thus compare the resulting composites with those from the literature with respect to mechanical properties and oxidation resistance.

Acknowledgments

Authors are deeply grateful to Claudio D'Amico and Paolo Fino from the Department of Applied Science and Technology of the Politecnico di Torino for having performed the TGA analysis on the phenolic resin.

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