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SYNTHESIS OF NANOCRYSTALLINE TITANIUM CARBIDE BY SPARK EROSION

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Introduction

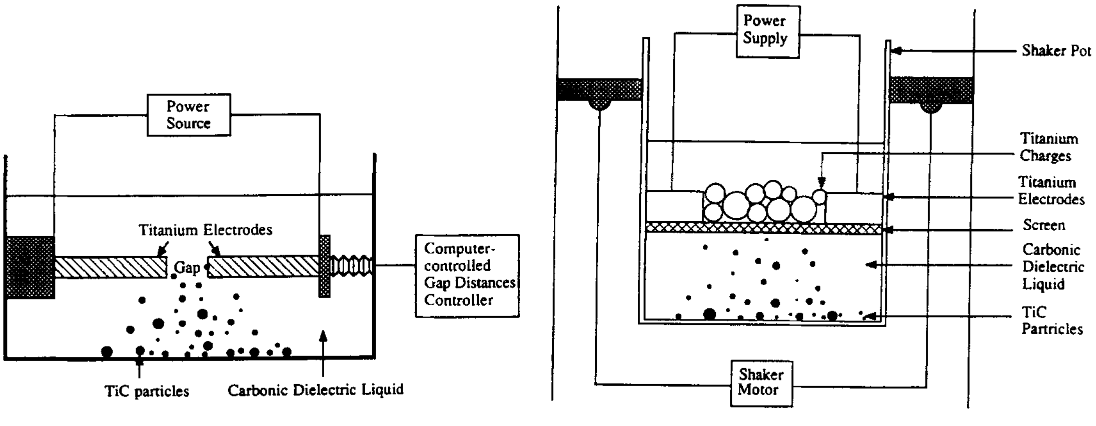
Interest in nanocrystalline ceramic powders is due to their attractive processing and mechanical properties. The disadvantages of conventional ceramics, such as large internal flaws, negligible ductility, high-temperature processing, can possibly be eliminated or minimized by starting with finegrained powders. A previous study on the sinterability of nanocrystalline ceramic powders showed that high densities can be achieved at lower temperatures, both with and without the application of pressure [1]. In addition, it is remarkable that superplastic behavior has been reported in nanocrystalline ceramics at room temperature [2]. One of the novel methods for preparing nanocrystalline ceramic powders is reactive spark erosion [3-5]. An important feature of this method is the capability to synthesize new materials by reacting the eroded particles with the dielectric liquid. This technique utilizes two metal or conducting electrodes sparked in a suitable dielectric liquid that reacts with the particles to produce the desired ceramic powders. The high temperature provided by the spark results in vaporization of the electrodes and the surrounding dielectric liquid; the reaction products formed between the various vapor species are quenched in the liquid and produce spherical particles. The aim of the present note is to report on the titanium carbide particle formation in a carbonic dielectric liquid (pentane) with titanium electrodes and charges. The nanocrystalline titanium carbide was produced in a wide range of particle size distribution and in the form of single phase spheres.

Experimental Procedures

A schematic illustration of the spark erosion system is shown in Figure 1(a). This system can be used to produce research quantities of nanocrystalline TiC powders.This system was developed by Berkowitz and Walter [4]. Electrodes of titanium rods submerged in a carbonic dielectric liquid (pentane) were used. In order to produce large quantities of ultrafine TiC powders, a shaker pot set-up was used, which is shown in Figure 1(b). Experiments were conducted using two different sizes of spherical titanium charge (1.0 and 1.5 cm in diameter) and an operating voltage of about 250V with a current ranging from 100 to 150A. In order to obtain short capacitor charging time, a small capacitor (about 1.3 μF) was used in this study. The X-ray diffraction was performed with an operating voltage of 50 kV and current of 32.5 mA, and Co Kα radiation was used. A Cambridge Stereoscan 360 scanning electron microscope (20 kV accelerating voltage) was used to examine the general size distribution. The specimen for transmission electron microscopy was made from a drop of the mixture of the powders and toluene on a copper grid with an amorphous carbon film and was examined in a Philips CM30 electron microscope at an accelerating voltage of 300 kV. The as-produced particles were mounted in epoxy and then polished down and the cross section was examined by both secondary electrons and back scattered electrons in the scanning electron microscope.

Results and Discussion

In order to determine the types of reaction products after spark erosion in the shaker pot set-up, X-ray diffraction analysis was performed. The result shown in Figure 2 confirms that the face centered cubic TiC phase was formed from the sublimated or melted Ti reacted with pentane. Furthermore, the lattice parameter calculated from the x-ray peaks of TiC was 0.4315 μm. The lattice parameter of TiC varies within the compositional range of TiC_x ($0.53<x<0.95$) [5], and the present result indicates that the C/Ti ratio (atomic) is



(a) (b)

Fig. 1. (a) Sketch of basic spark erosion experimental set-up, and (b) sketch of high yield shaker-pot spark erosion experimental set-up.

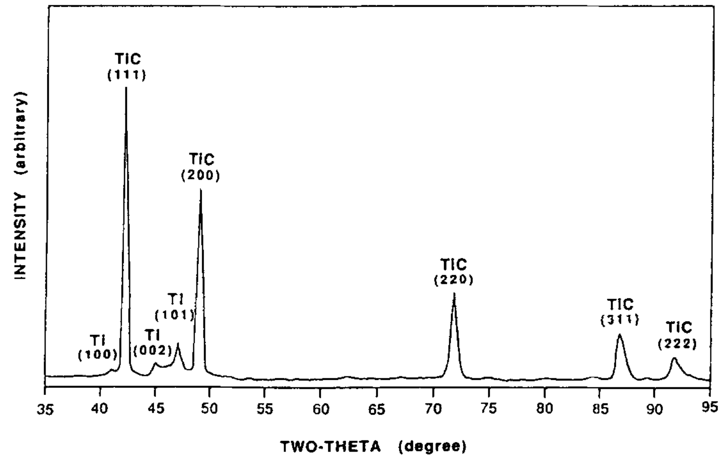


Fig. 2. X-ray diffraction pattern of TiC particles synthesized by spark erosion (Co Kα radiation)

about 0.6. However, Ti peaks were also observed in this spectrum. One possible explanation is that Ti has not fully reacted with pentane, indicating that there exists Ti inside or on the surface of TiC particles. Another possibility is that some unmelted irregular-shaped Ti fragments drop into dielectric liquid due to the milling effect of the charges. The present result favors the former hypothesis and confirms Ayers and Moore's observations [5]. They suggested that most of the powders were single phase TiC with the remainder containing TiC plus either Ti or graphite when Ti and graphite electrodes are used. Scanning and transmission electron microscopic analysis (Figures 3 and 4(a)) revealed that two size ranges were obtained, one in a range of 5 to 50 nm and the other one in a range of 5 to 20 μm. This bimodal distribution of particle

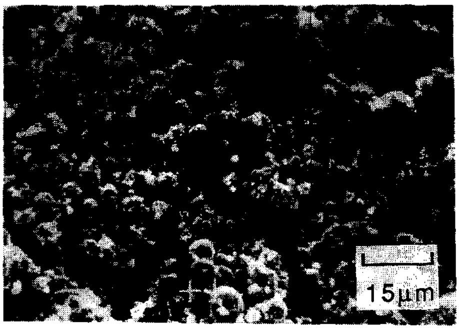


Fig. 3. Scanning electron micrograph showing bimodal particle size distribution.

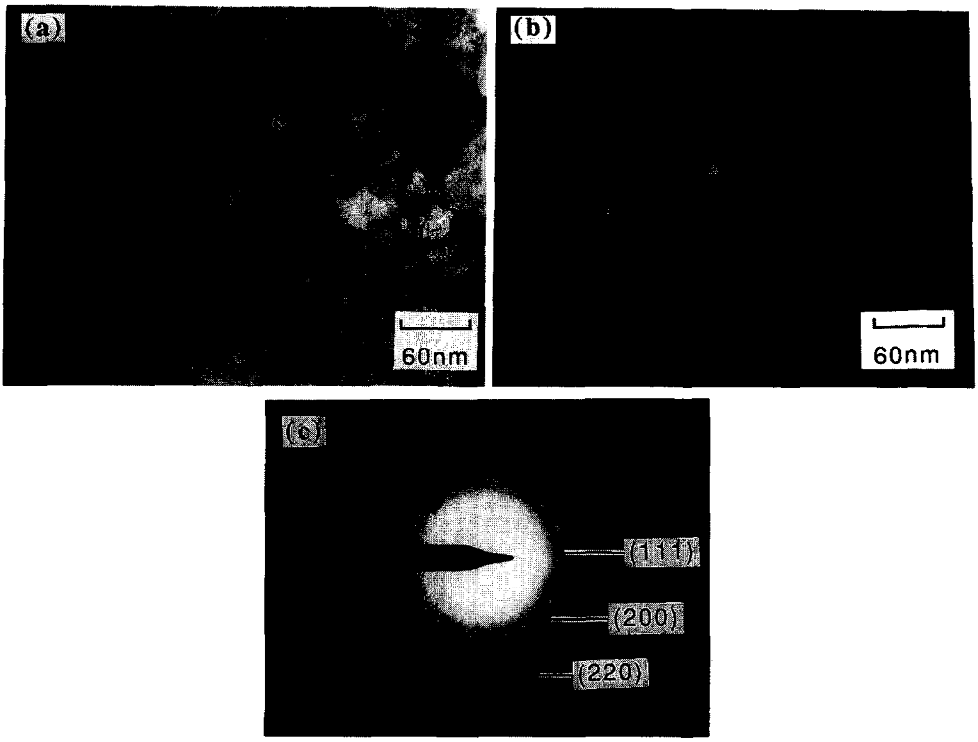


Fig. 4. Transmission electron micrograph for nanocrystalline TiC particles showing some facets, (a) bright field;(b) dark field, and (c) corresponding selected area diffraction pattern.

sizes in the spark erosion process has been found by Svedberg in 1924 [7], and is consistent with other works [4,8]. It is believed that the nanocrystalline particles were formed as a result of rapid condensation of vaporized reacted TiC, whereas the larger particles (5-15 μm)were produced by the solidification of molten TiC droplets. The selected area diffraction pattern shown in Figure 4(c) revealed that there is only cubic TiC phase in the smaller size particles indicating that those particles are fully reacted. .The bright field image shows some facets among the spherical particles due to the surface energy minimization, and the fact that those small particles are monocrystalline is confirmed by the dark field image in which only several (220) diffraction spots were collected by the objective aperture and reflected the corresponding particles in the image (Figures 4(b)). The reason is that the ultra-rapid spark energy deposition produces sublimation of the particle followed by a rapid solidification via heat conduction into the dielectric liquid, which promotes the tendency for this single crystal structure. The scanning electron micrograph in Figure 5(a) of the polished or fractured TiC particle cross section shows the homogeneity of the larger size particle; this is more obviously revealed in the backscattered electron (BSE) image presented in Figure 5(b). As seen in the picture, there is no second phase inside the particle, even if the size is as large as about 20 μm. This might imply that the particles formed in the reaction are mostly single-phased, Ti-rich TiC, and the weak Ti peaks in the X-ray spectrum come from some unreacted Ti on the surface of a small portion of TiC particles which were not observed here.

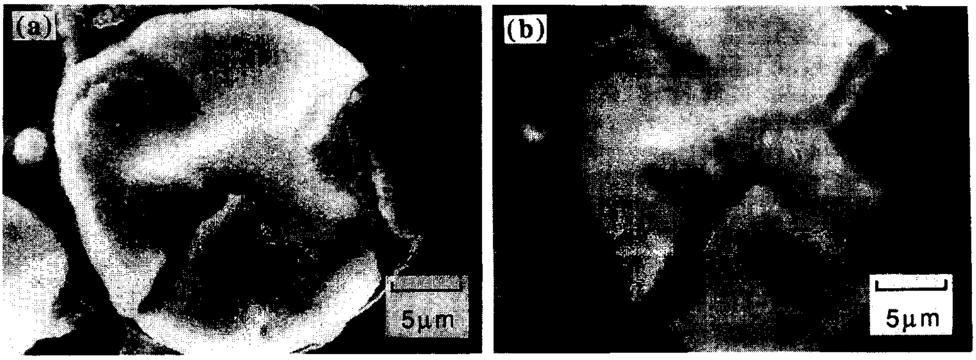


Fig. 5. (a) Scanning electron micrograph of polished or fractured TiC particle cross section, and (b) corresponding backscattering electron image.

Acknowledgements

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References

1. H. Hahn, J. Logas, and R. S. Averback, J. Mater. Res. 5(3), 609 (1990).
2. J. Karch, R. Birringer, and H. Gleiter, Nature 330, 556 (1987).
3. A. Kumar and R. Roy, J. Mater. Res. 3(6), 1373 (1988).
4. A. E. Berkowitz and J. L. Walter, J. Mater. Res. 2(2), 277 (1987).
5. E. K. Storms, The Refractory Carbides, p. 1, Academic Press, New York (1967).
6. J. D. Ayers and K. Moore, Metall. Trans. A 15, 1117 (1984).
7. T. Svedberg, Colloid Chemistry (Chemical Catalog, New York, 1924), Part I.
8. M. A. Lunina and Yu. A. Novozhilov, Colloid J. USSR 31, 370 (1969).