Available online at www.sciencedirect.com
ScienceDirect
Journal of the European Ceramic Society 27 (2007) 715–718
www.elsevier.com/locate/jeurceramsoc

Synthesis of nano-titanium diboride powders by carbothermal reduction

Shin H. Kang, Deug J. Kim *

Department of Materials Science and Engineering, Sungkyunkwan University, Suwon 440-746, Republic of Korea

Available online 16 May 2006

Abstract

The nano-sized titanium diboride particles were synthesized by carbothermal reduction process. In this study, carbothermal reduction process was used by controlling reaction rate and duration time. TiO_2, B_2O_3 and carbon resin were used as starting materials with a molar composition; TiO_2:B_2O_3:C = 1:2:5. The mixture was placed in a graphite crucible and pushed into a heating zone maintained at 1500 °C and Ar was flown for a period of 20 min. After reaction, the crucible was pulled out from the heating zone to cooling zone of the furnace for the rapid cooling. The average particle size of the agglomerated product was found to be ~500 nm, which was composed with small primary particles of <100 nm in size. After milling, the large agglomerate was reduced to primary particles.

Keywords: Carbothermal reduction; Powders-solid state reaction; Grain growth; TiO_2

1. Introduction

Titanium diboride (TiB_2) has attracted great interest in excellent mechanical properties, chemical resistance and good thermal and electrical conductivities. So it is widely applied as cutting tool composites, wear resistant parts, metal melting crucibles and electrode materials.[1–4] TiB_2 has a HCP structure with lattice parameters of $a = 3.03034$, $c = 3.22953$ and $c/a = 1.066$.[5,6] Several methods have been utilized in the synthesis of TiB_2 materials. A number of processes exist for synthesizing TiB_2 powder such as direction reaction of Ti and B,[7] metal-thermal reduction,[8] arc-plasma method[9,10] and gas-phase combustion (flame) method.[11] Normally, TiB_2 powder is commercially produced by reduction of titanium oxide with either boron oxide and carbon or an alkali metal and boron oxide.[15–17] Among above mentioned processing techniques, the carbothermal reduction process is commercially used by far the cheapest because of inexpensive raw materials and simple process. Also for each mole of TiB_2 produced, the process generates CO gas which will release energy when burnt with oxygen.

Generally, carbothermal reduction process has a strong exothermic reaction and requires long reaction periods, during which the grain growth of TiB_2 particles and bonding of the individual particulate was occurred.[12–15,18] The present study describes the production of ultrafine sized TiB_2 particles by carbothermal reduction which was used by controlling reaction speed and time, using the mixtures prepared from TiO_2, B_2O_3 and carbon.

2. Experimental

Fig. 1 shows the TiO_2 particles (P25, Degussa Co., Germany) used as a titanium source. The average size and specific surface area of the TiO_2 powder was 20–30 nm and $50 \pm 15\ m^2\ g^{-1}$, respectively. TiO_2, B_2O_3 (>99.9%, High Purity Chemicals, Japan) and carbon resin (Kangnam Chemical, Korea) were mixed at a molar composition ratios of TiO_2:B_2O_3:C = 1:2:5. These powders were mixed using planetary ball mill for 2 h in engineering plastic jar with acetone. After milling, the slurry was dried in a rotary evaporator at 70 °C and granulated using 100-mesh sieve. The mixture was fired at 500 °C for 60 min in an argon atmosphere for burn out of resin. The mixture was placed in a graphite crucible and pushed into heating zone maintained at 1500 °C and Ar was flown. After reaction, the product was pulled out from the heating zone to cooling zone of the furnace for the rapid cooling. The temperature of cooling zone was maintained at 150 °C when the reaction temperature was 1500 °C and the moving rate of the crucible to heating or cooling zone was approximately 2 min.

After synthesis, the products was milled by planetary mill for a period of 12 h in an engineering plastic jar with methanol to

* Corresponding author. Tel.: +82 31 290 7394; fax: +82 31 290 7410.
E-mail address: kimdj@skku.ac.kr (D.J. Kim).

0955-2219/$ – see front matter © 2006 Elsevier Ltd. All rights reserved.
doi:10.1016/j.jeurceramsoc.2006.04.053

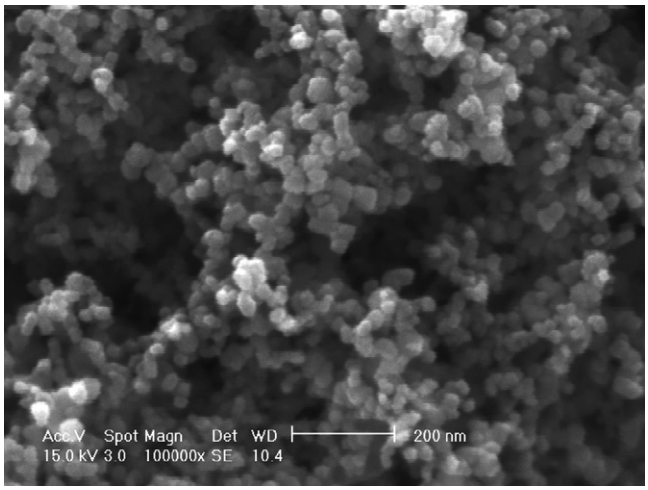

Fig. 1. SEM image of the TiO_2 particles.

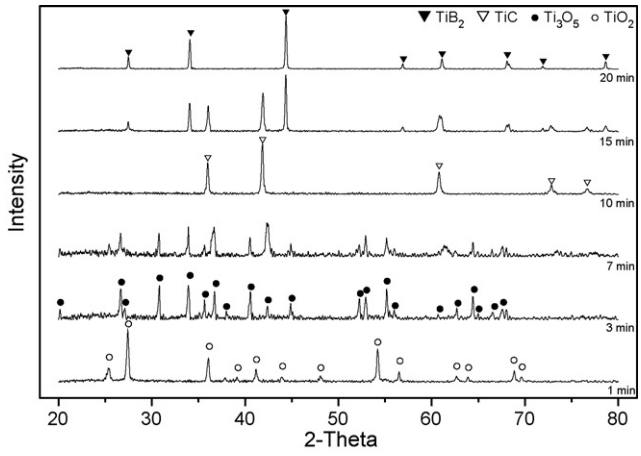

Fig. 2. XRD patterns of the products formed by carbothermal reduction with rapid heating and cooling at 1500 °C for various time.

crush of the agglomerated particles and to remove the unreacted boron oxides.[13]

X-ray diffraction (XRD, Regaku) was performed to identify the phase of product particles. The average particle size was measured by laser particle size analyzer (PSD, Mastersizer Microplus, Malvern Instrument Ltd.) and morphology was observed by environmental scanning electron microscopy (ESEM, XL30, Philps). The structure of the particles was determined by analyzing the high-resolution transmission electron microscopy (HRTEM, JEM-3011, JEOL) and X-ray photoelectron spectroscopy spectrum (XPS, ESCA2000, VG Microtech Ltd.). Oxygen and carbon contents of the products were analyzed by infrared detection in a NO and CS determinator (NO900 and CS2000, Eltra Gmbh.), respectively.

3. Results and discussion

In the carbothermal synthesis of TiB_2 from a mixture of TiO_2, B_2O_3 and carbon, solid–solid reactions are involved. TiC was rapidly formed by the reaction of TiO_2 and carbon, which then was changed to TiB_2 by the reaction with B_2O_3 and carbon.[13–15,19,20]

$$TiO_2(s) + B_2O_3(s) + 5C(s) \rightarrow TiB_2(s) + 5CO(g) \quad (1)$$

The overall reaction of carbothermal reduction of TiO_2 to TiB_2 proceeded as described by the reaction shown as Eq. (1), which consists of the following Eqs. (2) and (3), respectively:

$$TiO_2(s) + 3C(s) \rightarrow TiC(s) + 2CO(g) \quad (2)$$

$$TiC(s) + B_2O_3(l) + 2C(s) \rightarrow TiB_2(s) + 3CO(g) \quad (3)$$

Fig. 2 shows the XRD patterns of the product particles reacted from the mixture by carbothermal reduction with rapid heating and cooling at 1500 °C for various time under flowing argon atmosphere. In the figure, Ti_3O_5 peaks were observed with subsequent disappearance of TiO_2 peaks, after firing for 3 min. And there after, Ti_3O_5 peaks rapidly disappeared and those due to TiC peaks emerged until 10 min, after the beginning of the firing. The TiB_2 peaks were gradually appeared at temperature of 1500 °C for 15 min. The phases in the powder produced at 1500 °C for 15 min were TiB_2 and TiC as determined by XRD technique. Finally, the formation of TiB_2 was complete at 1500 °C for 20 min under flowing argon atmosphere. The

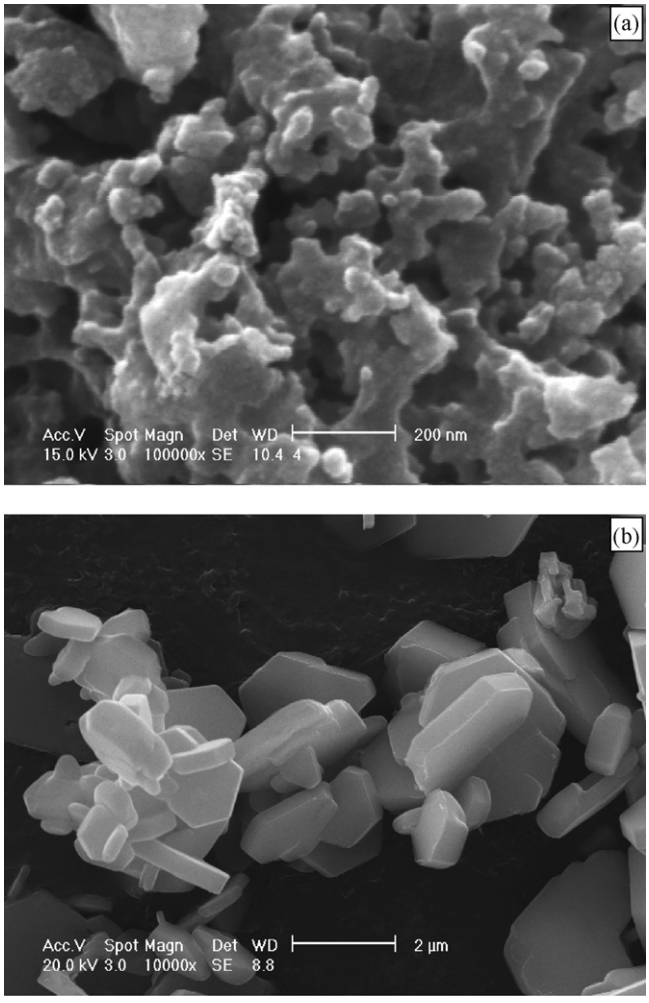

Fig. 3. ESEM image of the product formed by carbothermal reduction with rapid cooling (a) and without rapid cooling (b) at 1500 °C for 20 min.

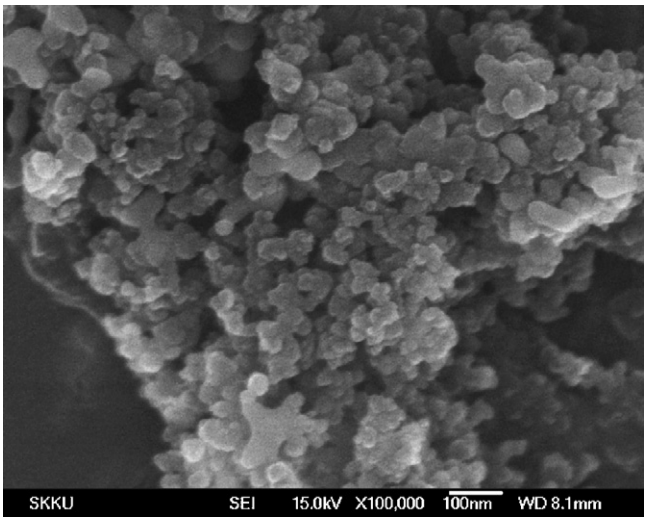

Fig. 4. Morphology of the synthesized TiB_2 particles formed by carbothermal reduction with rapid heating and cooling at 1500 °C for 20 min after milling for 12 h.

present result shows that the carbothermal reduction of TiO_2 to TiB_2 proceeded through TiC as stated in Eqs. (2) and (3).

Fig. 3 shows the morphology of the synthesized TiB_2 particles formed by carbothermal reduction with rapid cooling (a) and without rapid cooling (b) at 1500 °C for 20 min under flowing argon atmosphere. The rate of heating and cooling was 10 °C/min in the carbothermal reduction without rapid cooling. In the rapid cooling reduction, the average size of the agglomerated product was found to be 500 nm. The agglomerates were composed of small primary particles ~100 nm in size. However, it was found that formation of TiB_2 by carbothermal reduction without rapid cooling had a hexagonal platelet morphology with layer parallel to the (0 0 1) basal plane. These microstructure revealed that TiB_2 crystals are likely to grow by condensation of the vapor phase. It is well known that in some crystals deposited from the vapor phase, thin plates are often formed, and it is probable that these are separated by faulted layer.[21] The particles had grown ~2 μm in diameter. Grain growth occurred mainly along the basal plane direction.

Fig. 4 shows the morphology of the product particles after planetary milling for a period of 12 h which formed by carbothermal reduction with rapid heating and cooling at 1500 °C for 20 min under flowing argon atmosphere, the large

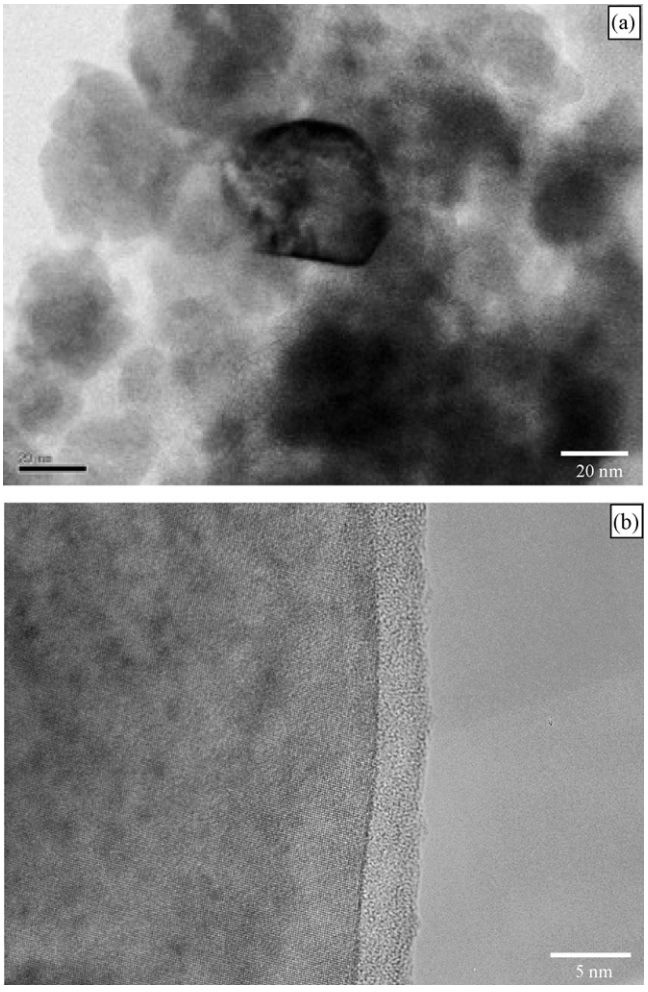

Fig. 5. TEM micrograph of the synthesized TiB_2 particles formed by carbothermal reduction with rapid heating and cooling at 1500 °C for 20 min.

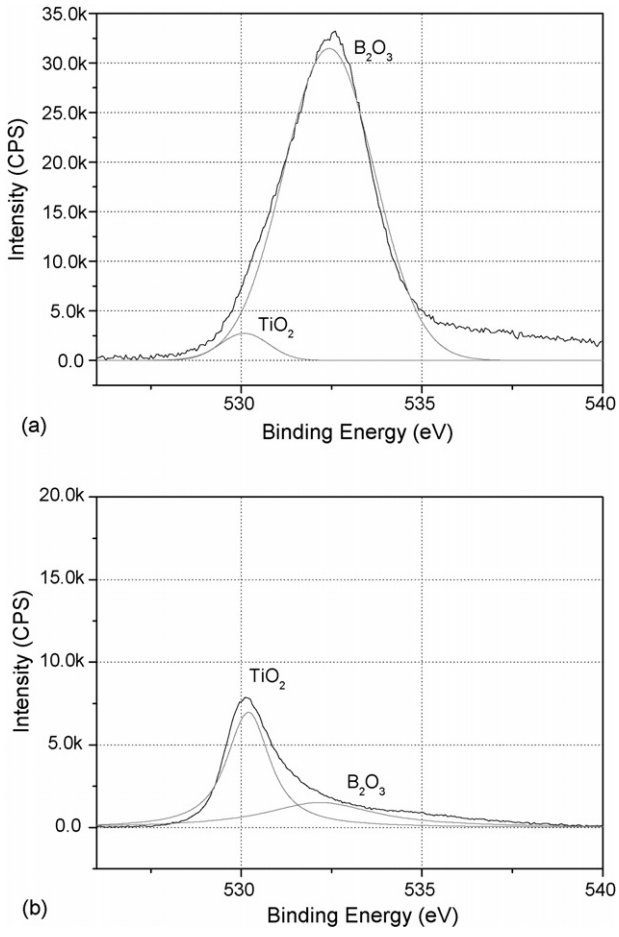

Fig. 6. XPS spectra of the synthesized TiB_2 particles formed by carbothermal reduction with rapid heating and cooling at 1500 °C for 20 min (a) and milling with methanol for 12 h (b).

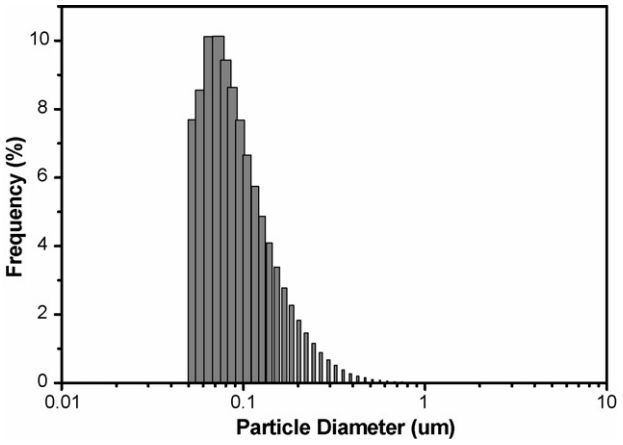

Fig. 7. Particle size distribution of the synthesized TiB_2 particles formed by carbothermal reduction with rapid heating and cooling at 1500 °C for 20 min after milling for 12 h.

agglomerate was reduced to fine particles with dimension of 80 nm.

Fig. 5 shows the TEM micrograph of synthesized TiB_2 particles formed carbothermal reduction with a rapid heating and cooling at 1500 °C for 20 min. From HRTEM image (Fig. 5(b)), it appears that the synthesized TiB_2 particles were covered with oxide amorphous layer. The amorphous layer of synthesized TiB_2 particles was determined by XPS. Fig. 6 shows the XPS spectra for the TiB_2 particles. From the O 1s spectra of the TiB_2 particles in Fig. 6(a), it can be seen that the synthesized TiB_2 particles gives two peaks, which are assigned to the TiO_2 and B_2O_3 species at surface. However, after planetary milling with methanol for 12 h, B_2O_3 peak was almost disappeared as shown in Fig. 6(b).

The average particle size of the synthesized TiB_2 particles formed by carbothermal reduction with rapid heating and cooling at 1500 °C for 20 min was 80 nm which was measured by PSD (Fig. 7). And the residual carbon and oxide content in the product were 10.3% and 7.0%, respectively.

4. Conclusions

Nano TiB_2 powders were synthesized successfully by carbothermal reduction with rapid heating and cooling from the mixture with TiO_2, B_2O_3 and carbon resin. The carbothermal reduction of TiO_2 to TiB_2 proceeded two step through TiC. When the mixture was reacted at 1500 °C for 20 min under Ar-atmosphere conditions with rapid heating and cooling, ultra fine TiB_2 particles were completely synthesized. The large agglomerated TiB_2 particles were reduced to fine particles by planetary milling for 12 h. The average particle size of the synthesized TiB_2 particles was found to be 80 nm.

Acknowledgement

The authors gratefully acknowledge the financial support from the Korean Ministry of Science and Technology through the "National R&D Project for Nano Science and Technology".

References

1. Tennery, V. J., Finch, C. B., Yust, C. S. and Clark, G. W., *Structure-Property Correlations for TiB_2-Based Ceramics Densified Using Active Liquid Metals, Science of Hard Materials*, ed. R. K. Viswanadham, D. J. Rowcliffe and J. Gurland. Plenum Press, New York, 1983, pp. 891–909.
2. Ferber, M. K., Becher, P. F. and Finch, C. B., Effect of microstructure on the properties of TiB_2 ceramics. *J. Am. Ceram. Soc.*, 1983, **66**(1), C-1–C-4.
3. Morz, C. and Titanium, D., *Am. Ceram. Soc. Bull.*, 1995, **74**(6), 158–159.
4. Martin, C., Cales, B., Viver, P. and Mathieu, P., Electrical discharge machinable ceramic composites. *Mater. Sci. Eng. A*, 1989, **109**, 351–356.
5. Samsonov, G. V., Hagenmuller, P. and Lundstrom, T., *Boron and Refractory Borides, The Nature of the Chemical Bond in Borides*, ed. V. I. Matkovich. Springer-Verlag, New York, 1977, 19–30.
6. Holleck, H. L., Leiste, H. and Schneider, W., *High Tech Ceramics*, ed. P. Incenzini. Elsevier Science Publishers, Amsterdam, 1987, p. 2609.
7. Neronov, V. A., Korchagin, M. A., Aleksandrov, V. V. and Gusenko, S. N., Investigation of the interaction between boron and titanium. *J. Less-common Met.*, 1981, **82**, 125–129.
8. Walker, J. K., Synthesis of TiB_2 by the borothermic/carbothermic reduction of TiO_2 with B_4C. *Adv. Ceram. Mater.*, 1988, **3**(6), 601–604.
9. Axelbaum, L., A flame process for synthesis of unagglomerated, low oxygen nano-particles: application to Ti and TiB_2. *Metal. R. Mater. Trans. B*, 1997, **28**, 1199–1211.
10. Baumgartner, H. R. and Steiger, R. A., Sintering and properties of titanium diboride made from powder synthesized in a plasma-arc heater. *J. Am. Ceram. Soc.*, 1984, **67**(3), 207–212.
11. Butes, S. E., Synthesis of titanium boride(TiB)(2) nanocrystallites by solution-phase processing. *J. Mater. Res.*, 1995, **10**(10), 2599–2612.
12. Schwartzkopf, P. and Kieffer, R., *Refractory Hard Metals: Borides, Carbides, Nitrides and Silicides*. Macmillan, New York, 1953, p. 447.
13. Saito, T., Fukuda, T., Maeda, H., Kusakabe, K. and Morooka, S., Synthesis of ultrafine titanium diboride particles by rapid carbothermal reduction in a particulate transport reactor. *J. Mater. Sci.*, 1997, **32**(15), 3933–3938.
14. Welham, N. J., Formation of nanometric TiB_2 from TiO_2. *J. Am. Ceram. Soc.*, 2000, **83**(5), 1290–1292.
15. Weimer, A. W., Moore, W. G., Roach, R. P., Hitt, J. E., Dixit, R. S. and Pratsinis, S. E., Kinetics of carbothermal reduction synthesis of boron-carbide. *J. Am. Ceram. Soc.*, 1992, **75**(9), 2509–2514.
16. Stanley, D. R., Birchall, J. D., Hyland, J. N. K., Thomas, L. and Hodgetts, K., Carbothermal synthesis of binary (MX) and ternary (M^1, M^2X) carbides, nitrides and borides from polymeric precursors. *J. Mater. Chem.*, 1992, **2**, 149–156.
17. Maeda, H., Yoshikawa, T., Kusakabe, K. and Morooka, S., Synthesis of ultrafine NbB_2 powder by rapid carbothermal reduction in a vertical tubular reactor. *J. Alloys Compd.*, 1994, **215**(1/2), 127–134.
18. Licko, T., Figusch, V. and Puchyova, J., Synthesis of silicon nitride by carbothermal reduction and nitriding of silica: control of kinetics and morphology. *J. Eur. Ceram. Soc.*, 1992, **9**(3), 219–230.
19. *JANAF Thermochemical Tables* (*3rd ed.*). American Chemical Society/American Institute for Physics/National Bureau of Standards, 1986.
20. Turkdogan, E. T., *Physical Chemistry of High Temperature Technology*. Academic Press, New York, 1980, pp. 5–26.
21. William, H. R. and Raynor, G. V., *The Structure of Metal and Alloys*. The Institute of Metals, London, 1972, pp. 325–329.