Microstructural evolution of SiC powder in molten silicon

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ARTICLE INFO	ABSTRACT
Keywords: A Grain growth B Composites B Microstructure-final B X-ray methods D SiC E Structural applications	SiC_{powder}/Si_{matrix} composites represent a new class of microstructurally toughened materials. The interactions between molten silicon and submicronic SiC powder have been considered since it could originate some limitations on the final properties of the material. Experiments putting in interaction a SiC powder and molten Si were performed while heating up to final values ranging between 1450 and 1600 °C for duration up to 8 h. The volume ratio of SiC and silicon was equal to one and SiC particles were freely dispersed within the liquid. X-ray diffraction analyses demonstrated that the apparent crystallites size increase of SiC powder followed a ripening law corresponding to a limitation either by volume diffusion or by dissolution into the liquid. Depending on the relevant mechanism, the activation energy of the crystallites' growth has been found equal to $357 \pm 50 \, kJ \, mol^{-1}$ or $441 \pm 57 \, kJ \, mol^{-1}$. An agglomeration-coarsening process of SiC particles was also identified which promoted a quick formation of larger particles.

1. Introduction

SiC compound has a great importance in a broad range of applications because of its very attractive properties: wide band gap, good oxidation resistance, high thermal stability and conductivity, low density and strong toughness. However, to obtain the best performances, the chemical behavior of this compound must be understood while it is synthetized and used. Many studies deal with the synthesis of SiC-based materials by a wide range of processes [1–10]. On the basis of these previous studies, one has to focus attention on the interactions between a liquid phase and SiC because they could have some influences on the resulting properties. The microstructure transformations observed during the interaction between a liquid metal and a ceramic were especially discussed by Lee et al. [11]. It was thus demonstrated that the presence of a low quantity of liquid during the SiC sintering at 1970 °C for 6 h was able to control the grain growth kinetic and the microstructure during the dissolution-precipitation transformation of β-SiC to α-SiC by generating a core/rim microstructure [12]. Several recent studies have also evidenced dissolution-precipitation processes during the infiltration of molten silicon into B_4C-based materials [13–15]. Moreover, the study reported by Kim et al. relative to the β-SiC grain growth at 1800 °C in presence of an oxynitride liquid suggested that the dissolution-growth mechanism is controlled by the diffusion of the species in the liquid [16]. Another study revealed that the grain growth of SiC particles in the presence of molten Si depends on the initial grain size [9]. Indeed, the authors found that the reactive

sintering at 1600 °C for 2 h in argon of a α-SiC powder with an initial 0.2 μm size led to a final grain size up to 4.0 μm. Such a phenomenon was not observed by the authors in similar conditions except a starting powder exhibiting a mean grain size of 23.65 μm. This can be explained by the highest surface of contact between the liquid and the SiC powder with the finer grain size, which promotes the grain growth [17–20]. The study about α-SiC coarsening during sintering at 1950 °C in presence of a liquid phase was realized by Sigl and Kleebe by addition of yttrium aluminum garnet (YAG) [21]. It was showed that coarsening occurs primarily by a solution-precipitation process, called Ostwald ripening, with the growth of the larger grains at the expense of the smaller ones. H. Ye et al. also examined the coarsening of α-SiC during YAG-liquid phase sintering [22]. Their results also suggested that Ostwald ripening controls the sintering mechanism. Yet, the sintering of SiC materials actually implies a high temperature of heating close to 2000 °C with an obvious grain growth [21–23]. The use of nanometric SiC powders is expected to considerably reduce the temperature, the time, the quantity of additives and to improve the properties of the final materials by promoting a very fine and dense microstructure [24–26]. Nevertheless, the sintering of such a pure powder remains laborious and requires high pressure, elevated temperature and more or less important quantities of additives [27–29]. In a recent study, Zhou et al. demonstrate the benefit of using silicon as sintering additive for a nano-scaled SiC powder to produce pure and dense ceramic [30]. Prior to the sintering, the authors have chemically treated the surface of the SiC grains in order to generate a carbonized layer able to consume silicon during the sintering

and to produce a pure SiC material with promising properties. Schmidt et al. have succeeded in producing nano-sized SiC particles with diameter between 2 et 7 nm by precipitation in a Si-B-C-N amorphous matrix without liquid phase [31]. The SiC particles size rises up to 40 nm by a coarsening mechanism controlled by the diffusion in the matrix with an activation energy of 770 kJ mol^{-1}. This value has to be compared to the ones of pure SiC nanograin growth which were reported to be in a range of 430–1060 kJ mol^{-1} depending on the densification mechanism [32]. In this way, the chemical interaction between molten silicon and a submicronic SiC powder is reported in the present paper. As, it is of importance to identify the effect of molten silicon on SiC transformations. Although SiC$_{powder}$/Si matrix composites represents a new class of potentially important structural materials, the evolution occurring during the silicon melt infiltration into a SiC powder remains poorly documented. Therefore, an investigation of a submicronic SiC powder dispersed in molten silicon is relevant. This is the purpose of this paper with the aim of providing a better understanding of the transformations occurring at micro- and macroscopic scales.

2. Materials and experimental procedures

A commercially available Si powder (99.995 wt% Si, grade AX-20, Starck, Germany) was used in the experiments, with a mean particle size of 7.5 μm. The SiC powder (99.8 wt%, Alfa Aesar, USA) contains 90% β-SiC and 10% α-SiC, with a particles size distribution characterized by d_{10} = 350 nm, d_{50} = 550 nm and d_{90} = 1000 nm (Fig. 1). SiC and Si powders were mixed and then compacted together with a volume ratio of 1:1 for a total mass of about 1 g, the final porosity being of about 50%. The volume ratio was carefully selected because it promotes the solid-liquid interactions. This ratio is also suitable to prevent the collapse of the pellets and the gravitational sedimentation of SiC particles induced by an excess of molten silicon. The heating treatments of the pellets at 1450, 1500, 1550 and 1600 °C were performed in an inductively heated graphite susceptor in the presence of hafnium powder as oxygen getter. A continuous flow of high purity argon under normal pressure was applied to prevent oxygen pollution. The temperature was increased rapidly (50 °C min^{-1}) up to the sintering temperature. The samples were then rapidly cooled (50 °C min^{-1}) at the end of heating. The determination of the crystallite sizes was performed by X-ray diffraction since it has been previously reported that this method is accurate up to crystallite sizes of about 100 nm or even 200 nm for a Cu-radiation [33–35]. Then, the samples were crunched to perform XRD experiments in Bragg-Brentano geometry with a Bruker D8 Advance diffractometer using a Cu Kα radiation fitted with a one-dimensional position sensitive silicon strip detector (Bruker, Linxeye). XRD patterns were recorded using a step size of 0.01° for a 2θ range of
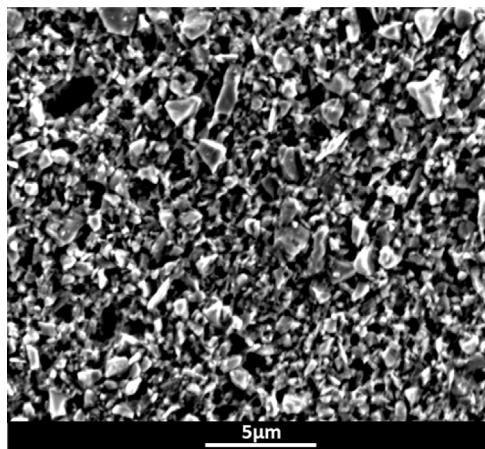

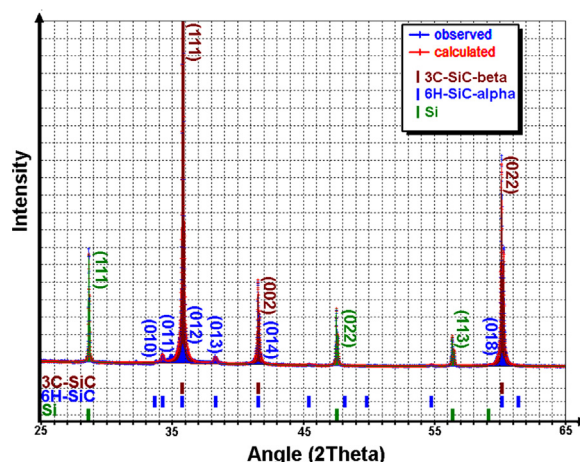**Fig. 1.** SEM image of the starting SiC powder.

Fig. 2. X-ray diffraction pattern and phases indexation of the SiC/Si sample heat treated at 1450 °C for 8 h.

20–140° and a counting time of 0.3 s per step. The freeware BRASS 2.0 was used for the profile fitting by Rietveld refinement including crystallite size calculations [36]. The instrumental broadening was defined using LaB$_6$ standard powder (NIST SRM660a). The zero shifts, roughness parameters, profile parameters, unit cell parameters, preferred orientation factor and isotropic temperature factors were refined in the Rietveld procedure using a pseudo-Voigt profile function. Atomic coordinates and site occupancies were however not refined since, in all cases, no significant effect from internal microstrain was identified. The Lorentzian size and the Gaussian size were refined in order to provide apparent crystallite values. The quality of the fitting was estimated visually on the basis of the difference curve and by the R$_{Bragg}$ factor which reaches values less than 5%. The microstructure of SiC grains was also analyzed by TEM (model 2100, JEOL).

3. Results and discussion

3.1. Crystallites growth

The size of SiC crystallites was estimated by Rietveld refinement from the X-ray diffraction patterns performed on 17 samples (Fig. 2) [37,38]. The value thus obtained is the radius corresponding to the equivalent spherical crystal noted *r*. The mean equivalent radius of the as-received powder was found close to 20 ± 1 nm. Prior to the heat treatments of the mixed Si and SiC powders, pellets of only SiC powder was heated at 1550 and 1600 °C during 6 h. In this case, the equivalent crystal radius increase was low; the calculated values were found to be less than 30 nm with an incertitude of 5%. It was thus considered that within the 1450–1600 °C range the crystal growth of isolated SiC powder was very weak. During heating between 1450 and 1600 °C, the weight loss of silicon by evaporation after heating was lower than 5%, so that it could be considered that the remaining silicon was sufficient to promote a practically constant interaction with the powder. The mean equivalent crystal radii were measured by Rietveld refinements from X-ray diffraction experiments performed on crushed pellets. The results obtained thus are plotted in Fig. 3-a). These plots indicate that an important crystal growth occurred during the first 60 min leading to *r* values of about 60 nm. The evolution of *r* strongly depends on the temperature; the highest value was measured close to 120 nm after a heating of 5 h at 1600 °C. An increase of the crystallites mean size during the heating is therefore confirmed. Theories of volume diffusion-controlled coarsening have been developed by Lifshitz, Slyozov [39] and Wagner [40] (LSW). In the LSW theory, the growth of SiC crystallites or particles in liquid phase, called Ostwald ripening, is predicted to obey to Eq. (1) [18]: