

Production of Fe-C Powders with Improved Structure

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Abstract

Production of Fe-C alloy powders by mechanical alloying was studied. Fe and graphite elemental powder mixtures containing 0.8 and 1.5wt.% graphite were mechanically alloyed using a planetary ball mill. The structural changes of powder particles during mechanical alloying were studied by x-ray diffractometry, scanning electron microscopy and microhardness measurements. For both compositions, mechanical alloying for 30h resulted in the development of a nanocrystalline structure with a typical grain size of 16nm containing nanoscale size Fe₃C phase. This structure exhibited high microhardness value of the order of 600Hv. The powder particles after 30h of milling had a nearly spherical morphology and narrow size distribution. The mean powder particle size for Fe-0.8wt.% graphite composition was 15μm, whereas the Fe-1.5wt.% graphite composition achieved a smaller particle size with a mean of 9μm due to higher graphite content.

Keywords: Powder preparation, Fe-C, Mechanical alloying, Nanomaterials.

Introduction

Studies of processing techniques which increase the range of obtainable microstructures and lead to improvements in properties are important for the development of new materials. Mechanical alloying (MA) as a non-equilibrium technique has been proved to meet this requirement¹⁾. Mechanical alloying is a solid-state processing route which involves the dry-milling of powders in a high energy mill. Severe plastic deformation, repeated cold welding and fracturing of powder particles, creation of a high density of lattices, defects, and materials transfer by diffusion of components during milling provide the means to synthesize materials with very fine microstructures and non-equilibrium phases. The resulting MA powders can subsequently be consolidated by standard powder metallurgy techniques into bulk materials with desirable properties.

The occurrence of mass transfer during MA makes it possible to synthesize commercial high melting point compounds at room temperature. For example metal carbides such as Al₄C₃, Fe₃C, WC, NbC, SiC and TiC have been produced directly by either milling of pure elements or milling of metal powders with hydrocarbons²⁻³⁾. Although a subsequent heat treatment was reported to be necessary to obtain carbide compounds in some alloy systems⁴⁾.

This has made MA a powerful tool for in-situ production of composites and dispersion-strengthened materials with high uniformity and fine microstructure¹⁾. The aim of present work was to study the behaviour of Fe-C powder mixtures during MA process. The development of Fe₃C phase during MA was of particular interest.

Experimental methods

99.8% pure Fe powder (from Ghazvin Powder Metallurgy Co.) and 99.98% pure graphite powder (from Merck) were used as starting materials. Figure 1. shows the morphology of as-received Fe and graphite powder particles. As can be seen, the Fe particles had a nearly uniform size of ~130μm with a morphology consisting of clusters of several small spherical particles. The graphite particles were angular in shape with narrow size distribution of 20μm.

The powders were weighed and mixed manually to give nominal compositions of Fe-0.8wt.% graphite and Fe-1.5wt.% graphite. Mechanical alloying was carried out, nominally at room temperature using a laboratory planetary ball mill. The milling media consisted of five 20mm diameter balls confined in a 120ml volume bowl. The bowl and ball materials were hardened chromium steel. In all MA runs the ball-to-powder weight ratio was about 6:1 and the angular velocity of the bowl was approx. 600rpm. The MA was interrupted after selected time intervals and a small amount of powder was removed for further characterization. Structural changes of samples were studied by x-ray diffraction (XRD) in a Philips X'PERT MPD diffractometer using filtered CuKα radiation (λ=0.1542nm). The particle morphologies

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were investigated by scanning electron microscopy (SEM) in a Philips XL30 operating at 30kV. Powder samples were fixed in small quantities on a sample holder by graphite sticky tape. At least 30 separate particles were chosen for the measurement of powder particle size. The hardness of powder particles was also determined by microhardness measurements using a Vickers indenter. Five indentations were made on each sample to obtain an average value of microhardness. Isothermal annealing was carried out to study the thermal behaviour of milled powders. MA samples were sealed and then annealed in a conventional tube furnace. The structural transitions occurred during annealing were determined by XRD.

Results and Discussion

a) Structural changes

Figure 2 shows XRD traces from Fe-1.5wt.% graphite powder mixture as-received and after different milling times. The XRD traces of the as-received powders showed diffraction peaks from pure crystalline Fe and graphite. Increasing milling time to 5h resulted in the crystalline graphite peaks vanishing while the sharp crystalline Fe peaks broadened and their intensities decreased due to the refinement of Fe grain size as well as the accumulation of internal strain. Increasing milling time to 10h and then 30h led to a further increase in Fe diffraction peaks width, indicating the progressive reduction of

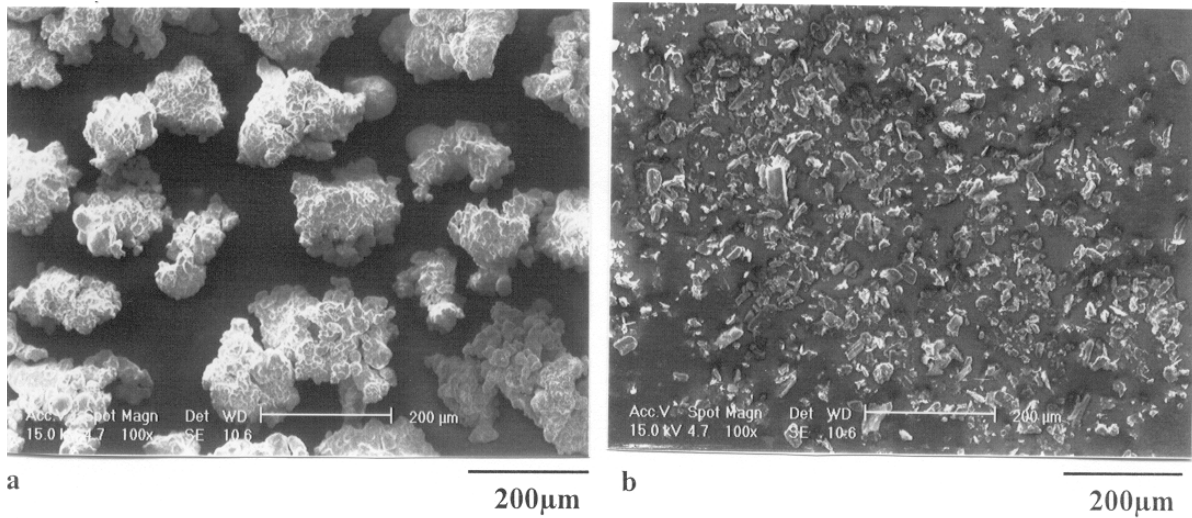


Fig. 1. SEM micrographs of as-received a) Fe and b) graphite powder particles.

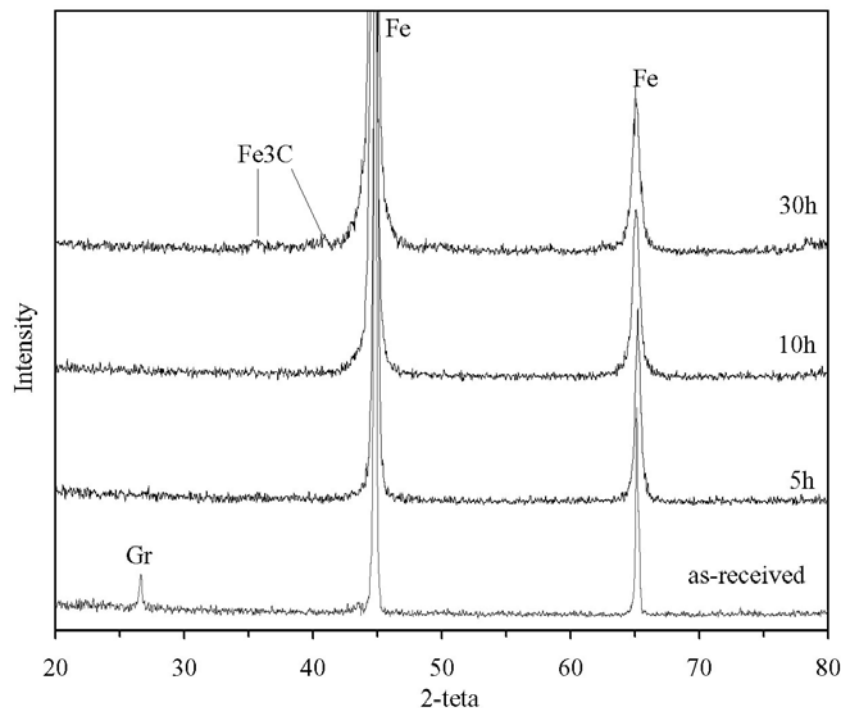


Fig. 2. XRD traces of Fe-1.5wt.% graphite powder mixture as-received and after different milling times.

grain size and enhancement of lattice strain in Fe. As shown in Figure 2 the traces of the diffraction peaks of Fe_3C phase were evident on the XRD traces only after 30h of MA. This observation suggests that numerous high speed diffusion paths such as dislocation networks and grain boundaries are necessary to permit a high diffusion rate at low temperature and therefore, allow the Fe-C reaction to take place kinetically.

No shift in Fe diffraction peaks was observed on the XRD traces during MA suggesting that there is no significant alloying between Fe and graphite prior to the formation of Fe_3C phase. These results are consistent with previous reports for MA of Fe-C powder mixture⁵⁻⁷.

The Fe grain size was estimated from broadening of XRD peaks using Scherrer's formula⁸:

$$t = \frac{0.9\lambda}{B\cos\theta} \quad (1)$$

Where t is the average grain size, λ is the $\text{CuK}\alpha$ wave length, B is the diffraction peak width at half-maximum intensity and θ is the Bragg diffraction angle. After 30h of MA, the Fe achieved a grain size of about 16nm. It is anticipated that this nanocrystalline structure could enhance both hardness and strength of materials¹). It also permits sintering of compacted powder at much lower temperatures¹). Grain refinement of powders to the nanometre size is governed by the plastic deformation induced during milling. At the early stage of milling, a very fine microstructure is obtained which contains some shear bands and many dislocations. The latter are converted into a dislocation cell structure which subsequently creates low-angle grain boundaries. With prolonged processing, this structure is transformed to a fully nanocrystalline structure with completely random orientation of neighbouring grains which are separated by high-angle grain boundaries⁹).

Similar results were also observed for Fe-0.8wt.% graphite composition.

b) Morphological changes

Changes in particles morphology during MA are produced by two simultaneous processes; cold welding and fracturing of the powder particles. The extent of these two events is determined by the mechanical properties of the elemental powders, such as ductility, yield stress and hardness, as well as the magnitude of the impact provided by colliding balls.

Elemental Fe and graphite powder particles had a mean size of $\sim 130\mu\text{m}$ and $\sim 20\mu\text{m}$ respectively. After 5 h of milling time, the Fe and powder particles got cold-welded to each other due to the heavy plastic deformation experienced by them during milling. At this time of milling, the particles varied in size, with an average of $\sim 30\mu\text{m}$, and also varied in shape. As MA proceeded further, the particle size decreased and their shape became progressively more uniform so that the final product after 30h of milling had a nearly spherical morphology and a narrow size distribution as shown in Figure 3. After 30h of milling time, Fe-1.5wt.% graphite particles had an average size of $9\mu\text{m}$ which was smaller than $15\mu\text{m}$ observed for Fe-0.8wt.% graphite particles after the same milling time. These results suggest that cold welding of the Fe particles is effectively hindered by the graphite as a solid surfactant. In such circumstances, the fracturing of powder particles becomes the dominant process, resulting in finer powder particles.

c) Thermal behaviour

Figure 4 shows XRD traces from the Fe-1.5wt.% graphite powder mixture after 30h mechanical alloying and also after subsequent heat treatment at 600°C for 1h. As shown after isothermal annealing, the diffraction peaks of the Fe_3C phase became more pronounced due to the further reaction of Fe and graphite during annealing to form Fe_3C compound. As pointed out earlier, no evidence of Fe_3C peaks was observed on the XRD traces of samples milled for 5h and 10h. Isothermal annealing

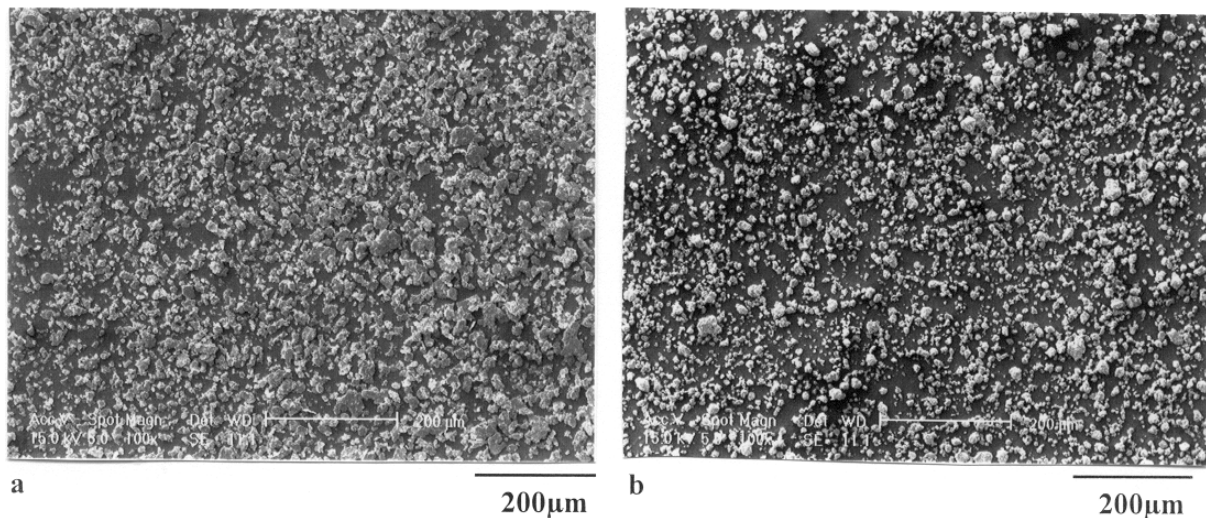


Fig. 3. SEM micrographs of a) Fe-0.8wt.% graphite and b) Fe-1.5wt.% graphite powder particles after 30h MA.

of these samples; however, led to the formation of Fe_3C phase. Although the annealing temperature (or time) needed to obtain the Fe_3C phase was higher for the sample milled for 5h compared with the sample milled for 10h. Because in this sample a lower density of lattice defects is available to facilitate the diffusion process during annealing.

XRD peak broadening analysis using Scherrer's equation showed that Fe_3C precipitates had a nanoscale size of about 13nm.

d) Microhardness measurements

Figure 5. shows the average value of microhardness of Fe-0.8wt.% graphite and Fe-1.5wt.% graphite powder particles as milled for 30h and after heat treatment at 600°C for 1h. The

microhardness value of as-received Fe powder is also included for comparison purposes. The original Fe powder particles had a microhardness value of 120Hv. As shown in Figure 5, mechanical alloying led to a drastic increase in hardness value of powder particles as a result of refinement of grain size, introduction of lattice defects and formation of Fe_3C phase. After 30h of milling time, the value of microhardness for Fe-0.8wt.% graphite powder particles was 650Hv while Fe-1.5wt.% graphite powder particles exhibited a greater value of 760Hv due to higher fraction of Fe_3C phase. After heat treatment, the microhardness values of the Fe-0.8wt.% graphite and Fe-1.5wt.% graphite powder particles decreased to 420 and 483Hv respectively. This decrease in hardness value is caused by annihilation of lattice defects as well as coarsening of Fe_3C phase during annealing process.

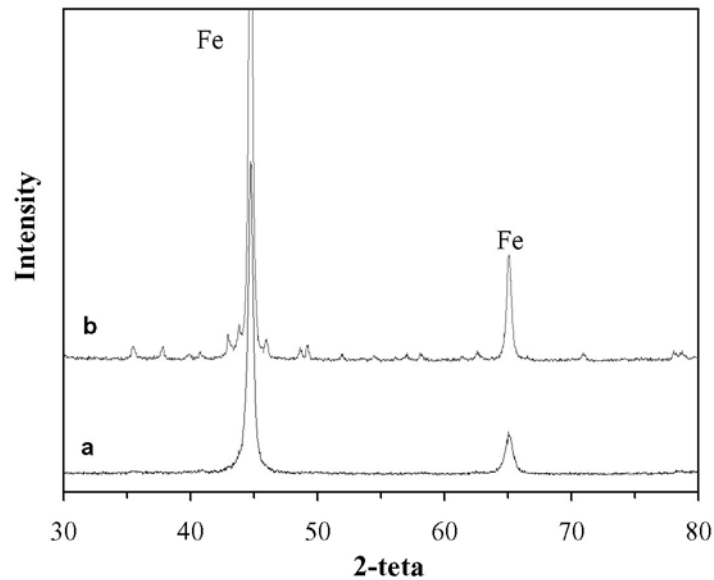


Fig. 4 .XRD traces of Fe-1.5wt.% graphite powder mixture a) as MA for 30h and b) after subsequent annealing.

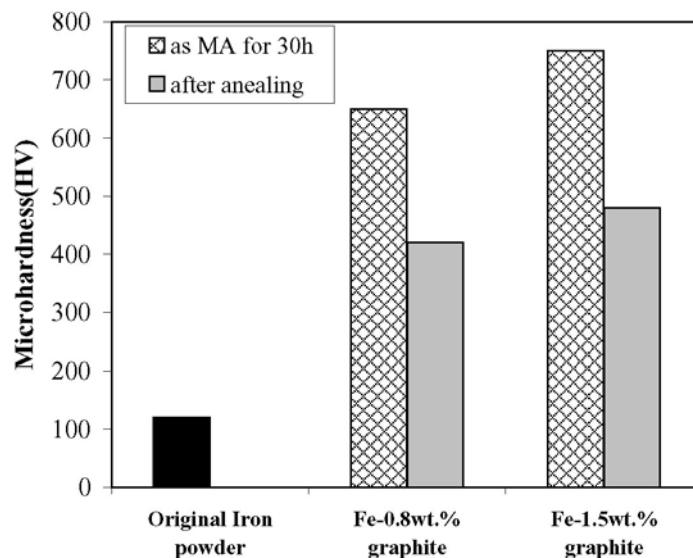


Fig. 5. Microhardness value of powder particles.

Conclusion

MA of Fe-0.8wt.% graphite and Fe-1.5wt.% graphite powder mixtures was studied. The results showed that for both compositions MA for 30h, directly led to the formation of nanoscale size Fe₃C phase without any intermediate stage (i.e. the development of an Fe-C solid solution). However, for milling times shorter than 30h, a subsequent heat treatment was needed to obtain Fe₃C phase. These results suggest that an adequate density of lattice defects is necessary to be created during MA to facilitate diffusion process and therefore the formation of Fe₃C phase. The powder particles, after 30h of milling time, had a nanocrystalline structure with a microhardness value of several hundred larger than the original Fe powder. Fe-1.5wt.% graphite powder, after 30h of MA, had a mean particle size of 9µm which was considerably smaller than 15µm observed for Fe-0.8wt.% graphite powder after the same milling time.

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