Journal of Alloys and Compounds 500 (2010) 220–223

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: www.elsevier.com/locate/jallcom

Mechanochemical synthesis of nano-structured TiC from TiO_2 powders

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ARTICLE INFO

Article history:
Received 11 January 2010
Received in revised form 25 March 2010
Accepted 1 April 2010
Available online 9 April 2010

Keywords:
TiC
Nanomaterials
Ceramics
Characterization methods

ABSTRACT

Nano-structured TiC was successfully synthesized from mixtures of TiO_2 and graphite through high-energy mechanical milling and subsequent heat treatment at a temperature that was considerably lower than that used in conventional carbothermal reduction synthesis of TiC. TiO_2 powders mixed with graphite were milled in a planetary ball mill for 30–90 h. The milled mixtures were then heat treated at 1200 °C and 1300 °C for 60 min. The as-milled and heat treated powders were characterized using SEM-EDAX, DTA, and XRD techniques. As revealed in SEM, agglomeration was found to be more pronounced after 30 h milling. Even though the formation of TiC was not detected in as-milled powders milled for durations between 30 h and 90 h, TiC appeared in the powder mass after heat treatment as revealed by the XRD patterns. The crystallite size of TiC as a function of milling time was estimated from the XRD data using Scherrer equation and it was found to be increased with increasing milling time after heat treatment.

1. Introduction

Titanium carbide is widely used in the fields of wear resistant tools, grinding wheels and aerospace materials due to its extremely high melting temperature, high hardness, high chemical resistance to oxidizing atmosphere, and good electrical conductivity. The bulk production of materials containing TiC as a component has been made possible by the extensive application of TiC powder consolidation using powder metallurgy techniques [1,2]. TiC can be synthesized by direct chemical reaction between Ti and carbon under vacuum at high temperature. This method, however, is rather expensive because of the high cost of elemental Ti and because it is an energy intensive process [3].

TiC is commercially produced by the carbothermal reduction of TiO_2 using carbon black as shown below [4]:

$$TiO_2(s) + 3C(s) = TiC(s) + 2CO(g) \tag{1}$$

The synthesis of TiC by means of carbothermal reduction of TiO_2, however, requires high temperature (1700–2100 °C) and a long reaction time (10–24 h). Since the reactants (TiO_2 and carbon) both react in solid states, the reaction rate is rather slow [5]. Nano-structured TiC was synthesized by methods such as liquid-magnesium reduction of vaporized mixture of $TiCl_4$ and CCl_4 solution. The corresponding reaction takes place as follows [1]:

$$TiCl_4(g) + CCl_4(g) + 4Mg(g) = TiC(s) + 4MgCl_2(l) \tag{2}$$

Thermal plasma has also been used for the synthesis of TiC using Ti and methane as starting materials [4]:

$$Ti(s) + CH_4(g) = TiC(s) + 2H_2(g) \tag{3}$$

Many reports are available on the formation of TiC by mechanical milling from Ti and C as the starting materials [6–10]. Even though titanium is the ninth most abundant element in the earth's crust, the high cost of production of this element is the major constraint for its wider applications. Titanium is produced by the Kroll process which needs high temperature and method, involving complicated multistep operations and high-energy consumption [11].

Very few researchers pointed to synthesis of nano-structured titanium carbide from TiO_2 powders. Setoudeh et al. [12] studied the reduction of anatase and rutile. Mixtures of TiO_2 and graphite were prepared in accordance with the stoichiometry given by reaction (1) (68% TiO_2 and 32% C). Seven grams of each mixture were milled under vacuum for 50 h in a tumbling ball mill. The mill was loaded with five 25.4 mm diameter stainless steel balls giving a very high ball to powder mass ratio of 43:1. After milling, samples were heated to 1400 °C in an alumina crucible at 20 °C/min under flowing argon (100 ml/min) atmosphere when the reduction and synthesis of TiC occurred. Ren et al. [13] also studied similar systems towards the synthesis of TiC. They used mixtures of pure TiO_2 and graphite with carbon-to-titanium dioxide molar ratios of 3: 1 and 4:1 and the high-energy milling was conducted using a modified Szegvari attritor. A milling speed of 600 rpm and BPR of 60:1 were employed. Application of ultra high BPR still poses as the major limitation towards the synthesis of TiC using mechanochemical route because the productivity of TiC decreases with higher BPR.

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doi:10.1016/j.jallcom.2010.04.007

It was concluded by the researchers that the reaction tendency between TiO_2 and carbon can be greatly enhanced by mechanical activation through high-energy ball milling. However, the conditions employed by the above researchers are still too energy intensive. In an attempt to make this synthesis possible at lower BPR (10:1) and lower milling speed (400 rpm), the present work was undertaken. TiO_2 is a cheap and abundant material [14]. Through high-energy mechanical milling under moderate conditions and subsequent heat treatment at a temperature which was still considerably lower compared to that used in conventional carbothermal reduction synthesis of TiC, and elimination of a number of intermediate steps and thereby the cost of production of pure Ti as the starting materials, this method was attempted towards an alternate cheaper route for TiC synthesis.

2. Experimental

In the present study, the starting materials chosen were TiO_2 powder (purity 99.5%, 80–250 μm) and graphite powder (purity 99.4%, 10–100 μm) for the synthesis of TiC. TiO_2 and C were mixed at the stoichiometric ratio for a total of 25 g in which 1 g of zinc stearate ($C_{36}H_{70}O_4Zn$) was added to promote de-agglomeration. The TiO_2 and C powder mixture was mixed thoroughly in a horizontal mixing machine at 20 rpm for 2 h. Then this mixture was milled in a high-energy planetary mill with stainless steel balls of 20 mm size (average). A constant ball to powder ratio (BPR) of 10:1 and a rotational speed of 400 rpm were maintained all throughout. The powder mixture was milled for various milling durations (30–90 h) with intermittent sampling. A portion of the milled samples was heat treated at 1200 °C and 1300 °C under an argon protective atmosphere for 60 min in a tube furnace with a constant heating rate of 10 °C/min. Characterization of the samples was done using SEM-EDAX, and the phases evolved in the reaction products were investigated using XRD patterns.

3. Results and discussion

3.1. Observation of microstructures under SEM

At the early stage of milling, the powders were fine and continuous milling created new surface on particles and enabled the powders to weld together and form large particles (agglomeration). This stage indicated that cold welding was dominant than fracturing of the particles as shown in Fig. 1. These SEM micrographs clearly show the different morphologies of powders milled for short and long milling time.

The heat treatment of the milled mixtures of TiO_2 and graphite at 1300 °C proceeded by three steps as follows. First, partially reduced TiO_2 particles were conglomerated in the initial stage of the heat treatment. During the intermediate stage, porosities among the particles due to the release of CO were observed and particles were separated to finer sizes. Finally, the homogeneous and fine powders containing TiC particles formed at 1300 °C as shown in Fig. 2.

3.2. Differential thermal analysis (DTA)

Differential thermal analysis (DTA) studies were performed on the fresh as-milled samples where the samples were heated from room temperature to 1300 °C at a constant heating rate of 10 °C/min under ambient air atmosphere. Exothermic and endothermic peaks in the mixture of TiO_2 and graphite without milling or with milling were observed. Samples without milling indicated weak exothermic and endothermic peaks which might be due to the oxidation of graphite and transformation to lower oxides of Ti respectively. With milled samples, exothermic peaks might have occurred due to the oxidation of graphite and due to the formation of TiC [15,16]. Endothermic peaks might be due to the transformation to lower oxides of Ti [17]. Lower oxides of Ti are indicated in Fig. 3. The phase transition from anatase to rutile was not investigable by DTA because the exothermic effect was immeasurably low [18]. Samples milled for 90 h seemed to be more reactive compared to the other samples as shown in Fig. 3.

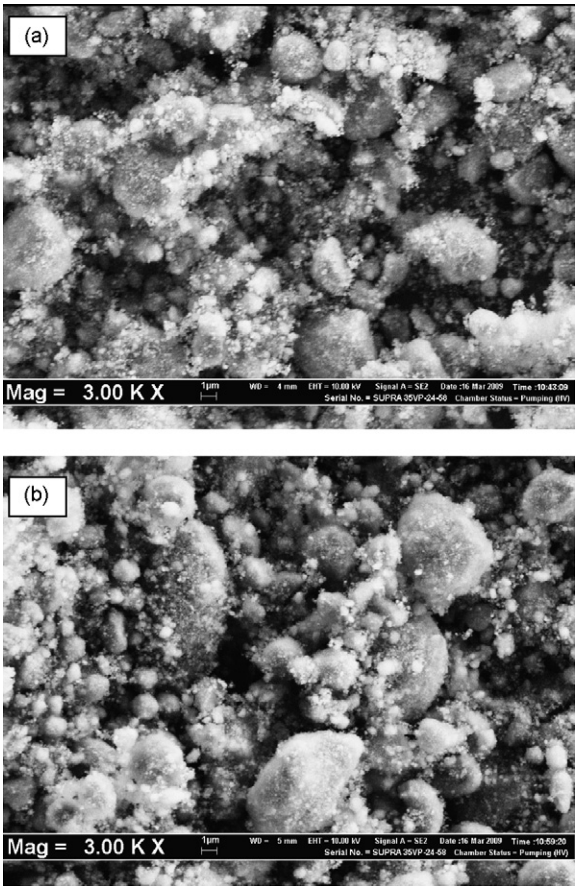

Fig. 1. SEM images of TiO_2–graphite mixtures milled for (a) 30 h and (b) 90 h (both 3000×).

The DTA trace (a) in Fig. 3 did not reveal any strong peak. It indicated a possible reaction at about 950 °C referring to the oxidation of graphite. Trace (b) also showed a similar pattern as that of trace (a) as it did not contain any strong peaks except that it indicated a possible reaction at a temperature of about 850 °C. As the sample was further activated, a drop in this temperature was expected. Trace (c) displayed a relatively stronger exothermic peak at 750 °C which also referred to the oxidation of graphite and stronger endothermic peaks at 900 °C referring to the formation of lower oxides of Ti. The lowering in temperatures compared to that obtained in trace (b) was due to the higher activation due to extended milling. The other peaks at 1120 °C and 1270 °C might refer to the formation of TiC. Graphite powders thus tended to oxidize at lower temperatures with increasing milling time. Such a phenomenon corroborates with the observation made by Welham and Williams [19].

3.3. X-ray diffraction analysis

Fig. 4 shows the XRD patterns of as-milled mixtures of TiO_2 and graphite milled for different durations indicating the phase transformation from anatase to rutile taken place due to the application of mechanical energy through milling (mechanochemical process). Even though no TiC peaks were noticed in the XRD patterns, the powders got activated leading to the possibility of chemical reaction between them towards the synthesis of TiC in further processing steps e.g. heat treatment.

Broadening of the peaks as shown in Fig. 4 indicates the decrease in crystallite size and increase in lattice strain which occur by increasing milling time [20]. Decreases in crystallite size and

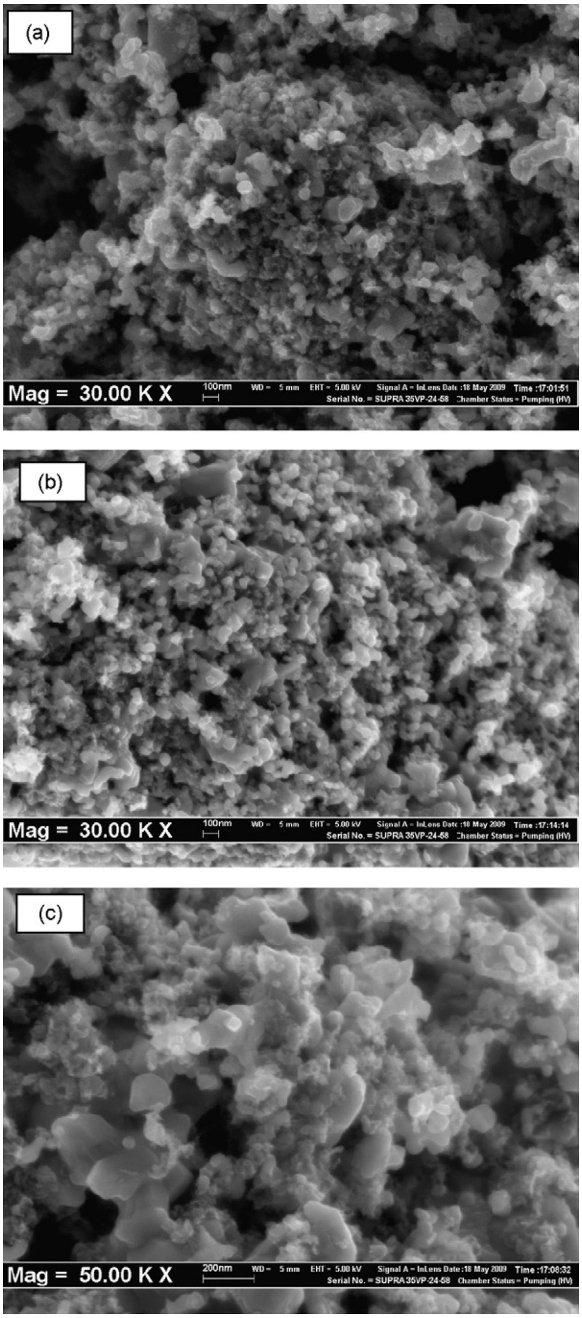

Fig. 2. SEM images of titanium carbide agglomerated with fine particles obtained from milled mixtures of TiO_2 and graphite followed by heat treatment at 1300 °C for 1 h. (a) 30 h milling; (b) 90 h milling (30,000×); (c) 90 h milling (50,000×).

consequent increase in grain boundary area therefore increases the free energy of the system, thus leading to easier phase transformation and formation of products as a means of reducing the free energy of the system [21,22].

The peaks of graphite were not found particularly after 30 h milling in Fig 4 due to the amorphization of graphite and/or originated from the fact that the absorption of X-ray by titanium is much stronger than graphite, leading to extremely weak diffraction peaks of graphite relative to those of TiO_2 [19,13]. The application of lower BPR than the other researchers [12,13] may prove to be useful to make the synthesis economically viable.

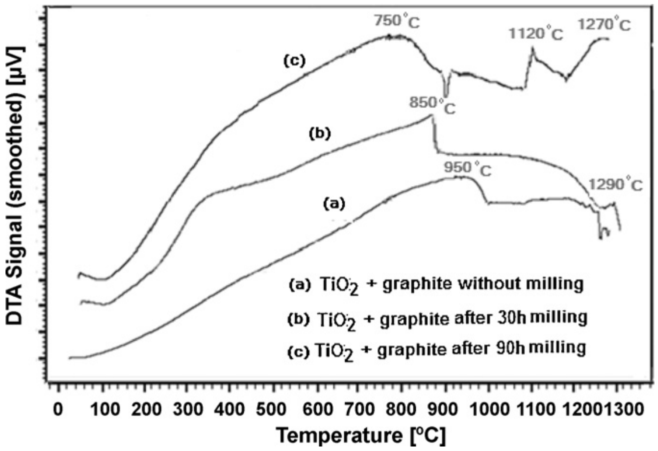

Fig. 3. DTA traces for TiO_2 and graphite powder mixture samples without milling and with milling for 30 h and 90 h.

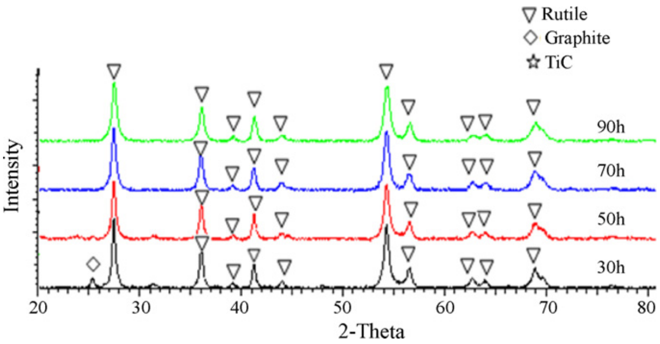

Fig. 4. XRD traces for mixtures of TiO_2 and graphite milled for various durations (30–90 h).

From initial DTA analysis, the peaks at 1120 °C and 1270 °C might refer to the formation of TiC which occurred at temperatures much lower than those used in the conventional carbothermic reduction which is due to the mechanical activation process that enhanced the reactivity of the reactants as well as the reaction kinetics [13]. Heat treatment temperatures were thus chosen depending on the initial DTA analysis. The actual heat treatment temperature employed was marginally higher than these temperatures to ensure the formation of TiC at a reasonably faster rate as shown in Figs. 5 and 6.

The peaks of graphite appear on the XRD patterns with short milling time after heat treatment due to the separation of agglomerates which produce unreacted graphite (free amount) after recrystallization by heat treatment. The peaks of graphite decrease with increasing milling time at both the temperatures of 1300 °C and 1200 °C. This is due to the reaction of graphite with TiO_2 to produce TiC and due to the differential absorption of X-ray.

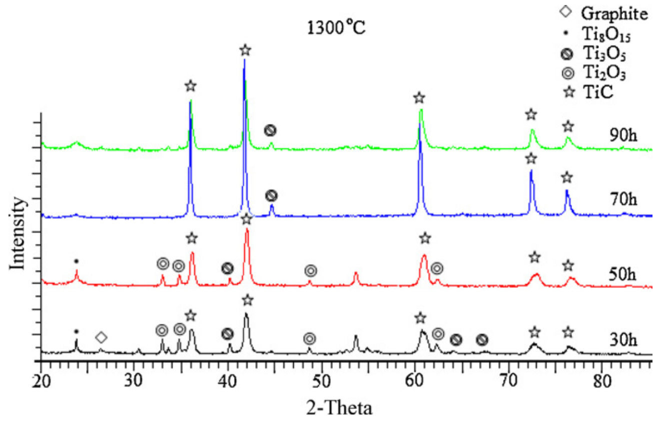

Fig. 5. XRD traces for mixture of TiO_2 and graphite milled for different durations and further heat treated at 1300 °C.

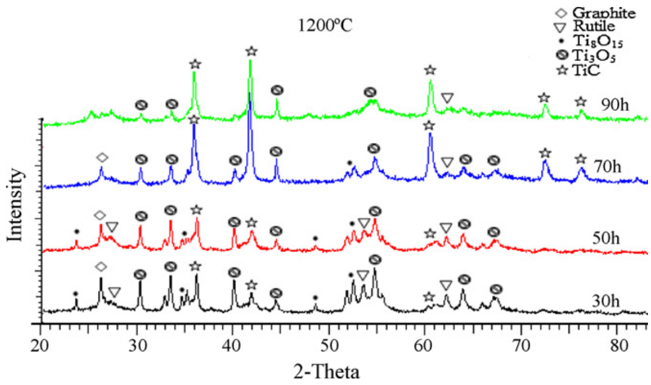

Fig. 6. XRD traces for mixture of TiO_2 and graphite milled for different durations and heat treated at 1200 °C.

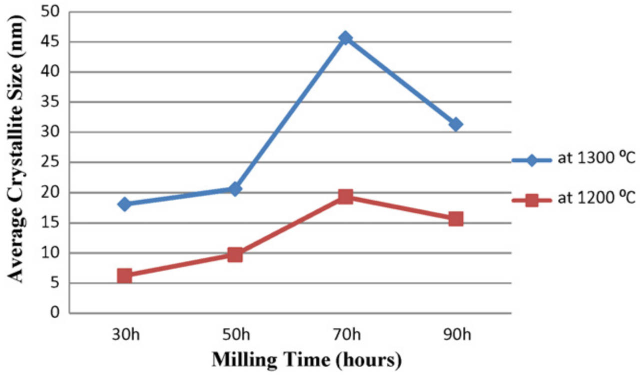

Fig. 7. Change in average crystallite size of TiC with milling durations at different heat treatment temperatures.

The formation of lower oxides of Ti such as Ti_3O_5 and Ti_2O_3 were found after milling for 30 h. Only a small amount of Ti_3O_5 was observed in the powders after milling for 70 h and 90 h and heat treated at 1300 °C for 60 min and most of the oxides of Ti have been transformed into TiC after 90 h milling due to the enhanced reactivity of the reactants as well as improved reaction kinetics due to the mechanical activation process. At 1200 °C, the formation of lower oxides of titanium such as Ti_3O_5 was found with 30–70 h milling. With 70 h milled sample, peaks of Ti_3O_5 and TiC appeared indicating that there was no complete reduction at 1200 °C as shown in Fig. 6. Lower oxides of Ti and TiC were observed and the possible reactions of lower oxides of Ti and C are as the following [17]:

$$4TiO_2(s) + C(s) \rightarrow Ti_4O_7(s) + CO(g) \qquad (4)$$

$$3Ti_4O_7(s) + C(s) \rightarrow 4Ti_3O_5(s) + CO(g) \qquad (5)$$

$$Ti_3O_5(s) + 8C(s) \rightarrow 3TiC(s) + 5CO(g) \qquad (6)$$

The XRD traces showed that the peak intensities were reduced with increasing milling duration due to the refinement of the crystallites and contaminations.

The average crystallite size of TiC was estimated from the XRD traces in Figs. 5 and 6 using the Scherrer formula, $D = k/B\cos\theta$, where D is the average crystallite size, k is the CuK_α wave length, B is the diffraction peak width at half-maximum intensity and θ is the Bragg diffraction angle [23]. The crystallite size of TiC after milling for 30 h, 50 h, 70 h, and 90 h and further heat treated at 1300 °C were 12.3 nm, 17.1 nm, 45.7 nm, and 24.2 nm respectively. On the other hand, the crystallite size of TiC after milling for 30 h, 50 h, 70 h, and 90 h and heat treated subsequently at 1200 °C were 6.23 nm, 9.72 nm, 19.38 nm, and 15.70 nm respectively as shown in Fig. 7.

Average crystallite size of TiC as calculated from the XRD traces was found to increase with increasing milling time up to 70 h at both the temperatures. This was due to the pronounced mechanical activation with increasing milling time which led to enhance the formation and growth of TiC crystallites during heat treatment. On the other hand, with further extended milling to 90 h, the average crystallite size of TiC was found to be smaller than the average crystallite size due to the increasing contaminations and amorphous phase formation which hindered the formation and growth of TiC crystallites [24,25]. At any particular milling time, samples treated at 1300 °C had larger average crystallite size than the same obtained with 1200 °C as higher heat treatment temperature promoted larger grain growth.

4. Conclusions

TiC has been synthesized directly from mixtures of TiO_2 and graphite through a moderate condition of mechanical activation and subsequent heat treatment. In the proposed technique, the synthesis of TiC was completed at temperature much lower than those used in the conventional carbothermic reductions due to the mechanical activation process which enhanced the reactivity of the reactants as well as enhanced reaction kinetics. The milling conditions employed were also less severe. With increasing milling time, the mechanical activation increased which led to enhance the formation of TiC crystallites. The average crystallite size of the TiC formed under all the conditions was in the nano range.

Acknowledgement

Financial support from FRGS, Govt. of Malaysia (Grant No. 203.PBAHAN.6071127) to conduct the study is gratefully acknowledged.

References

[1] M. Razavi, M.R. Rahimipour, Ceram. Int. 35 (2009) 3529–3532.
[2] D.W. Lee, B.K. Kim, Scripta Mater. 48 (2003) 1513–1518.
[3] R. Koc, J.S. Folmer, J. Mater. Sci. 32 (1997) 3101–3111.
[4] L. Tong, R.G. Reddy, Scripta Mater. 52 (2005) 1253–1258.
[5] Y. Gotoha, K. Fujimuraa, M. Koikea, Y. Ohkoshia, Mater. Res. Bull. 36 (2001) 2263–2275.
[6] E.S. Chernikova, I.I. Timofeeva, L.V. Uvarova, A.I. Bykov, V.V. Skorokhod, V.P. Smirnov, Powder Metall. Met. Ceram. 37 (5–6) (1998) 65.
[7] L.L. Ye, M.X. Quan, Nanostruct. Mater. 5 (1) (1995) 25–31.
[8] D.P. Xiang, Y. Liu, M.J. Tu, Y.Y. Li, W.P. Chen. 27 (2009) 111–114.
[9] M. Razavi, M.R. Rahimipour, A.H. Rajabi-Zamani, J. Alloys Compd. 436 (2007) 142–145.
[10] Z.G. Liu, K. Tsuchiya, M. Umemoto, J. Mater. Sci. 7 (2003) 1229–1235.
[11] Z. Yong, M. Meng, W. Dihua, J. Kai, H. Xiaohong, J. Xianbo, G.Z. Chen, Chin. Sci. Bull. 20 (51) (2006) 2535–2540.
[12] N. Setoudeh, A. Saidi, N.J. Welham, J. Alloys Compd. 390 (2005) 138–143.
[13] R. Ren, Z. Yang, L.L. Shaw, J. Mater. Sci. 35 (2000) 6015–6026.
[14] H. Han, L. Zan, J. Zhong, X. Zhao, J. Mater. Sci. 40 (18) (2005) 4921–4923.
[15] J.M. Skowrotski, J. Therm. Anal. 27 (1983) 69–76.
[16] C.H. Cho, D.K. Kim, J. Mater. Synth. Process. 10 (2002) 127–134.
[17] Y.C. Woo, H.J. Kang, D.J. Kim, J. Eur. Ceram. Soc. 27 (2007) 719–722.
[18] A. Daffier, A. Feltz, J. Jung, W. Ludwig, E. Kaisersberger, J. Therm. Anal. 33 (1988) 803–809.
[19] N.J. Welham, J.S. Williams, Carbon 36 (1998) 1309–1315.
[20] H.J. Niu, D.P. Hampshire, Physica C 372 (2002) 1145–1147.
[21] C. Suryanarayana, Prog. Mater. Sci. 46 (2001) 1–184.
[22] M.H. Enayati, Z. Sadeghian, M. Salehi, A. Saidi, Mater. Sci. Eng. A 375–377 (2004) 809–811.
[23] E. Gaffet, F. Bernard, J.-C. Niepce, F. Charlot, C. Gras, G. LeCaer, P. Delcroix, A. Mocellinc, J. Mater. Chem. 9 (1999) 305–314.
[24] A. Mergen, Ceram. Int. 35 (2009) 1151–1157.
[25] J. Wang, J.M. Xue, D.M. Wan, B.K. Gan, J. Solid State Chem. 154 (2000) 321–328.