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Phase analysis and wear behavior of *in-situ* spark plasma sintered Ti_3SiC_2

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Abstract

In-situ synthesis of dense near-single phase Ti_3SiC_2 ceramics from 3Ti/SiC/C/0.15Al starting powder using spark plasma sintering (SPS) at 1250 °C is reported. Systematic analysis of the phase development over a range of sintering temperatures (1050–1450 °C) suggested that solid state reactions between intermediate TiC and Ti_5Si_3 phases lead to the formations of Ti_3SiC_2. The effect of starting powder composition on phase development after SPS at 1150 °C was also investigated using three distinct compositions (3Ti/SiC/C, 2Ti/SiC/TiC, and Ti/Si/2TiC). The results indicate that the starting powder compositions, with higher amounts of intermediate phase such as TiC, favor the formation of Ti_3SiC_2 at relatively lower sintering temperature. Detailed analysis of wear behavior indicated that samples with higher percentage of TiC, present either as an intermediate phase or a product of Ti_3SiC_2 decomposition, exhibited higher microhardness and better wear resistance compared to near single phase Ti_3SiC_2.

Keywords: A. Sintering; B. Microstructure; C. Hardness; C. Wear resistance; D. Carbides

1. Introduction

Ti_3SiC_2 is a representative member of a family of layered ternary phases called as $M_{n+1}AX_n$ phases (M is a transition metal; A is an A group (mostly IIIA and IVA) element; X is C and/or N; and $n=1$–3) [1]. The presence of metallic, covalent, and ionic type chemical bondings in Ti_3SiC_2 gives the material remarkable combinations of properties of metallic and ceramic materials [2]. These materials are often referred to as "ductile ceramics" and exhibit properties such as lower density, high melting point, excellent electrical and thermal conductivity, good machinability, thermal shock resistance, damage tolerance, and fatigue, creep and high temperature oxidation resistance [3–5].

Ti_3SiC_2 was first synthesized by Jeitschko and Nowotny via chemical reaction between TiH_2, Si, and graphite in 1967 [6]. Over the years from 1967 to present, several methods, including magnetron sputtering [7], arc melting and post-annealing [8], chemical vapor deposition (CVD), pulsed laser deposition (PLD) [9], self-propagating high temperature synthesis (SHS) [10], mechanical alloying [11], and combustion synthesis with hot isostatic pressing [12], were employed for Ti_3SiC_2 synthesis. However, these processes almost always result in the formation of Ti_3SiC_2 accompanied with large amounts of undesired ancillary phases like TiC, Ti_5Si_3, and $TiSi_2$. Barsoum et al. synthesized almost single phase Ti_3SiC_2 from Ti, graphite, and SiC powders by employing hot isostatic pressing (HIP) at 1600 °C [13]. In the recent years, a novel solid state consolidation technique spark plasma sintering (SPS), where uniaxial compaction pressure is applied to the powder along with pulse direct current, was employed for synthesis of nanostructured/ultra-fine grained materials, difficult-to-sinter materials, and metastable/non-equilibrium phases. SPS presents tremendous potential for the processing of fully dense materials at relatively lower sintering temperature and in shorter sintering time without significant grain growth compared to conventional hot pressing [14]. SPS of Ti_3SiC_2 from Ti/Si/TiC [15,16], Ti/Si/C [17], Ti/SiC/TiC [18], Ti/$TiSi_2$/TiC [19], TiH_2/SiC/C [20] starting powder has been reported. However, similar sintering process applied to Ti/SiC/C starting composition

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resulted in the formation of Ti_3SiC_2 with higher amount of ancillary TiC (nearly 10%) [21]. Excess Si in starting composition was used to compensate for the evaporation of Si at higher temperature, resulting in decreased amount of ancillary TiC [22]. However, the higher percentage of Si content also resulted in appearance of a new ancillary phase, $TiSi_2$ [23]. Addition of small amount of aluminum in the starting powder is reported to favor the nucleation and growth of Ti_3SiC_2 [24]. In this paper, systematic investigation on the effect of sintering temperature, in the range of 1050–1450 °C, on the phase development during SPS of 3Ti/SiC/C/0.15Al powder is presented. The reaction mechanisms leading to formation of Ti_3SiC_2 and the possibility of formation of $Ti_3(Si_{1-x}Al_x)C_2$ solid solution during SPS are critically analyzed. Also, the effect of starting powder composition on phase development after SPS at 1150 °C is investigated using three distinct compositions (3Ti/SiC/C, 2Ti/SiC/TiC, and Ti/Si/2TiC). The effect of phase constituents in sintered Ti_3SiC_2 samples on the wear behavior (wear weight loss and coefficient of friction) is also presented.

2. Experimental procedure

Commercially available powders of Ti (< 44 μm), SiC (2–10 μm), graphite (< 44 μm), and Al (< 2 μm) were used for the synthesis of Ti_3SiC_2 phase. The starting powder, weighted according to molar ratio of Ti/SiC/C/Al (3:1:1:0.15), was milled for 1 h in a high energy planetary ball mill (Make: Fritsch; Model:Pulverisette 7). The mechanical milling was conducted using tungsten carbide milling media with an operating speed of 500 rpm and powder to ball ratio of 10:1. The ball milled powder was then compacted loosely in a 20 mm in diameter graphite die. The samples were then sintered using SPS in a temperature range of 1050–1450 °C with a uniaxial pressure of 50 MPa, soaking time of 15 min, and heating rate of 100 °C/min (Make: Thermal Technology, Inc.; Model: 10-3). To investigate the effect of starting powder composition on phase development, three different powder mixtures (3Ti–SiC–C, 2Ti–SiC–TiC and Ti–Si–2TiC) were also sintered using SPS at 1150 °C with a uniaxial pressure of 50 MPa and soaking time of 15 min. The phase constituents and microstructure of the ball milled powder and sintered samples were analyzed using X-ray diffractometer (Make: Philips Norelco; Model: PW1830) operating with CuK_α radiation ($\lambda = 1.54178$ Å) and Scanning Electron Microscope (SEM) (Make: JEOL; Model: JSM-633OF) equipped with energy dispersive X-ray spectroscopy (EDS) detector. Microhardness of the samples was measured using a Vickers hardness tester (Clark Instruments; Model: CM-700AT) operated with the normal force of 9.8 N and holding time of 15 s. About ten hardness readings were taken on each sample and the average value was reported along with positive and negative error bars. Wear tests were conducted using a ball-on-disk configuration (Make: Nonovea; Model: MT/60). Polished surfaces of 20 mm diameter sintered discs were slid against 6 mm diameter aluminum oxide (Al_2O_3) ball to form 4 mm diameter wear tracks on the surfaces. The wear tests were conducted with a normal force of 10 N and sliding velocity of 200 rpm. The wear weight loss data for the samples was recorded after every 10 min interval with total wear test duration of 1 h. The depth profiles across the wear tracks were measured out using a non-contact optical 3D profilometer (Make: Nanovea; Model: PS50).

3. Results and discussion

3.1. Analysis of phases in starting powder and spark plasma sintered samples

X-ray diffraction (XRD) patterns from ball milled powder (Ti/SiC/C/Al) and samples spark plasma sintered at different sintering temperatures in a range of 1050–1450 °C are presented in Fig. 1. The XRD pattern from the ball milled powder showed peaks corresponding to major constituents, Ti and SiC, in the starting composition. Note that the ball milling was conducted to mix the starting power uniformly and not to initiate any new phase formation. The SPS sintering with the investigated processing parameters (temperature range of 1050–1450 °C, uniaxial pressure of 50 MPa, and soaking time of 15 min) resulted in *in-situ* reactions forming new phases. The peaks corresponding to starting constituents Ti and SiC were absent in the XRD patterns of all the sintered samples. For the samples sintered at relatively lower temperatures (1050–1150 °C), the peaks corresponding to new phases, TiC and Ti_5Si_3, were observed in the XRD patterns. In this temperature range, Ti seems to react with free C and SiC to form TiC and Ti_5Si_3. The XRD pattern indicated the

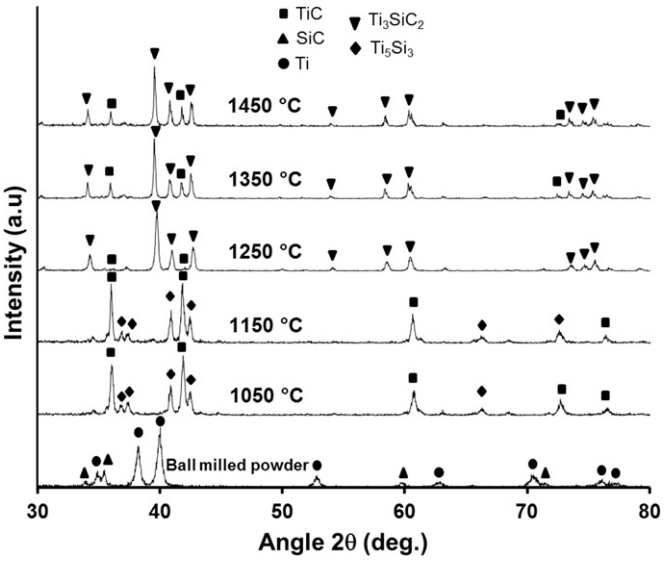

Fig. 1. X-ray diffraction patterns from ball milled 3Ti/SiC/C/0.15Al powder mixture and samples spark plasma sintered at 1050 °C, 1150 °C, 1250 °C, 1350 °C, and 1450 °C.