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Influence of mechanical alloying on Ti_3SiC_2 formation via spark plasma sintering technique from Ti/SiC/C powders

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Abstract

Ti_3SiC_2 was elaborated by two different methods: (i) Spark plasma sintering of 5Ti/2SiC/C powders and (ii) mechanical alloying of powders followed by Spark plasma sintering. The results showed that mechanical alloying was not advantageous for pure Ti_3SiC_2 formation but it can significantly improve the density of the obtained bulk material via the particles refinement as well as the microhardness by increasing the TiC content. It was found that the relative density was increased up to 98.58% for the sintered mechanically alloyed sample whereas it was not more than 96.04% for the sintered 5Ti/2SiC/C starting powders. The Vickers microhardness measured for both bulk samples demonstrates a high improvement for the previously mechanically alloyed powder mixture, as it was of about 1282 Hv and only 581.2 Hv for the alloy obtained from 5Ti/2SiC/C starting powders.

Keywords: C. Hardness; Ti_3SiC_2; Mechanical alloying; Spark plasma sintering technique

1. Introduction

Ternary compound Ti_3SiC_2 has received more and more attention due to its remarkable combination of the best properties of ceramic and metals and particularly the stable mechanical and electrical behavior at high temperature. In fact, like metals it is a good electrical and thermal conductor, easily machinable, relatively soft and highly thermal shock resistant. Like ceramics, it is very stiff, oxidation resistant and stable to at least 1700 °C [1–6].

Moreover, Ti_3SiC_2 has the individual combination of strength and ductility at elevated temperatures as well as resistance to thermal shock and excellent machinability that has never been observed in other materials [7]. This extraordinary grouping of properties makes Ti_3SiC_2 to be thought about as a promising material for many important industrial applications.

Therefore, it is important to make fully dense bulk Ti_3SiC_2 samples with high purity. Zhou et al. [8] were the first who synthesized the ternary compound via chemical reaction between TiH_2, Si and graphite at 2000 °C, followed by the work of Nickl et al. [9] by using the chemical vapour deposition (CVD) method. During the last decades diverse methods have been employed for the synthesis of bulk Ti_3SiC_2 such as arc melting [10], hot isostatic pressing (HIP) [11], hot pressing (HP) [12], reactive sintering [13], heat treatments in vacuum [14] and others. However, the synthesis process of all these mentioned techniques are either much time consuming or involving high pressure and high temperature.

The spark plasma sintering technique (SPS) also called the pulse discharge sintering (PDS) method, a relatively newly developed technique, has several advantages over similar processes. Indeed, with the help of this sintering method, materials can be sintered or synthesized at lower temperature and with shorter soaking time thus avoiding any exaggerate grain growth. Therefore metals and ceramic can be obtained with fine particles leading to materials

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with superior properties [15]. There are several reported works on the simultaneous synthesis and consolidation of Ti_3SiC_2 through the SPS process starting from different powder mixtures including: Ti/Si/C [16,17], Ti/SiC/C [17], Ti/Si/TiC [17,18] and Ti/SiC/TiC [19].

Nevertheless, regardless of the several starting powder mixtures cited above a single phase is often difficult to be obtained and TiC, SiC and/or Ti_5Si_3 and $TiSi_2$ inevitably appear after the synthesis.

Mechanical alloying is a low cost process appropriate to the formation of a big variety of powder materials. Furthermore, it is considered to be the most powerful technique for synthesizing nanocrystalline carbide materials at room temperature [20–22]. Nevertheless, high purity of Ti_3SiC_2 ceramic is difficult to synthesize via mechanical alloying alone [23].

In recent years, more and more attention has been paid to mechanical alloying in order to fabricate Ti_3SiC_2 because using highly deformed and reactive powders could reduce the sintering temperature and the holding time [24].

Liang and co-workers [25] obtained high purity of Ti_3SiC_2 through the combination of mechanical alloying and SPS (MA–SPS) at a temperature 300 °C lower than that reported in the literature. They obtained full dense Ti_3SiC_2 with a purity of 99.3% by adding an appropriate amount of Al and starting from the powders mixture of 3Ti/Si/2C.

Zhang et al. [26] established that Ti_3SiC_2 can be rapidly synthesized using the pulse discharge technique starting from Ti/SiC/C powder mixture at a relatively low temperature of 1250–1300 °C under a pressure of 50 MPa. They demonstrated that by adjusting the molar ratio of the starting composition to 5:2:1 the purity of Ti_3SiC_2 could be improved to about 93%.

From the synthesis processes as well as the starting composition used in the past for Ti_3SiC_2 elaboration, it is found that the purity of Ti_3SiC_2 could be further improved by adding an excess of Si to the starting powders [16]. The previous results [26] showed that a high purity of Ti_3SiC_2 could be obtained by SPS using an optimum temperature that ranges between 1250 and 1300 °C, a short soaking time of 15 min under a constant pressure of 50 MPa.

The objective of this work is to study the mechanical alloying (MA) effect on Ti_3SiC_2 purity using the SPS technique starting from a powders mixture of Ti/SiC/C at a molar ratio of 5:2:1. Two synthesis processes will be adopted in this work: direct spark plasma sintering (SPS) of Ti, SiC and C powders and the sintering of the previous mechanically alloyed powder mixture of Ti/SiC/C (MA–SPS). A comparison will be completed between the two processes in terms of Ti_3SiC_2 purity and the mechanical properties of the obtained bulk materials as well as their relative densities.

2. Experimental details

Starting powders of coarse Ti (< 40 μm, 98%, Prolabo), C (99%, Fischer Scientific) and SiC (< 44 μm, 99%, Alfa Aesar) were used in this study. The powder mixtures were placed into a shaker for 48 h for better homogeneity and the stoichiometric molar ratios were fixed at 5:2:1. The mechanical alloying procedure was conducted at room temperature using the Pulverisette 7 planetary ball mill. The Ti/SiC/C powders were sealed into stainless steal vials (45 ml in volume) with 5 stainless steal balls (15 mm in diameter) in a glove box under argon protective atmosphere. The ball-to-powder weight ratio was about 67:2. The powder mixtures were mechanically alloyed for 6 h with a rotation speed of 350 rpm. The starting powder mixture of 5Ti/2SiC/C and the previously mechanically alloyed one were respectively referred to as M1 and M2 samples.

In order to study the mechanical alloying effect on the mechanical properties of the powder mixtures, the starting powder mixtures as well as the alloyed ones were consolidated as pellets, by spark plasma sintering using an SPS-515 S SYNTEX apparatus. Based on the previous results [26], the temperature was set to 1300 °C at a heating rate of 60 °C/min. The soaking time was fixed to 10 min under a constant pressure of 64 MPa.

Before the SPS process, all the powders were well mixed during 48 h in a shaker. The powders were then, compacted into a graphite die of 8 mm in diameter and sintered in vacuum at fixed temperature of 1300 °C and pressure of 64 MPa. The soaking time at the maximum temperature was within 10 min. A constant heating rate of 60 °C/min was employed during all the sintering process. During the SPS process, the pressure was set to 54 MPa during the first 500 s. Then it was increased to 64 MPa and remained constant between 600 and 1800 s (Fig. 1). The temperature was maintained constant around 600 °C until 500 s and then increased to 1300 °C and remained constant after 1150 s until 1750 s (Fig. 2).

The starting powders as well as the bulk samples were characterized by X-ray diffraction (XRD) using a (θ–2θ) Panalytical XPERT PRO MPD diffractometer operating with Cu Kα radiation (λ=0.15406 nm). The existing

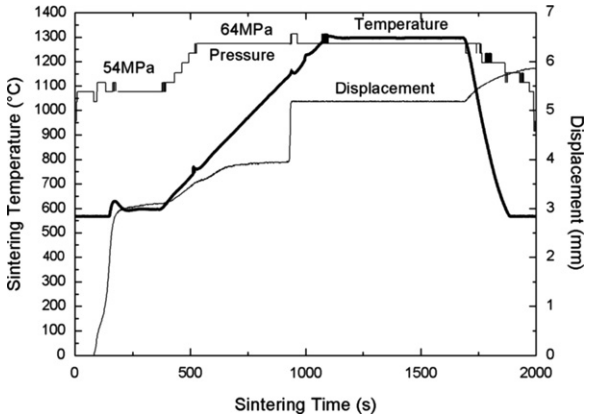

Fig. 1. Variation of sintering temperature, sample shrinkage and applied pressure during the SPS process for Ti/SiC/C powder mixture (M1) heated at 1300 °C for 10 min. Left *y*-axis corresponds to the sintering temperature and right *y*-axis corresponds to shrinkage curve.