Tribosynthesis of $Fe_{3-x}Mn_xC$ Phases *via* Mechanical Alloying and Annealing

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Z. Naturforsch. **2013**, *68b*, 1180 – 1184 / DOI: 10.5560/ZNB.2013-3194
Received July 15, 2013

Powderous crystalline materials of the composition $Fe_{3-x}Mn_xC$ have been prepared by first synthesizing Fe_3C *via* mechanical alloying in a planetary mill followed by the addition of elemental manganese and arc-plasma melting or *via* the classic ceramic route in an electric furnace. The milling time for the synthesis of Fe_3C was significantly reduced through adjusting the parameters of the planetary ball mill. When the ball-to-powder ratio was lowered, significantly larger batches were possible. Sintering in a fired tubular furnace was found to be the method of choice for the aftertreatment of the nanocrystalline $Fe_{3-x}Mn_xC$ powders as exemplified by X-ray Rietveld refinements.

Key words: Cementite, Rietveld Refinement, Mixed Carbides, Tribochemistry, Planetary Mill, Manganese Steel

Introduction

Despite having been used for centuries already, steel still is and continues to be a construction material of paramount importance, in particular in the 21st century. Recent research concerning high-performance steels is focusing on the understanding of the underlying mechanisms of mechanical properties such as strain hardening, twinning-induced plasticity (TWIP) or transformation-induced plasticity (TRIP) in high-manganese steels [1 – 3]. These effects result in extraordinary material strength and formability. Materials showing such behavior are of great interest for the automotive industry as well as for general construction because they offer a possible reduction in weight and material of up to 40 weight percent [4].

As steel is not a homogeneous material, understanding why different phases are formed is of uttermost importance for the future development of "tailor-made" steels. The present study concentrates on the formation of $Fe_{3-x}Mn_xC$ phases with $0 < x < 1.5$, derived from cementite (Fe_3C), which is a steel-hardening phase. Because *manganese* is much cheaper than alternative alloying metals such as chromium, nickel, silicon, cobalt, or molybdenum, the use of manganese as an alloying metal seems promising for industrial use. A variety of these mixed carbides has already been successfully synthesized and characterized [5 – 10].

Cementite crystallizes in the orthorhombic cohenite type with space group *Pnma*, and the metal atoms are situated on the two different crystallographic sites 4*c* and 8*d* [11]. The structure of Fe_3C has been studied extensively by Wood *et al.* [12] arriving at lattice parameters of $a = 6.744$, $b = 5.090$ and $c = 4.525$ Å (Fig. 1).

The lattice parameters of the isostructural Mn_3C are $a = 6.772$, $b = 5.080$ and $c = 4.530$ Å [13]. Many of the mixed phases $Fe_{3-x}Mn_xC$, however, are yet to be studied, especially with a focus on high-manganese alloys. In fact, some of these phases are already contained in several industrial steels (*e. g.*, Hadfield or Strømhard), but their formation has only been studied empirically. For a better understanding of the aforementioned compounds, theoretical calculations on $Fe_{3-x}Mn_xC$ with $0 < x < 3$ using density-functional theory have been carried out quite recently. A possible preference of manganese occupying the 8*d* site was suggested and would be in accord with antiferromagnetic ground states found in ferromanganese carbides with high manganese contents [14]. In order to validate the theoretical calculations, it is necessary to synthesize and carefully characterize these compounds [15].

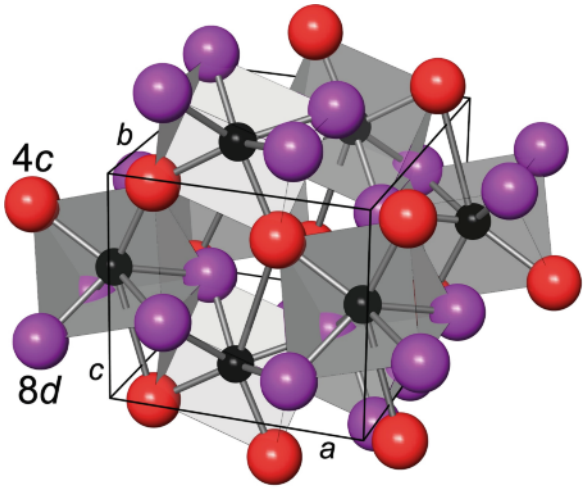

Fig. 1 (color online). View into the orthorhombic cementite crystal structure containing both corner- and edge-sharing trigonal prisms formed by the metal atoms located on Wyckoff positions 8*d* (lilac) and 4*c* (red) around the central carbon atoms (black).

Herein we report on a study of the formation of mixed carbides in the $Fe_{3-x}Mn_xC$ system by monitoring their crystallinity using X-ray Rietveld refinements. Starting with the mechanical alloying (MA) of cementite in a planetary mill, elemental manganese is added and sintered or melted using an arc-plasma in order to obtain the mixed carbides. Furthermore, the synthesis of pure Mn_3C *via* MA has been attempted.

Experimental Section

Synthesis and characterization

For the preparation of Fe_3C *via* mechanical alloying, 9.333 g iron powder (99.998 %, Alfa Aesar) and 0.667 g graphite flakes (99.8 %, Alfa Aesar) were weighed into the milling bowl of a planetary mill. Opposed to the work of Chaira *et al.* [15], the circumferential speed was strongly enlarged to 750 instead of 450 rpm in order to increase the energy input. The aftertreatment of the obtained nanocrystalline product was carried out either in a plasma arc furnace or in an electric oven.

Planetary ball mill

A planetary micro mill of the type "Pulverisette 7 premium" (Fritsch) was used. The grinding bowl ($V = 20$ mL) was filled with the respective amounts of elemental powders, and 7 – 11 milling balls were added. Subsequently, the mill was locked inside an Ar glovebox with a gas lid. The grinding bowl and the milling balls had been coated by the manufacturer with highly inert Si_3N_4 to prevent mechanical damage, wear and surface reactions. The total milling time in argon atmosphere was 40 h. The milling cycles were set to 5 min milling time at 750 rpm followed by a 30 s pause to allow the powder to cool. The milling cycles were performed with alternating rotational directions to ensure homogeneous milling. Samples for X-ray analysis were taken every 10 h of milling time in an Ar glovebox.

Plasma arc

The milled powders mixed together with elemental manganese were weighed in the corresponding stoichiometric ratio (total mass about 0.2 g). They were then pressed into pellets at a pressure of 1.2 t for 10 min. The pelletized powders were arc-melted on a water-cooled copper crucible (first electrode) under an Ar pressure of 1.2 bar using a tungsten tip as a second electrode and by applying a direct current of 10 – 50 A until homogeneous melting occurred. The argon had been purified before over silica gel, molecular sieves, and titanium sponge kept at a temperature of 950 K. Small weight losses during the melting process occurred, but the vaporization of graphite and manganese was neglegible because of the short periods of arc melting (1 – 5 s). The metallic lustrous reguli were mechanically cracked and pulverized using a mortar and a pestle for final X-ray examination.

Electric oven

The pellets were prepared as described before. They were then placed inside quartz-glass containers which were eventually evacuated and placed in the middle of a three-zone electric oven. The sintering temperatures were varied between 500 and 700 °C. Sintering time was set between 30 and 120 min. After heating, the samples were either allowed to slowly cool to room temperature or directly quenched in ice water.

Analysis

X-Ray powder methods were applied for the phase identification and determination of the lattice parameters at room temperature, using a Huber G670 Guinier powder diffractometer in transmission geometry, a Ge monochromator, Cu$K_{\alpha 1}$ radiation ($\lambda = 1.54059$ Å) and an image-plate detector. As additional measurement time for Co$K_{\alpha 1}$ radiation was rather limited, only highly crystalline samples were measured using a Stoe Stadi MP powder diffractometer in transmission geometry, a Ge monochromator, Co$K_{\alpha 1}$ radiation ($\lambda = 1.78919$ Å) and a linear position-sensitive detector (PSD).

Rietveld analyses were carried out for the powder data by full-matrix least-squares refinements implemented in

the FULLPROF program. The starting models used originated from the previously reported structures of Fe_3C, $Fe_{1.8}Mn_{1.2}C$, and $Fe_{1.2}Mn_{1.8}C$ [12, 13, 16].

Results and Discussion

The tribochemical synthesis of Fe_3C has been carried out successfully. The experimental data given in Table 1 clearly show that a milling time of 30 h with alternating milling directions is sufficient to obtain X-ray-pure Fe_3C. Additional milling did not lead to further improvement. An overview of the diffraction data and their time evolution is given in Fig. 2.

As the method of choice for aftertreatment, sintering at 600 °C with subsequent quenching leads to much better results compared to arc-plasma treatment. Probably due to the insufficient temperature control in the melt of an arc-plasma furnace, there is the occurrence of additional side phases. Sintering, however, leads to phase-pure Fe_3C with an average crystallite size of 58 nm. The Rietveld refinement of the powder-diffraction data performed in the orthorhombic cohenite type (*Pnma*) and statistically corrected according to Bevar in terms of standard deviations arrives at Fe_3C lattice parameters of $a = 6.7508(2)$, $b = 5.0890(1)$ and $c = 4.5267(1)$ Å for 30 h of milling time and $a = 6.7523(2)$, $b = 5.0900(2)$ and $c = 4.5280(2)$ Å for 40 h, respectively. The corresponding Rietveld refinements are given in Fig. 3 for both data sets.

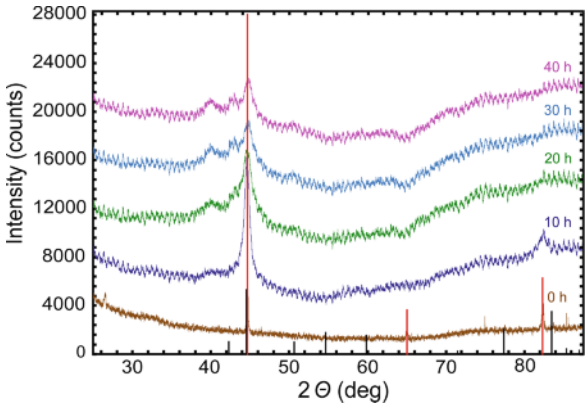

Fig. 2 (color online). Time evolution of the XRD patterns of the tribochemical synthesis of Fe_3C measured with Cu$K_{\alpha 1}$ radiation showing the reflections of the elemental powders (brown) and of the powders after 10 (dark blue), 20 (green), 30 (light blue) and 40 h (pink). The theoretical Bragg positions of graphite (black) and α-Fe (red) are also given.

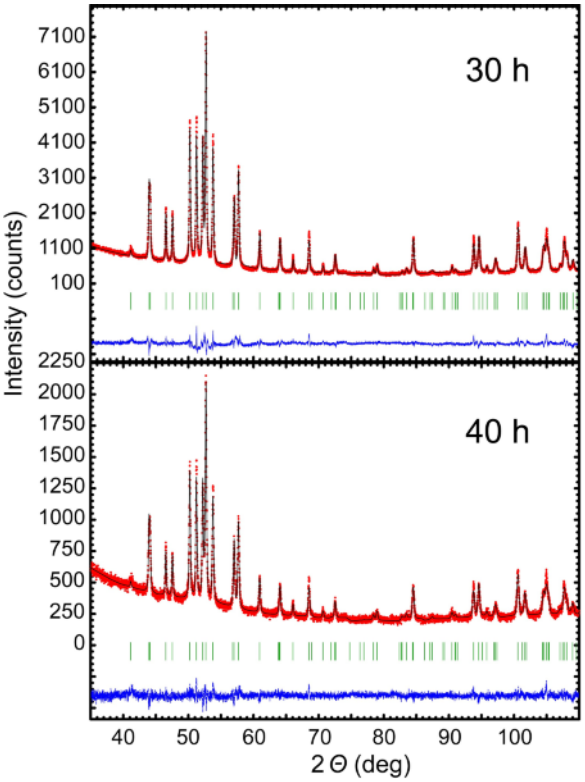

Fig. 3 (color online). Result of the Rietveld refinement of Fe_3C on the basis of Co$K_{\alpha 1}$ radiation after 30 h (top) and 40 h (bottom) of milling time and subsequent tempering at 600 °C for 1 h, with the measured (red) and refined (black) intensities, the observed Bragg peaks of the main phase (upper bars), as well as the difference-intensity curve (bottom).

We note that the refined lattice parameters are in good agreement with the literature [6]. As the milling was carried out without any anti-caking agent, surprisingly enough it is clear that no such additive is needed, at least at the laboratory scale. We also note that the milling time could be reduced by 25 % when compared to the literature simply due to modified milling parameters. As a consequence of the large energy input, the ball-to-powder ratio was reduced from 10 : 1 to 3.5 : 1.

Solid solutions

The synthesis of mixed carbides has also been carried out and the X-ray data (see also Table 1) suggest that various compositions between $Fe_{2.7}Mn_{0.3}C$ and $Fe_{1.8}Mn_{1.2}C$ were obtained. Experiments with 10 weight percent manganese treated in arc-plasma

Table 1. Lattice parameters of various cementite samples obtained after heat treatment; the imperfect crystallinity of the $Fe_{1.5}Mn_{1.5}C$ samples treated in the electric furnace did not allow for a reliable lattice parameter determination.

Mn content (weight-%)	Nominal composition	*a* (Å)	*b* (Å)	*c* (Å)
Electric furnace				
0	Fe_3C	6.745(6)	5.090(3)	4.529(3)
10	$Fe_{2.7}Mn_{0.3}C$	6.752(6)	5.085(6)	4.525(6)
20	$Fe_{2.4}Mn_{0.6}C$	6.745(6)	5.083(12)	4.525(6)
30	$Fe_{2.1}Mn_{0.9}C$	6.743(15)	5.081(6)	4.525(9)
40	$Fe_{1.8}Mn_{1.2}C$	6.740(9)	5.082(9)	4.523(9)
50	$Fe_{1.5}Mn_{1.5}C$	–	–	–
Arc plasma furnace				
0	Fe_3C	6.747(6)	5.083(3)	4.520(3)
10	$Fe_{2.7}Mn_{0.3}C$	6.748(9)	5.078(6)	4.519(6)
20	$Fe_{2.4}Mn_{0.6}C$	6.747(9)	5.055(3)	4.518(3)
30	$Fe_{2.1}Mn_{0.9}C$	6.722(9)	5.066(9)	4.519(9)
40	$Fe_{1.8}Mn_{1.2}C$	6.722(9)	5.066(9)	4.519(9)
50	$Fe_{1.5}Mn_{1.5}C$	6.763(9)	5.067(9)	4.521(9)
for comparison				
Fe_3C [12]		6.7443	5.0896	4.5248
$Fe_{2.7}Mn_{0.3}C$ [11]		6.7462	5.0598	4.5074
$Fe_{1.8}Mn_{1.2}C$ [16]		6.7573	5.0742	4.5212
Mn_3C [13]		6.772	5.080	4.530

led to a crystalline phase with lattice parameters of $a = 6.747(6)$, $b = 5.083(3)$ and $c = 4.520(3)$ Å, very close to the parameters of $Fe_{2.7}Mn_{0.3}C$. A quantitative phase analysis *via* Rietveld refinement further clarified that the crystalline phase consisted of 94 weight percent cementite phase but also 6 weight percent α-Fe, a promising result for future studies. Not too surprisingly, however, it was impossible to obtain single crystals, and the resolution of the powder XRD data is insufficient to fully determine all crystallographic details, *e. g.*, the site occupation factors of Mn and Fe. Nonetheless, all obtained lattice parameters were in the expected region and confirm the successful synthesis of the mixed carbides.

Addition of 30 weight percent or more of manganese enhanced the formation of unwanted side phases (such as α-Fe and Fe carbides) which is also not surprising at all since manganese tends to substitute iron. In order to suppress the formation of other carbide phases, more graphite was added to the powders in slightly overstoichiometric amounts with respect to the expected iron excess. The results based on arc-plasma experiments indeed corroborate the occurrence of fewer side phases. Since the temperature control during arc-plasma treatment is very difficult, however, the results were not always reproducible.

As a different approach, sintering and quenching of the mixed powders resulted in more satisfactory results in terms of crystallinity. In addition, the deposition of α-Fe did not occur as frequently as in the arc-plasma experiments.

Summary

Fe_3C was successfully synthesized in a planetary ball mill. It was possible to significantly reduce the milling time by 25 % through adjusted milling parameters. In addition, no added anti-caking agents were necessary at the laboratory scale. It was shown that sintering in an electric tubular furnace increases the crystallite sizes and leads to X-ray-pure Fe_3C.

The X-ray diffraction results for the series of mixed iron/manganese carbides are in good agreement with that of the previously reported structures of $Fe_{2.7}Mn_{0.3}C$ and $Fe_{1.8}Mn_{1.2}C$. Further research is necessary to understand the influence of stress and other mechanical effects on the lattice parameters in order to reliably calculate the constitution from the latter. It is also interesting to note that the compounds turned out to be much more stable than expected. The literature suggests the formation of other side phases (*e. g.*, α-Fe, iron oxides and manganese oxides) under these conditions even for small oxygen contaminations.

Acknowledgement

It is a pleasure to thank Sabine Schäfer for experimental assistance and Deutsche Forschungsgemeinschaft (DFG) for financial support through Sonderforschungsbereich 761 ("Steel *ab initio*").

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