

Preparation of Al–SiC–Al₂O₃ metal matrix composite powder by mechanochemical reaction between Al, SiO₂ and C

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In this Letter, Al–SiC–Al₂O₃ metal matrix nanocomposite powder was successfully synthesised employing a mechanical alloying technique, through a mechanochemical reaction among aluminium (Al), silicon dioxide (SiO₂) and carbon (C). For commercial purposes, the materials (Al, SiO₂ and C powders) and also the method of synthesis (mechanical alloying) is considered to be cost-effective for production of Al–SiC–Al₂O₃ nanocomposite. The structural evaluation of powder particles after different milling times was conducted by X-ray diffractometry, and scanning electron microscopy. The results showed that during ball milling Al, SiO₂ and C reacted through a mechanochemical reaction producing Al–SiC–Al₂O₃ metal matrix nanocomposite powder after 50 h of ball milling and annealing at a temperature of 650°C for 1 h. The crystallite sizes of phases remained in nanometric scale.

1. Introduction: Al matrix materials have been widely used for aircraft and automotive applications because of their high strength to weight ratio, environmental resistance, high stiffness and good wear resistance [1–3]. The mechanical strength and wear resistance of Al will be improved when reinforced with ceramic particles [3–6].

The most commonly used ceramic particles as reinforcement for the Al matrix are SiC and Al₂O₃ [7, 8]. SiC is a proper choice for high-temperature applications because of its good strength and hardness, acceptable corrosion resistance, low thermal expansion coefficient and high thermal conductivity [9]. Also, Al₂O₃ can increase the strength and fatigue crack resistance of Al [10].

Property enhancement of target composite by the reinforcing particles is directly dependent on the amount, size and distribution of the particles [11, 12]. Nanostructured Al matrix composites with average crystalline size of a few nanometres have improved properties that are much more attractive than conventional microstructured composites in industrial use and as a result, many investigators have recently made this the focus of their research [13, 14]. Generally, making the nanostructured materials increases the hardness, diffusivity, specific heat and ductility and reduces the density and elastic modulus [15, 16].

The Al matrix nanocomposite can be produced by two different approaches: (i) direct mixing of nanosize Al₂O₃ particles, or (ii) displacement reaction during ball milling of aluminium with a suitable oxide [17]. Although direct mixing of nanoparticles is an easy approach to produce aluminium matrix nanocomposites, expensive starting materials and a heterogeneous microstructure can be the two major drawbacks of this technique [18]: mechanical alloying is generally more successful in achieving the fine distribution of ceramic nanoparticles [19]. This technique, which is usually employed in powder metallurgy, is well known in the fabrication of composites using mechanochemical synthesis [20, 21]. The chemical precursors can be a mixture of oxides, chlorides and metals that react during milling or the following heat treatment [22]. Repeated cold welding, fracturing and rewelding can uniformly disperse the reinforcement particles into the matrix which is usually in complete nanosize structures

because of the high degree of deformation during milling [23–25].

For commercial purposes, the initial materials and the production methods must be cost-effective. In the work reported in this Letter, we investigated the formation of a novel Al–SiC–Al₂O₃ nanocomposite powder employing inexpensive materials and methods for the first time. Hence, the main objective of this reported work was the production of Al–SiC–Al₂O₃ nanocomposite powder using Al, SiO₂ and C powders instead of mixing Al, SiC and Al₂O₃, as the first group are less expensive compared with the second one. Moreover, the method of production was mechanical alloying which is an inexpensive technique for the manufacturing of nanocomposite powders.

2. Materials and methods: A mixture of commercial Al, SiO₂ and C was milled in a planetary ball mill to produce the Al–SiC–Al₂O₃ nanocomposite powder. Mechanical alloying was carried out at ambient temperature in a planetary high energy ball mill, via a hardened chromium steel vial and balls. The mechanical alloying parameters are presented in Table 1. To study the thermal behaviour of milled powders, isothermal annealing was carried out. The samples were sealed and then annealed in a conventional tube furnace. The annealing conditions are displayed in Table 1.

Phase structure analysis was carried out by an X-ray diffractometer (XRD, Philips Xpert) using Ni filtered Cu K α ($\lambda_{\text{Cu K}\alpha}$ = 0.154186 nm, radiation at 40 kV) over the 2 θ range of 10–90°.

Table 1 Mechanical alloying parameters and annealing conditions of SiO₂, Al and C

Value	Parameters
600	rotational speed, r/min
15:1	ball to powder weight ratio
15 min, 24 h and 50 h	ball milling time
Ar	protective atmosphere
650, 750 and 920	annealing temperature, °C
1	holding time, h

The obtained experimental patterns were compared with the standards compiled by the Joint Committee on Diffraction Pattern and Standards. The crystallite size was estimated by broadening the XRD peaks using the Williamson-Hall equation [24]

$$B \cos \theta = 0.89\lambda/D + 2\varepsilon \sin \theta \quad (1)$$

in which λ is the wavelength of the X-ray (nm), B is the full width of the diffraction peak under consideration (rad) in the middle of its height, considered after computer fitting of the X-ray data using a Gaussian line shape and θ is the Bragg's angle ($^\circ$). Thus, when $B \cos \theta$ was plotted against $\sin \theta$, a straight line was obtained with the slope of 2ε and the intercept as $(0.89\lambda/D)$. Thus, the crystallite size, d (nm), could be calculated.

A scanning electron microscope (SEM) (Philips XL 30: Eindhoven, The Netherlands) equipped with an energy dispersive spectra analyser, utilising ZAF corrections and elemental mapping was used for the microstructural studies.

3. Results and discussion: The XRD patterns of the Al-SiO₂-C powder mixture after 15 min, 24 and 50 h of milling times are presented in Fig. 1. The diffraction peaks of the initial powders (Al, SiO₂ and C) are clearly visible at the mixed powder after 15 min milling and no sign of the reaction between the Al-SiC-C powder mixtures is detected by the XRD pattern. By increasing the milling time from 15 min to 24 h, the intensity of the Al, SiO₂ and C diffraction peaks gradually decreased. The SiO₂ and C diffraction peaks disappeared completely in the samples milled for 50 h. Also, by increasing the milling time from 15 min to 50 h, the XRD peaks broadened. Broadening of the diffraction peaks after 24 h indicates that the grain size of the powder is decreased. According to the Williamson-Hall method, the grain sizes for SiC after 24 and 50 h ball milling were 39 and 16 nm, respectively.

Mechanical alloying induces intensive plastic deformation to powder particles at an extremely high strain rate, creating a high density of lattice defects, mainly dislocations. At the same time, recovery phenomenon can take place, reducing the density of dislocations. The progressive accumulation and interaction of dislocations lead to formation of dislocation cell configuration, which consequently builds low-angle grain boundaries. By continuing the procedure, this configuration is changed to high-angle grain boundaries and a fully nanocrystalline structure can be formed [1].

According to Fig. 1, after 50 h of milling, the SiO₂ and C peaks disappeared in the XRD pattern. However, no SiC and Al₂O₃ peaks were detected. In fact, during milling Al, SiO₂ and C react to form SiC and Al₂O₃ particles. It is reported that the SiC and Al₂O₃ particles formed during milling are very small in size (under 25 nm) and have an amorphous structure [21, 26]. Once amorphous SiC and Al₂O₃ are formed at low temperature, the strong Si-C and Al-O bond will suppress the atomic mobility necessary for the development of crystalline SiC and Al₂O₃. Therefore the alumina remains amorphous, which cannot clearly be identified in the XRD patterns.

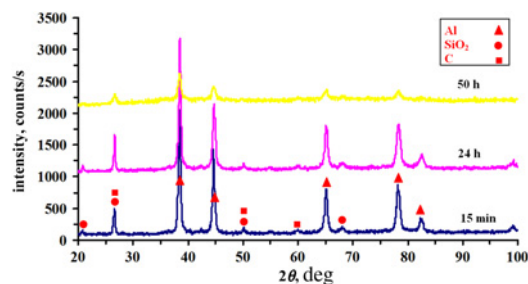


Figure 1 XRD patterns of Al-SiO₂-C powder mixture after 15 min, 24 and 50 h of milling time

Figs. 2a-d, respectively, show the SEM photomicrographs of the Al-SiO₂-C powder mixture after 15 min, 1 h, 24 h and 50 h milling times. The black, grey and white regions in the backscattered SEM photomicrographs refer to the three phases of Al, SiC and Al₂O₃, respectively, according to their density. An inhomogeneous lamellar structure was identified in the powder particles according to Fig. 2a. After 1 h of milling, a layered microstructure consisting of three phases is formed by cold welding and the powder particles are extensively flattened (Fig. 2b). At this stage, the structure is coarse and non-uniform. Increasing the milling time to 24 h led to the refinement of the composite microstructure because of the repeated cold welding and fracturing of powder particles (Fig. 2c). On the other hand, by increasing the milling time to 24 h, owing to the work hardening of powders, the size of the powder particles decreased. This fine microstructure includes an extensive interface area between phases, which promotes the inter diffusion of atoms through high diffusivity paths (dislocations and grain boundaries), and can therefore increase the reaction kinetics at ambient temperature [5]. Thus, the microstructures of the composites after 24 h (Fig. 2c) and 50 h (Fig. 2d) milling times indicated a nearly homogeneous distribution of two phases in a composite matrix. After 50 h of milling time the powder particles become nearly equiaxed in shape. In fact, by increasing the milling time, the rate of fracturing increased because of the work hardening of powders; as a result, the size of particles decreased.

A heat treatment after milling is needed to improve the structural properties [6]. The thermal behaviour of Al-SiO₂-C nanocomposite powders was studied by annealing at 650, 750 and 920°C for 1 h. Fig. 3 shows the XRD patterns of as received powders after ball milling for 50 h and after annealing at 650, 750 and 920°C. The grain size of Al and SiC at different annealing temperatures in the 50 h as-milled Al-SiO₂-C nanocomposite powders are presented in Table 2. During annealing at relatively low temperatures (650°C), the clear peaks corresponding to Al, SiC and Al₂O₃ were detected. The possible reason for the formation of Al, SiC and Al₂O₃ between annealing processes can be the movement of vacancies and dislocations as discussed in [8]. It may cause atoms in the disordered or distorted positions to rearrange and/or move into the more thermodynamically equilibrated ordered lattice positions [8]. It enhances the degree of ordering and crystallinity. The width of the XRD peaks of Al and SiC decreased and

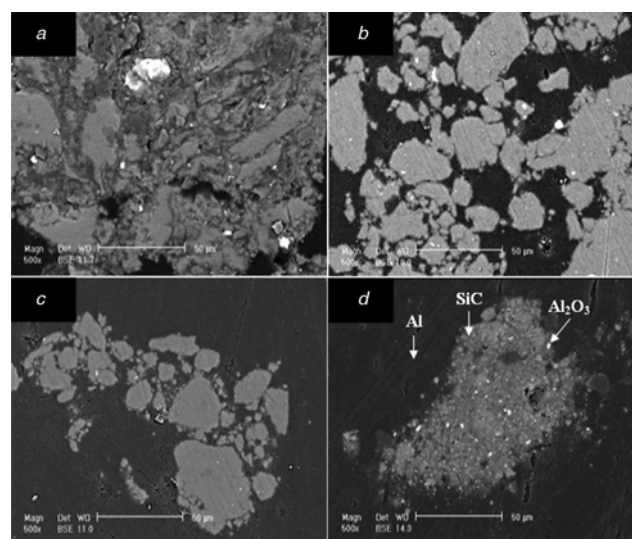


Figure 2 SEM photomicrographs of the Al-SiO₂-C powder mixture after 15 min, and 1, 24, 50 h milling times

a 15 min
b 1 h
c 24 h
d 50 h

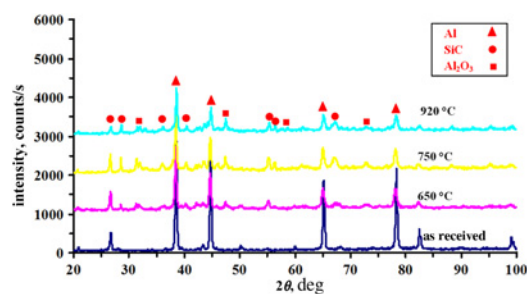


Figure 3 XRD patterns of the as-received powders after ball milling for 50 h and after annealing at 650, 750 and 920 °C

Table 2 Grain size of Al and SiC at different annealing temperatures on the 50 h as-milled Al–SiO₂–C nanocomposite powders

Element temperature, °C	Al, nm	SiC, nm
650	97	47
750	190	92

their intensity increased after annealing because of the reduction of lattice strain as well as grain growth. Nanocrystalline structures are thermodynamically unstable because of excess free energy stored in their grain boundaries. According to Table 2, the grain size of Al is increased from 97 to 327 nm by annealing from 650 to 920 °C. In addition, this range of annealing causes the grain size growth of SiC from 47 to 247 nm. At high temperatures, the vacancy annihilation process competes with the triple defects [9]. Therefore the vacancy concentration first decreases very slightly with increasing temperature and then increases when the temperature is rising [3]. On the other hand, the reordering is caused by the difference of energy between the ordered and disordered states [1]. Thus, if this difference in energy is overcome by thermal activation, the alloy will be disordered and the grain size will increase significantly to above 100 nm for the annealing temperature above 650 °C. Thus, according to our results, 1 h annealing at 650 °C would be necessary for the production of Al, SiC and Al₂O₃ in the nanometre scale.

Figs. 4a–c, respectively, show the SEM photomicrographs of as-milled powder for 50 h after annealing at 650, 750 and 920 °C.

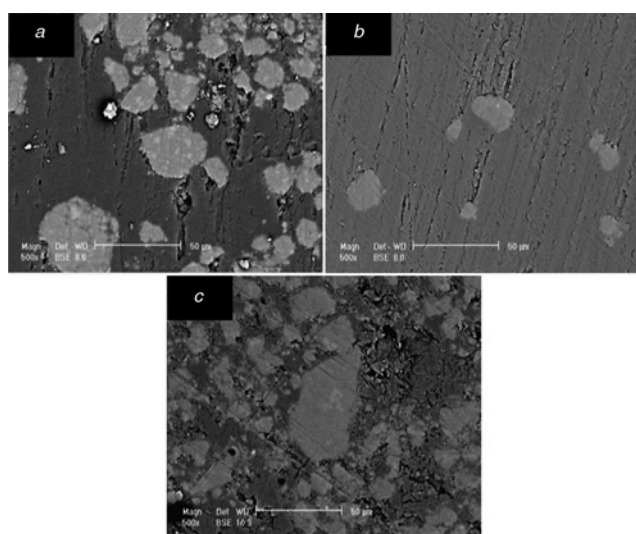


Figure 4 SEM photomicrographs of as-milled powder for 50 h after annealing at 650, 750, 920 °C

a 650 °C
b 750 °C
c 920 °C

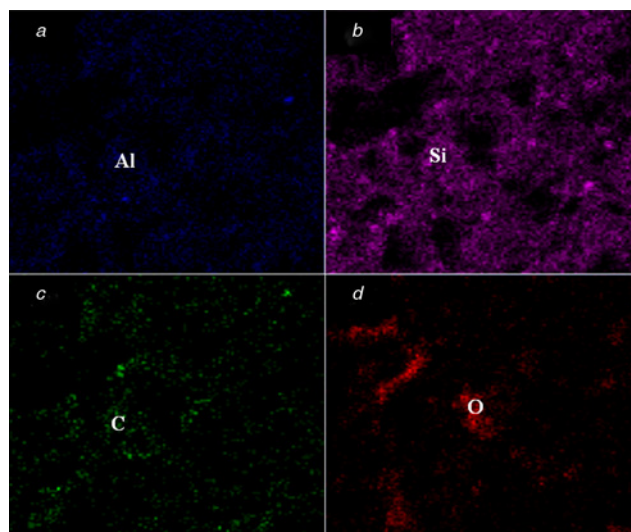


Figure 5 Elemental mapping of the as-milled powders for 50 h after annealing at 650 °C

The elemental mapping of the as-milled powders for 50 h after annealing at 650 °C is presented in Fig. 5. According to Fig. 4, the black, grey and white zones in the backscattered SEM photomicrographs correspond to the three phases of Al, SiC and Al₂O₃ in the microstructure. The presence of C (Fig. 5a), Si (Fig. 5b), Al (Fig. 5c) and O (Fig. 5d) can be regarded as confirmation of the presence of Al, SiC and Al₂O₃ in the structure of the nanocomposite powder.

Also, overlapping the elements by elemental mapping of the as-milled powder for 50 h after annealing at 650 °C is shown in Fig. 6. According to this Figure, the overlapping of Si and C (Fig. 6a) and Al and O (Fig. 6b) show not only the presence of SiC and Al₂O₃ in the structure but it also shows a nearly homogeneous distribution of SiC and Al₂O₃ in the structure of the nanocomposite powder.

Mechanical alloying can enhance the kinetics of reactions via: (i) introducing excess energy into materials in the form of structural defects, (ii) creating high diffusion paths, (iii) providing an extensive interface area between materials during repeated fracturing and cold welding of powder particles and (iv) local temperature rise [14]. In mechanical alloying, gradual interdiffusion of components occurs leading to the formation of products by increasing milling time. In other words, the reaction may extend to a very small volume during each collision, resulting in a gradual transformation [15]. An effective method used for the preparation of a powder nanocomposite in low temperatures is mechanical alloying using the well-known exothermic reduction reactions of oxides (M_xO_y) with active metals such as Al [26]

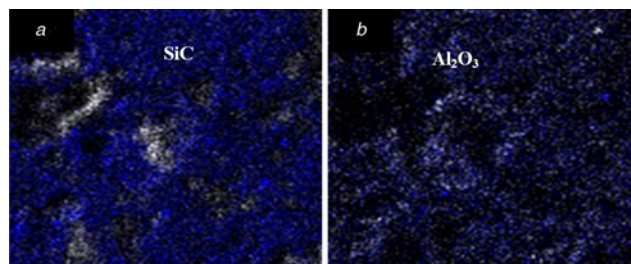
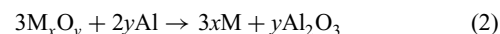
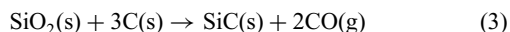


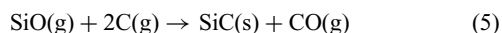
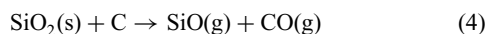
Figure 6 Overlapping the elements by elemental mapping of the as-milled powder for 50 h after annealing at 650 °C

The possibility of the synthesis of the nanocomposite powder is caused by the presence of metals (reduced M and excess aluminum) in the reaction zone.

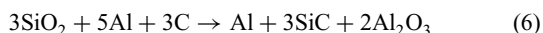
The overall reaction of formation for SiC through carbothermic reduction is normally written as [27]



Although the reaction (3) involves both reactants in solid form, the carbothermic reduction of silica consists of gas–solid reactions in two steps. The most accepted reaction mechanism for the gas–solid carbothermic synthesis of SiC at low temperatures is given in the following equations [28]



Moshtaghion *et al.* [28] have reported that silicon carbide nanopowders have been synthesised from carbothermic reduction of nanosilica with graphite in a 2.45 GHz microwave field in nitrogen atmosphere after 40 h milling. At 1150°C, the synthesis of SiC is started but it is not completed even with increasing duration time. In the present research, by milling SiO₂ and C, the reduction temperature decreases from 1150 to 650°C. There are several reasons for this phenomenon: (i) the mechanical activation of powders and (ii) promotion of the diffusion process because of increase in grain boundary and defects, which needs a lower energy and provides more rapid pathways for solid-state diffusion. Increasing contact areas between the particles is another reason for the starting reaction temperature decrease [27]. Mechanical alloying can enhance the kinetics of reaction by creating a high diffusivity path, providing an extensive interface area between reactants and by the dynamic removal of the reaction product from interfaces because of the repeated fracturing and cold welding of powder particles [19]. Thus, the Al–SiC–Al₂O₃ metal matrix nanocomposite powder can be produced by a displacement reaction between the Al, SiO₂ and C powder mixture according to the following reaction



4. Conclusion: In this Letter, Al–SiC–Al₂O₃ metal matrix nanocomposite powder was successfully synthesised by mechanical alloying. 50 h ball milling of Al, SiO₂ and C and 1 h annealing at a temperature of 650°C results in the production of Al–SiC–Al₂O₃ metal matrix nanocomposite powder through a mechanochemical reaction. The crystallite sizes of the phases were in nanoscale after this process.

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6 References

- [1] Stearns L.C., Zhao J., Harmer M.P.: 'Processing and microstructure development in Al₂O₃–SiC nanocomposites', *J. Eur. Ceram. Soc.*, 1992, **10**, pp. 473–477
- [2] Mohammad Sharifi E., Karimzadeh F., Enayati M.H.: 'Fabrication and evaluation of mechanical and tribological properties of boron carbide reinforced aluminum matrix nanocomposites', *Mater. Des.*, 2011, **32**, pp. 3263–3271
- [3] Hosseini N., Karimzadeh F., Abbasi M.H., Enayati M.H.: 'Tribological properties of Al6061–Al₂O₃ nanocomposite prepared by milling and hot pressing', *Mater. Des.*, 2010, **31**, pp. 4777–4785
- [4] Sabooni S., Mousavi T., Karimzadeh F.: 'Mechanochemical assisted synthesis of Cu(Mo)/Al₂O₃ nanocomposite', *J. Alloys Compd.*, 2010, **497**, pp. 95–99
- [5] Mohammad Sharifi E., Karimzadeh F., Enayati M.H.: 'Mechanochemically synthesized Al₂O₃–TiC nanocomposite', *J. Alloys Compd.*, 2010, **491**, pp. 411–415
- [6] Hosseini S.N., Karimzadeh F., Enayati M.H.: 'Development and characterization of CoAl/Al₂O₃ intermetallic matrix nanocomposite', *Mater. Chem. Phys.*, 2012, **136**, pp. 341–346
- [7] Tavosi M., Karimzadeh F., Enayati M.H., Heidarpour A.: 'Bulk Al–Zn/Al₂O₃ nanocomposite prepared by reactive milling and hot pressing methods', *J. Alloys Compd.*, 2009, **475**, pp. 198–201
- [8] Mohammad Sharifi E., Karimzadeh F., Enayati M.H.: 'Preparation of Al₂O₃–TiB₂ nanocomposite powder by mechanochemical reaction between Al, B₂O₃ and Ti', *Adv. Powder Technol.*, 2011, **22**, pp. 526–531
- [9] Grigoryeva T.F., Novakova A.A., Yu Kiseleva T., Barinova A.P., Ancharov A.I., Talako T.L.: 'Mechanochemical production of nanocomposites of metal/oxide and intermetallic/oxide systems', *J. Phys.*, 2009, **144**, pp. 1–4
- [10] Tavosi M., Karimzadeh F., Enayati M.H.: 'Fabrication of Al–Zn/α-Al₂O₃ nanocomposite by mechanical alloying', *Mater. Lett.*, 2008, **62**, pp. 282–285
- [11] Mousavi T., Karimzadeh F., Abbasi M.H., Enayati M.H.: 'Investigation of Ni nano crystallization and the effect of Al₂O₃ addition by high-energy ball milling', *J. Mater. Process. Technol.*, 2008, **204**, pp. 125–129
- [12] Karimzadeh F., Enayati M.H., Tavosi M.: 'Synthesis and characterization of Zn/Al₂O₃ nanocomposite by mechanical alloying', *Mater. Sci. Eng. A*, 2008, **486**, pp. 45–48
- [13] Candan E., Ahlatci H., Imenoglu H.C.: 'Abrasive wear behaviour of Al–SiC composites produced by pressure infiltration technique', *Wear*, 2001, **247**, pp. 133–138
- [14] Suryanarayana C.: 'Mechanical alloying and milling', *Prog. Mater. Sci.*, 2001, **46**, pp. 1–184
- [15] Botta W.J., Tomasi F.R., Pallone E.M.J.A., Yavari A.R.: 'Nanostructured composites obtained by reactive milling', *Scripta Mater.*, 2001, **44**, pp. 1735–1740
- [16] Yang X.Y., Huang Z.W., Wu Y.K., Ye H.Q.: 'HREM observations of the synthesized process of nano-sized SiC by ball milling of Si and C mixed powders', *Mater. Sci. Eng. A*, 2001, **300**, pp. 278–283
- [17] Wu J.M.: 'Nano-sized amorphous alumina particles obtained by ball milling ZnO and Al powder mixture', *Mater. Lett.*, 2001, **48**, pp. 324–330
- [18] Dashtbayazi M.R., Shokuhfar A.: 'Statistical modeling of the mechanical alloying process for producing of Al/SiC nanocomposite powders', *Comput. Mater. Sci.*, 2007, **40**, pp. 466–479
- [19] Yang Y., Lin Z.M., Li J.T.: 'Synthesis of SiC by silicon and carbon combustion in air', *J. Eur. Ceram. Soc.*, 2009, **29**, pp. 175–180
- [20] Ruggles-Wrenn M.B., Christensen D.T., Chamberlain A.L., Lane J.E., Cook T.S.: 'Effect of frequency and environment on fatigue behavior of a CVI SiC/SiC ceramic matrix composite at 1200°C', *Comput. Sci. Technol.*, 2011, **71**, pp. 190–196
- [21] Wrbanek J.D., Fralick G.C., Zhu D.: 'Ceramic thin film thermocouples for SiC-based ceramic matrix composites', *Thin Solid Films*, 2012, **520**, pp. 5801–5806
- [22] Costil S., Lukat S., Bertrand P., Langlade C., Coddet C.: 'Surface treatment effects on ceramic matrix composites: case of a thermal sprayed alumina coating on SiC composites', *Surf. Coat. Technol.*, 2010, **205**, pp. 1047–1054
- [23] Hosseini N., Karimzadeh F., Abbasi M.H., Enayati M.H.: 'A comparative study on the wear properties of coarse-grained Al6061 alloy and nanostructured Al6061–Al₂O₃ composites', *Trib. Int.*, 2012, **54**, pp. 58–67
- [24] Williamson G.K., Hall W.H.: 'X-ray line broadening from filed aluminium and wolfram', *Acta Metall.*, 1953, **1**, pp. 22–31
- [25] Larpiattaworn S., Ngerchuklin P., Khongwong W., Pankurdee N., Wada S.: 'The influence of reaction parameters on the free Si and C contents in the synthesis of nano-sized SiC', *Ceram. Int.*, 2006, **32**, pp. 899–904
- [26] Santhosh Kumar S., Devaiah M., SeshuBai V., Rajasekharan T.: 'Mechanical properties of SiCp/Al₂O₃ ceramic matrix composites prepared by directed oxidation of an aluminum alloy', *Ceram. Int.*, 2012, **38**, pp. 1139–1147
- [27] Moshtaghion B.M., Poyato R., Cumbreira F.L., de Bernardi-Martin S., Monshi A., Abbasi M.H.: 'Rapid carbothermic synthesis of silicon carbide nano powders by using microwave heating', *J. Eur. Ceram. Soc.*, 2012, **32**, pp. 1787–1794
- [28] Moshtaghion B.M., Monshi A., Abbasi M.H., Karimzadeh F.: 'A study on the effects of silica particle size and milling time on synthesis of silicon carbide nanoparticles by carbothermic reduction', *Int. J. Refract. Metal. Hard Mater.*, 2011, **29**, pp. 645–650