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Development of Fe_3C, SiC and Al_4C_3 compounds during mechanical alloying

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Abstract Mechanical alloying process, as a solid-state technique, is a very useful method for fabrication of high melting point compounds like metal carbides and nitrides, which additionally have nanocrystalline structure with improved properties. In this work the development of several carbides including iron, aluminium and silicon carbides by the mechanical alloying process and the effect of subsequent heat treatment were investigated. Mixtures of elemental powders of Fe–C, Si–C and Al–C were mechanically alloyed, nominally at room temperature using a laboratory planetary ball mill. Structural changes of samples were studied by X-ray diffraction (XRD) and scanning electron microscopy (SEM). The results showed that the aluminium carbide (Al_4C_3) could not be synthesized by mechanical alloying process alone, even after long milling times. A suitable subsequent heat treatment was required to allow Al–C reaction to take place kinetically. In contrast mechanical alloying of Fe–C as well as Si–C systems directly led to the formation of Fe_3C and SiC carbides after sufficient milling time. In all cases the end product had a nanosized structure.

Introduction

The metal carbides generally have high melting points and therefore these compounds are frequently referred to as ‘‘refractory materials’’. While these materials are refractory, their main commercial importance stems from their extreme hardness. The metal carbides form the basis for cemented carbide cutting tools and wear-resistant parts and surfaces. Because they have high strength, particularly at high temperatures, high values of Young’s modulus, high chemically stability and good thermal shock resistance and thermal conductivity, they can also be used as structural materials. But at room temperature they are brittle which limits their applications [1].

Metal carbides are usually prepared by powder metallurgy route. The metal or oxide powder is reacted with carbon, pressed, and sintered. The preparation of homogeneous samples is, however, a difficult task. Very high temperatures (>1,000 °C) and good vacuum conditions or highly purified gases are generally required [1]. One recently developed method for preparing homogeneous metal carbides is mechanical alloying (MA).

Mechanical alloying is a solid-state synthesis route using a milling process. The starting powder, often a mixture of elemental constituent powders, is charged into a suitable mill and processed for several hours depending on experimental conditions as well as desired microstructure and properties. Repeated ball-powder-ball collisions during MA lead to the material transfer by diffusion, which is significantly accelerated by lattice defects and by a momentary increase in temperature of particles trapped between colliding balls. The occurrence of mass transfer during MA makes it possible to synthesize the commercial high melting metal carbides directly at room temperature by either milling of pure elements or milling of metal powders with hydrocarbons [2, 3]. Although a subsequent heat treatment was reported to be necessary to obtain carbide compounds in some alloy systems [4]. MA has the advantage over other fabrication techniques as the final product has a nanocrystalline structure with superior properties to those of conventional coarse grained materials. Thereby, conventional rather brittle and hard materials like

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metal carbides exhibit improved ductility (and hence, formability) and even superplasticity in the nanocrystalline state, especially at evaluated temperature.

In this work the development of Al_4C_3, SiC and Fe_3C carbides during MA process was investigated. The effect of subsequent heat treatment on the metal–carbon reaction is discussed.

Experimental procedures

Mixtures of elemental powders of Fe–C, Si–C and Al–C were mechanically alloyed to produce Fe_3C, SiC and Al_4C_3 compound. Powder mixtures together with the steel balls (20 mm in diameter) were placed in a hardened chromium steel vial (120 mL volume). The weight ratio of the balls to the powder was 17:1. Dry milling was carried out in a planetary-type ball mill with a disc rotation speed of 200 rev min^{-1}. All milling runs were nominally at room temperature. At selected times, a small amount of the sample powders were taken out for structural analysis. The as-milled powders were characterized by a Philips X'PERT MPD X-ray diffractometer with CuKα radiation ($\lambda = 0.1542$ nm) and a Philips XL30 scanning electron microscopy (SEM) operating at 30 kV. Isothermal annealing was performed to study the thermal behaviour of milled powders. MA samples were sealed and then annealed in a conventional tube furnace. After annealing the specimens were cooled in air. The structural transitions occurred during annealing were determined by XRD.

Results and discussion

Figure 1 shows micrographs of as-received Fe, Si, Al and graphite powder particles. The Fe particles had a nearly uniform size of ~300 μm with a sponge morphology. The Si particles were angular in shape with a wide size distribution ranging from ~5 μm to 20 μm. The Al particles were irregular in shape with a size distribution of 20–100 μm. The graphite particles had an angular shape with a narrow size distribution of 20 μm.

MA of Fe–C

Figure 2 shows the XRD patterns of the Fe–C powders milled for 30 and 60 h and also after subsequent heat treatment. With prolonged milling time, the intensities of Fe peaks decreased, and the peaks were broadened owing to reduction in grain size and accumulation of lattice strain. After 60 h of MA several weak diffraction peaks of Fe_3C phase were found on the XRD patterns. The powder particles after 60 h MA were isothermally annealed at 950 °C for 1 h. As seen in Fig. 2c no evidence of Fe_3C peaks are observed on XRD patterns of heat treated sample. In contrast Enayati and Zakeri [5] found that a significant fraction of Fe_3C phase forms in Fe–1.5 wt% graphite powder

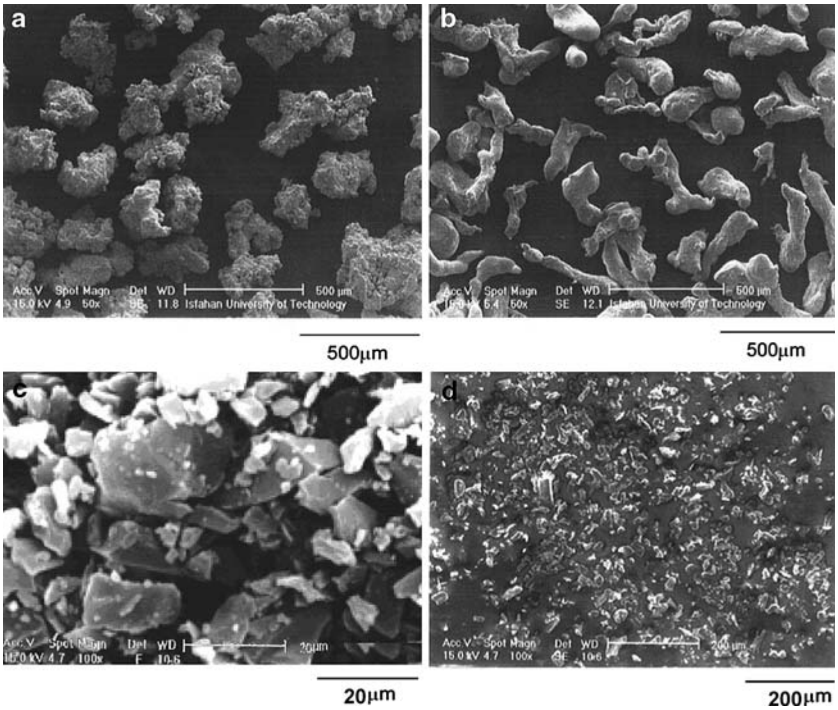

Fig. 1 SEM images of as-received powder particles: (**a**) Fe, (**b**) Al, (**c**) Si and (**d**) graphite

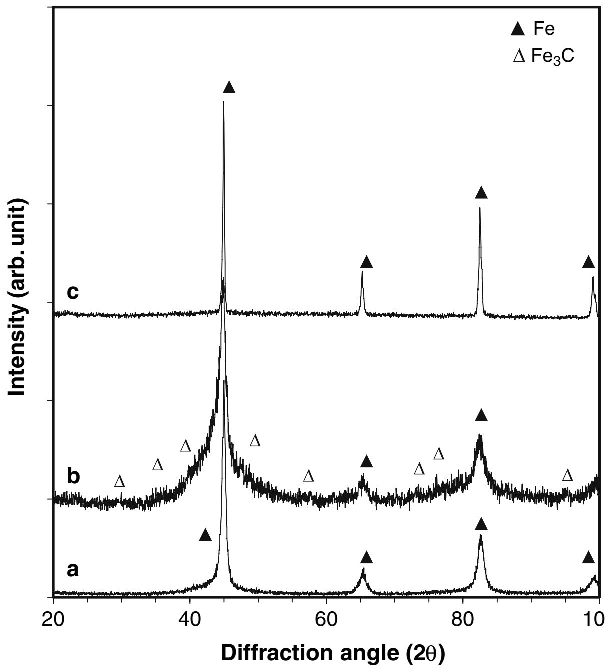

Fig. 2 XRD patterns of Fe–C powder mixture: (**a**) milled for 30 h, (**b**) milled for 60 h and (**c**) milled for 60 h followed by isothermal annealing at 950 °C for 1 h

mixture, milled for 30 h, after subsequent heat treatment at 600 °C for 1 h. In fact annealing process at 950 °C leads to the ferrite-to-austenite transformation. During subsequent cooling in air, the temperature of powder particles rapidly reduced, resulting in austenite-to-martensite transformation rather than the formation of Fe$_3$C phase.

MA of Si–C

The structural revolution of Si–C powder particles during MA process are shown in Fig. 3. Mechanical alloying for 30 h led to only the broadening of crystalline Si peaks without any indication of additional phases (e.g. SiC). XRD patterns of powder particles at longer milling time of 60 h include the crystalline peaks of SiC phase along with the Si peaks remaining from incomplete Si–C reaction. The SiC crystallite size was estimated from broadening of XRD peaks using the approximate Scherrer's formula, $D = \lambda/B\cos\theta$, where D is the average grain size, λ is the CuKα wave length, B is the diffraction peak width at half-maximum intensity and θ is the Bragg diffraction angle [6]. The results showed that SiC phase had a nanoscale size of about 8 nm. As seen in Fig. 3c subsequent annealing (at 450 °C for 1 h) of powder particles milled for 60 h had no significant effect on structure; no further increase in fraction of SiC phase was observed. Longer milling times and/or higher annealing temperatures may be necessary to form a fully SiC structure.

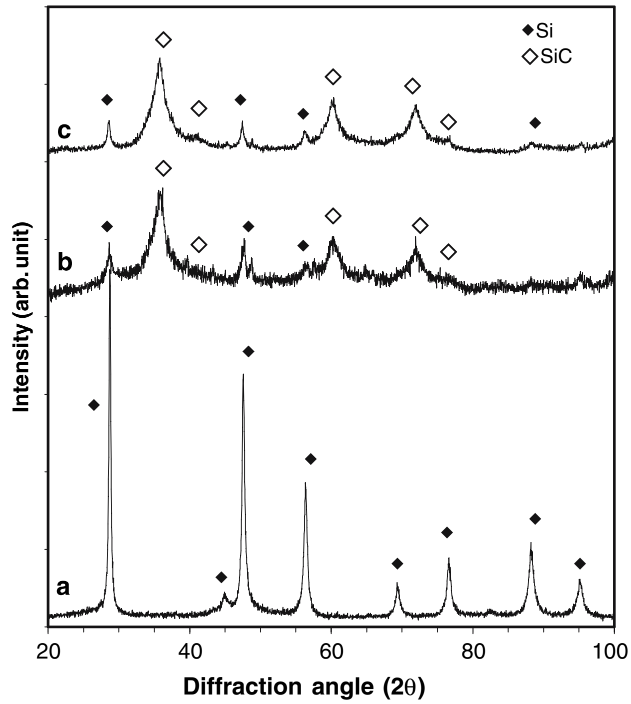

Fig. 3 XRD patterns of Si–C powder mixture: (**a**) milled for 30 h, (**b**) milled for 60 h and (**c**) milled for 60 h followed by isothermal annealing at 450 °C for 1 h

MA of Al–C

The XRD patterns of the structural evolution of the mechanically alloyed Al–C powders are shown in Fig. 4. The principle change observed consisted of a broadening of the Al peaks and a decrease of their peaks intensities. The crystalline graphite peaks disappeared after 60 h of milling time. The absence of any shift in the peak positions of Al lead to the conclusion that no reciprocal solid solution of carbon in aluminium had formed. No traces of the diffraction peaks of Al$_4$C$_3$ phase were evident on the XRD traces even after 60 h of milling time. This suggests that the mechanical alloying process for Al–C system is essentially a mixing process, which additionally involves a high density of lattice defects and progress refinement of Al crystallite size. Figure 4c shows the XRD traces from the Al–C powder mixture as-milled for 60 h after subsequent heat treatment at 450 °C for 1 h. After isothermal annealing the diffraction peaks of the Al$_4$C$_3$ phase appeared on the XRD patterns, although the traces of original Al peaks are still visible after annealing. These results are qualitatively in agreement with the previous result given by Jangg [7]. In contrast Wu et al. [8] reported that the Al$_4$C$_3$ phase is formed during milling of Al$_{72}$C$_{28}$ powder mixtures. This discrepancy may be related to the different milling conditions employed. For example Wu et al. chose a ball-to-powder weight ratio of 30:1, which is much higher

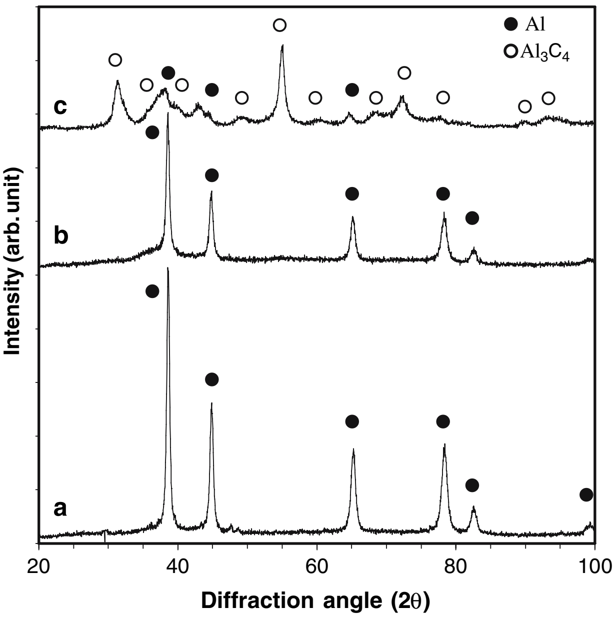

Fig. 4 XRD patterns of Al–C powder mixture: (**a**) milled for 30 h, (**b**) milled for 60 h and (**c**) milled for 60 h followed by isothermal annealing at 450 °C for 1 h

than that used here, 10:1. A higher ball-to-powder weight ratio reduces the start time of the formation of Al_4C_3 phase as the powder particles undergo greater number of collisions per unit time. XRD peak broadening analysis using Scherrer's equation suggests that Al_4C_3 phase has a nanosized structure with a crystalline size of about 15 nm.

Conclusions

The formation of metal carbide in three compositions, Fe–C, Si–C and Al–C was investigated by utilizing mechanical alloying process. It was found that MA of Fe–C as well as Si–C systems directly led to the formation of Fe_3C and SiC carbides after sufficient milling time. This observation suggests that numerous high-speed diffusion paths are necessary to allow a high diffusion rate at low temperature and therefore permits the metal–carbon reaction to take place kinetically. It was not possible to obtain Al_4C_3 compound by MA alone. In fact Al_4C_3 compound can be formed by a combination of MA and a suitable subsequent heat treatment. The metal carbides prepared by MA process found to have a nanocrystalline structure.

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