ELSEVIER

Chemical Engineering Science 62 (2007) 4885–4890

Chemical Engineering Science

www.elsevier.com/locate/ces

Mechanical and electric current activation of solid–solid reactions for the synthesis of fully dense advanced materials

A.M. Locci[a], R. Licheri[a], R. Orrù[a,b,*], A. Cincotti[a], G. Cao[a,b,*]

[a]*Dipartimento di Ingegneria Chimica e Materiali, Centro Studi sulle Reazioni Autopropaganti (CESRA), Unità di Ricerca del Consorzio Interuniversitario Nazionale di Scienza e Tecnologia dei Materiali, Università degli Studi di Cagliari, Piazza d'Armi, 09123 Cagliari, Italy*

[b]*Società Consortile PROMEA Scarl, c/o Dipartimento di Fisica, Cittadella Universitaria di Monserrato, S.S. 554 bivio per Sestu, 09042 Monserrato (CA), Italy*

Received 16 June 2006; received in revised form 6 December 2006; accepted 10 January 2007
Available online 26 January 2007

Abstract

The so-called spark plasma sintering (SPS) is used in this work as a new time-saving sintering/synthesis method for the preparation of fully dense TiC/TiB_2 ceramic composites and $NbAl_3$ intermetallics. In particular, mechanically activated powders of starting materials are reacted and simultaneously consolidated once crossed by an electric pulsed current.

Specifically, the effect of the most important parameters related to mechanical activation of starting reactants and synthesis/consolidation stage on process behavior and end-products characteristics is systematically investigated.

The general result found in this study is that milling time and current level applied during the synthesis/densification strongly affect process dynamics, kinetics of synthesis process, as well as product relative density and crystallite sizes, which are reduced down to nanometric levels.

Keywords: Solid–Solid reactions; Activation; Ball milling; Spark plasma sintering; Advanced materials

1. Introduction

Mechanical treatment of powders by ball milling (BM) is recognized capable to produce cold-welding, microstructure refinement, interface formation processes, which favor the occurrence of structural and chemical transformations up to the synthesis of equilibrium and far-from-equilibrium phases (Suryanarayana, 2001; Beyer and Clausen-Schaumann, 2005). Moreover, BM is found to affect significantly powders reactivity by the so-called mechanical activation (MA) (Charlot et al., 1999; Takacs et al., 2001; Khina and Formanek, 2006). Chemical and structural transformations involved during BM clearly depend on the corresponding intensity of mechanical treatment, which is typically tuned through the appropriate selection of milling time and charge ratio, i.e., the ball to powder mass ratio (Delogu et al., 2003).

Starting from powders processed by BM, several densification techniques, for instance hot pressing (HP) (Krasnowski and Kulik, 2003; Zheng et al., 2003) and shock consolidation (Korth and Williamson, 1995), are employed with the aim of fabricating bulk advanced materials, including nanostructured products. A novel sintering methods, the so-called spark plasma sintering (SPS), where the ball milled powders are crossed by an electric pulsating current, has been recently proposed (Lee et al., 2001; Orrù et al., 2001). It is generally found that SPS allows to perform sintering at lower temperatures and shorter times with respect to conventional HP.

In this work we examine the effect of mechanical pretreatment of the starting reactants by means of BM on the electric current activated simultaneous synthesis and densification of TiC/TiB_2 and $NbAl_3$ by means of SPS.

Both systems under investigation are very promising materials in several application fields due to their interesting

* Corresponding authors. Dipartimento di Ingegneria Chimica e Materiali, Centro Studi sulle Reazioni Autopropaganti (CESRA), Unità di Ricerca del Consorzio Interuniversitario Nazionale di Scienza e Tecnologia dei Materiali, Università degli Studi di Cagliari, Piazza d'Armi, 09123 Cagliari, Italy.
E-mail address: cao@visnu.dicm.unica.it (G. Cao).

0009-2509/$ - see front matter © 2007 Elsevier Ltd. All rights reserved.
doi:10.1016/j.ces.2007.01.009

Table 1
Starting powders used in the present investigation

Reactant	Vendor	Size	Purity
Ti	Sigma-Aldrich	−325 mesh	99.98%
B_4C	Alfa Aesar	1–7 μm	99.4%
C (amorphous)	Alfa Aesar	0.042 μm (average)	99.9 + %
Nb	Alfa Aesar	−325 mesh	99.8%
Al	Sigma-Aldrich	−200 mesh	99%

properties. Specifically, wear resistance and fracture toughness of TiC/TiB_2 composites are superior with respect to their constituent ceramic components (Bhaumik et al., 2000). In addition, niobium aluminides are considered optimal candidate for structural applications to be used beyond the operating temperatures of conventional nickel-base superalloys (Hanada, 1997).

2. Experimental materials and methods

Characteristics of the starting powders used in the present investigation are reported in Table 1. Powders were co-milled in the stoichiometric ratio according to the following reactions:

$$4Ti + B_4C + C \rightarrow 2TiC + 2TiB_2, \quad (1)$$

$$Nb + 3Al \rightarrow NbAl_3 \quad (2)$$

for the preparation of the composite or the aluminide products, respectively. BM experiments were conducted in a SPEX 8000 shaker mill, while an SPS 515S apparatus was used to synthesize/sinter the selected materials. The ranges of BM time (t_M) investigated are 0–24 h and 0–35 h, for the case of TiC/TiB_2 and $NbAl_3$, respectively, while the charge ratio, CR, was set equal to 1 for both systems. SPS experiments are carried out, for the case of TiC/TiB_2, by applying a previously set constant value of the electric current or following a selected temperature cycle, for the case of $NbAl_3$. Temperature, applied average current and voltage, mechanical load, and vertical displacement of the lower electrode were measured in real time and recorded. The latter parameter can be regarded as the degree of powder compact densification. However, the contribution of thermal expansion of electrodes and graphite spacers and plungers have to be subtracted to the recorded displacement, in order to obtain the sample shrinkage (δ). For the sake of brevity, details on experimental equipment and procedures have been reported elsewhere (Locci et al., 2006a,b).

3. Results and discussion

The mechanism of formation of the composite TiC/TiB_2 by SPS was recently studied starting from unmilled reactants ($4Ti + B_4C + C$) by simultaneously applying a constant pulsed electric current ($I = 800$ A) and mechanical pressure ($P = 20$ MPa), for time intervals (t_{SPS}) ranging from 60 to 600 s (Locci et al., 2006a). When applying such current level, it was found that the complete conversion to TiC and TiB_2 is achieved after 480 s.

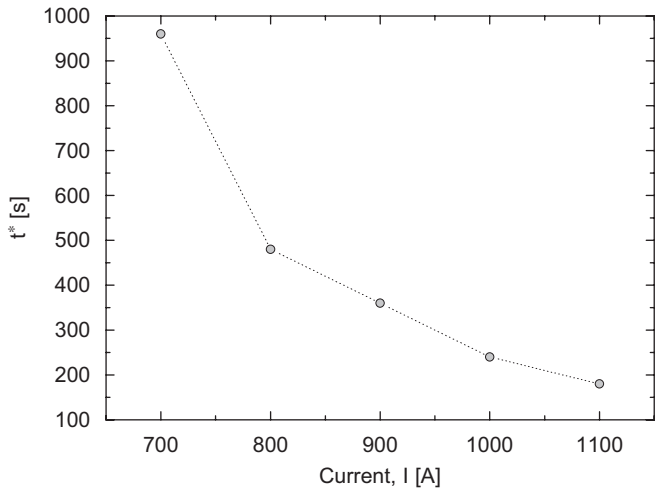

Fig. 1. Effect of the applied current on the time needed to obtain full conversion of reactants (Eq. (1)) into final desired product ($P = 20$ MPa).

The influence of current intensity on the SPS of TiC/TiB_2 composite is investigated in the range 700–1100 A ($P = 20$ MPa). The dependence of the synthesis time (t^*), i.e., the minimum time interval during which the applied current result in complete conversion, is shown in Fig. 1. It is seen that synthesis time decreases monotonically as current is increased, varying from 960 to 180 s in the range 700–1100 A. It is also observed that product densification increases as current is augmented, thus reaching 87% of the theoretical value, when 1100 A are provided for 180 s. It is then apparent that the increase of the applied current accelerates both densification and, especially, synthesis processes. These outcomes could be considered as a direct consequence of higher heating rates and temperature levels obtained by increasing the applied current. Moreover, in order to reach relatively high dense products, current needs to be applied for time intervals longer than those required for obtaining complete conversion. Specifically, a 98% dense product is obtained when $I = 1100$ A ($P = 20$ MPa) was applied for 240 s.

Fig. 2 shows the variation of the XRD patterns of the powder mixture as milling time, t_M is increased. It is seen that, the initially sharp diffraction peaks become broader due to powder crystallite size refinement and internal strain increase induced by BM. In addition, these XRD results indicate that, within the detection limit of this analysis, additional phases are not formed at t_M up to 6 h.

First evidence of product formation (TiC) is observed when $t_M = 12$ h. The TiC content clearly increased as t_M was extended up to 24 h. The apparent formation during milling of TiC before TiB_2 is consistent with the higher diffusivity of carbon into Ti as compared to that of boron (Lasker et al., 1990).

The milled powders were then processed in the SPS apparatus under optimized operating conditions ($I = 1100$ A, $P = 20$ MPa, $t_{SPS} = 240$ s) obtained when using unmilled powders. The sample shrinkage and temperature time profiles corresponding to unmilled ($t_M = 0$ h) and milled ($t_M = 24$ h) powders, are shown in Fig. 3. It is clearly seen that the milling