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Letter

Mechanical alloying of Cr–C mixtures and low temperature synthesis of chromium carbides

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Recently, new metastable carbides were produced by crystallization of a spattered amorphous $Cr_{1-x}C_x$ alloy with a concentration range $0.27<x<0.52$ [1]. In this work we attempted to obtain metastable Cr–C alloys by mechanical alloying (MA) in order to prepare chromium carbides in powder form. The Cr–C system is known as a non-self-sustained reacted system in contrast with *e.g.* the Ti–C system, MA of which is characterized by self-sustained formation of equilibrium carbides [2]. This means that in the case of the Cr–C system the MA process can easily be controlled in order to prepare a precursor for carbide synthesis. MA was used already for preparation of amorphous or crystalline alloys containing metals and non-metal elements, which can be used as precursors for preparation of borides [3], carbide-dispersion-strengthened copper alloys [4], intermetallics [5] and other materials.

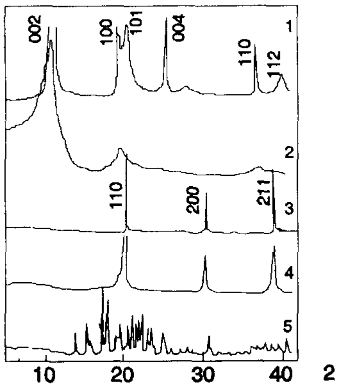

Fig. 1. X-Ray diffraction of the MA Cr–C system: 1, graphite; 2, graphite after 15 min MA; 3, Cr metal; 4, composition $Cr_{60}C_{40}$ after 5 min MA; 5, sample as in 4 after annealing at 1073 K for 3 h.

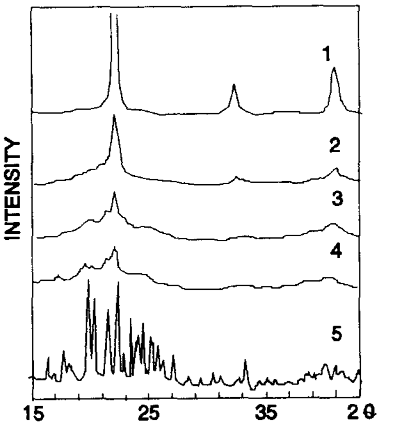

Fig. 2. X-Ray diffraction of $Cr_{60}C_{40}$ after different times of MA: 1, 5 min; 2, 10 min; 3, 15 min; 4, 40 min; 5, sample 4 annealed at 1073 K for 3 h.

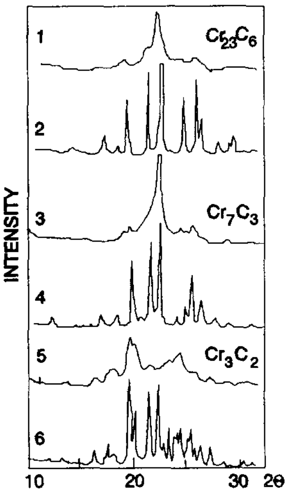

Fig. 3. X-Ray diffraction patterns after MA for 40 min (1, 3, 5) and after annealing at 1073 K for 3 h for different compositions (2, 4, 6): 1, 2, $Cr_{80}C_{20}$; 3, 4, $Cr_{70}C_{30}$; 5, 6, $Cr_{60}C_{40}$.

We have used mixtures of elemental Cr and graphite powders of different compositions: $Cr_{1-x}C_x$ ($x=0.2$, 0.3, 0.4) as starting material for MA. The mean size of the Cr particles was 150 μm and that of the graphite powder was about 100–300 μm. MA was performed using a planetary ball mill with water bearings at high energy milling mode (900 rev min^{-1}). The MA process was monitored using X-ray diffraction. Thermal transformation of the ball milled powders was carried out in a vacuum tube furnace at temperatures of 1073–1273 K. Transmission electron microscopy (TEM) and electron probe microanalysis (EPMA) were used to characterize as-milled and annealed samples.

For every composition the progress of the MA process was monitored every 5 min using X-ray diffraction. The

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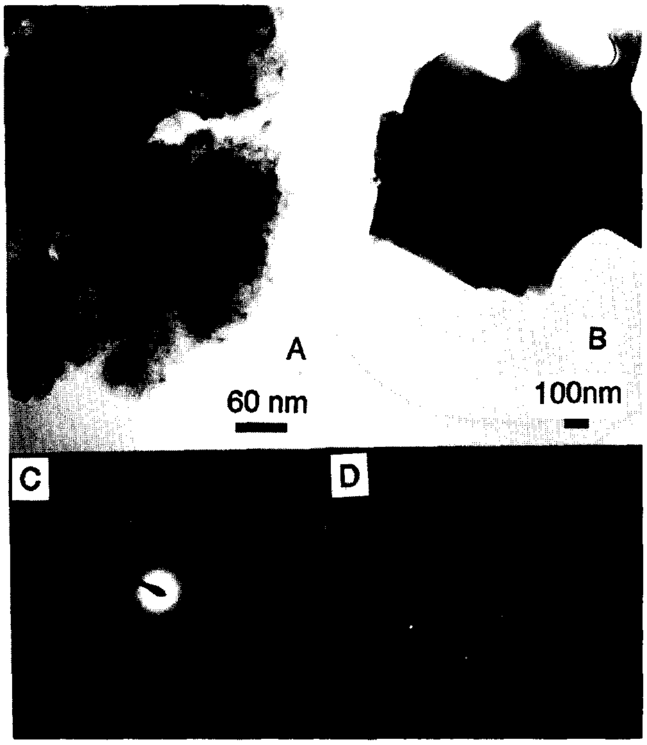

Fig. 4. TEM and specific area diffraction (SAD) patterns of $Cr_{60}C_{40}$. Mechanically alloyed $Cr_{60}C_{40}$ for 10 min: A, TEM image; C, SAD pattern. For the same sample annealed at 1073 K for 3 h: B, TEM image; D, SAD pattern.

X-ray diffraction patterns of Cr–C mixtures prior to milling clearly showed Cr and graphite reflections. In Fig. 1 Cr and graphite diffractograms are shown separately (3 and 1 respectively). After 5 min of MA of $Cr_{60}C_{40}$ the Cr reflections were broadened and graphite reflections disappeared. Milling of pure graphite as a reference experiment for 15 min resulted only in considerable broadening of (200) and (100) graphite reflections while other graphite reflections disappeared. Using a Scherer peak broadening formula, a corresponding grain size of about 9 nm was obtained for $Cr_{60}C_{40}$ mechanically alloyed for 5 min. The MA process at this stage did not result in the interaction of Cr and C. The X-ray patterns after further milling are shown in Fig. 2; after 10 min of MA weak reflections appeared as a result of carbide formation. After annealing the sample at 1073 K for 3 h the nanostructure transformed into a mixture of carbide phases according to the starting composition.

In Fig. 3 the X-ray patterns taken from mixtures of different compositions $Cr_{78.5}C_{21.5}$, $Cr_{70}C_{30}$ and $Cr_{60}C_{40}$ are presented both after milling for 40 min and after annealing at 1073 K for 3 h. For the annealed samples with the starting compositions $Cr_{78.5}C_{21.5}$ and $Cr_{60}C_{40}$ the carbides were identified as $Cr_{23}C_6$ and Cr_3C_2 respectively with the corresponding lattice parameters (Fig. 3, patterns 2 and 6). The phase composition of the annealed sample with the starting composition $Cr_{70}C_{30}$ was not identified as a single phase (Fig. 3, pattern 6).

In Fig. 4 TEM images are shown for MA $Cr_{60}C_{40}$ and for the same sample after annealing. The chemical composition before and after annealing was determined by EPMA and did not change.

We conclude that the combination of MA and thermal treatment can produce a fine powder of chromium carbides of the desired composition.

References

1 E. Bouzy, G. le Caër and E. Bouer-Grosse, *Mater. Sci. Eng., A133* (1991) 640–643.
2 P. Yu. Butiagin, V. Yu. Davydkin and L. I. Trusov, *Dokl. Akad. Nauk SSSR, 308* (1989) 405–409.
3 A. Galka, A. P. Radlinsky and R. Shanks, *Mater. Sci. Eng., A133* (1991) 555–559.
4 T. Takahashi and Y. Hashimoto, *Mater. Sci. Forum, 88–90* (1992) 175–182.
5 M. A. Morris, *J. Mater. Sci., 26* (1991) 1157–1164.