Advanced Powder Technology 25 (2014) 885–890

Contents lists available at ScienceDirect

Advanced Powder Technology

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

Original Research Paper

Effect of substitution of Si by Al on microstructure and synthesis behavior of Ti_5Si_3 based alloys fabricated by mechanically activated self-propagating high-temperature synthesis

Kian Kasraee [a,*], Ali Tayebifard [a], Esmaeil Salahi [b]

[a] Semiconductor Department, Materials and Energy Research Center, Karaj, Iran
[b] Ceramic Department, Materials and Energy Research Center, Karaj, Iran

ARTICLE INFO

Article history:
Received 5 September 2013
Received in revised form 7 December 2013
Accepted 11 January 2014
Available online 25 January 2014

Keywords:
Titanium silicide
Self-propagating high-temperature synthesis
Mechanical activation
Nanostructured

ABSTRACT

The effect of substitution of Si by Al and mechanical activation on microstructure, phase composition, ignition and combustion temperature of Ti_5Si_3 based alloys and composites that were prepared by mechanically activated self-propagating high-temperature synthesis (MASHS) method was investigated. For this purpose elemental powders of titanium, silicon and aluminum were mixed according to the $5Ti + 3(1 - X)Si + 3XAl$ formula, where $X = 0$, 0.2, 0.4, 0.6. The samples were characterized by X-ray diffraction (XRD) analytical technique and scanning electron microscope (SEM) equipped with an energy-dispersive spectrum (EDS) analyzer. The results have shown that formation of Ti_5Si_3 during milling stage is postponed by adding Al into the system. Presence of Al in the Ti–Si system have a significant effect on the phase composition of the final products. Substitutional solid solution of $Ti_5(Si, Al)_3$ and Ti_5Si_3–Ti_3Al composite are formed by increasing Al amount in the system. Furthermore combustion temperature and crystallites size of Ti_5Si_3 is reduced with addition of Al into the Ti–Si system. Moreover, solubility of Al in Ti_5Si_3 is increased with enhancing the X up to 0.4, after that, the solubility of Al in Ti_5Si_3 is ceased, due to achieving the solubility limit of Al in the Ti_5Si_3. The average crystallites size of Ti_5Si_3 are decreased with increasing milling time prior to the reaction.

1. Introduction

Ti_5Si_3 has gained significant attention as a high temperature structural material [1–6]. It has a high melting point (2130 °C), a low density (4.32 g/cm^3), a high hardness (11.3 GPa), a relatively high Young's modulus (225 GPa) [7], potential to save high strength up to 1200 °C, a good creep resistance below 850 °C [8–10], and its high silicon concentration may assists in the formation of a protective SiO_2 layer [11]. However, poor room-temperature fracture toughness of the Ti_5Si_3 is the major drawback, which severely limits its application [12]. The fracture toughness of Ti_5Si_3 shows a remarkable improvement with a decrease in grain size [12,13].

The high heat of formation of Ti_5Si_3 (-579 kJ mol^{-1}), can be economically utilized to formulate novel processing techniques. One of these methods is Self-propagating High-temperature Synthesis (SHS) [7]. In SHS process, highly exothermic reaction can becomes self-sustaining and once initiated will propagate through the reactants in the form of combustion waves [14]. SHS has advantages including lower energy requirement, simpler and cheaper equipment, higher product purity and higher sinterability compared to conventional methods [15,16]. The use of mechanical activation as a precursor to SHS results in the formation of nanostructured materials. In MASHS, the elemental powder mixture is milled for a short time at a given frequency and impact energy, and then it is used as a reactant in the SHS process. Actually, mechanical activation would promote the number of potential nucleation sites and produce finer crystallites. Since, the milling process refines the particle size therefore ignition temperature (Tig) decreases with the milling time. Consequently, crystallite growth is limited by lower temperature and large numbers of grains are formed at the same time [17]. Alloying by metal element has been seen as a possible way to improve the mechanical or physical properties of this compound [16]. Rosenkranz and Frommeyer have suggested that softer particles like titanium aluminides can improve the ductility of Ti_5Si_3 alloys [5]. Mitra has reported that the room-temperature fracture toughness of Ti_5Si_3 is enhanced considerably by adding 8 wt.% Al or 20 vol.% TiC [8]. He has also reported that substitution of Si sites by Al atoms in Ti_5Si_3 lattice alter covalent character of bonding, which in turn effects the fracture toughness and brittle to ductile transition temperature. Indeed, Al caused to increase

* Corresponding author. Tel.: +98 21 88448938; fax: +98 26 362018880.
E-mail address: kiankasraee@yahoo.com (K. Kasraee).

0921-8831/$ - see front matter © 2014 The Society of Powder Technology Japan. Published by Elsevier B.V. and The Society of Powder Technology Japan. All rights reserved.
http://dx.doi.org/10.1016/j.apt.2014.01.008

metallic-bond at the expense of the covalent bond, in Ti_5Si_3 lattice, thereby increasing the metallic nature of the Ti_5Si_3 [12]. This phenomenon has been reported by several researcher in the case of $MoSi_2$, where Substitution of Si atoms in the $MoSi_2$ lattice by Al leads to replacement of covalent Mo–Si bonds by metallic Mo–Al bonds and enhance the ductility of $MoSi_2$ [18,19].

Zha et al. [16] have reported that Ti_5Si_3–$TiAl_3$ composite can be synthesized with SHS method by adding 10–40 wt.% Al To 5Ti + 3Si. They have suggested that Al not only serves as a diluent but also participates in the SHS reaction process. Rao and Zhou [20] and Vysa et al. [21] have undertaken an investigation to study Characterization of mechanically alloyed Ti–Al–Si powder blends and their subsequent thermal stability, and discovered that $TiAl_3$ and $TiSi_2$ were formed at lower temperature while $Ti_5(Al,Si)_3$, (Ti,-Si)Al and $(Ti,Si)_3Al$ achieved through a long-time annealing at high temperature.

In the present work nanostructured Ti_5Si_3 and Ti_5Si_3 based alloys and composites were synthesized by using mechanically activated powders prior to the SHS reaction and investigated the effect of replacement of Si by Al in a systematic manner and mechanical activation time on the microstructure, phase composition, ignition and combustion temperature of Ti_5Si_3 based alloys and composites.

2. Experimental

Elemental powders of Ti (98%, 150 μm), Si (99%, 150 μm) and Al (99%, 100 μm), were mixed according to the following formula:

$$5Ti + 3(1 - X)Si + 3XAl \quad (1)$$

where X = 0, 0.2, 0.4, 0.6. Then, the reactant powders were milled by a planetary ball mill unit with stainless steel cup and balls. Ball-to-powder weight ratio (BPR) of approximately 10:1 and rotation speed of 250 rpm were used during the milling. For preventing excess agglomeration some process controlling agent (PCA) was used. To prevent oxidation during the milling process the cup was evacuated and filled with pure argon gas. The milling process was interrupted at intervals of 3 and 6 h and small amounts of milled powder were taken for examination. This operation was performed in a glove box under argon atmosphere. Then the milled powders were pressed in a steel die at a pressure of about 300 MPa into pellets. The combustion reactions were carried out in a tubular furnace under a continuous flow of argon. The phase compositions of the milled powders and combustion products were characterized by XRD (Philips PW 3710) using Cu Ka radiation at 40 kV and 30 mA. All XRD experiments were performed with a step size of 0.02° and a stoppage time of 1 s per step. The XRD peak broadening was used to determine the crystallite size and lattice strain via the Williamson–Hall relation. The microstructure of products was investigated by scanning electron microscope (Vega/Tescan) equipped with an energy-dispersive spectrum (EDS) analyzer. Combustion temperatures were detected by a pyrometer (AS 101 C-TPS) which reports 10 data per second. Repeated measurements were conducted for three times, and errors were calculated about ±20 °C.

3. Results and discussion

3.1. XRD analysis

Fig. 1 shows the XRD patterns of as-received, milled and synthesized powders with composition of $Ti_{62.5}Si_{37.5}$ (X = 0). According to XRD patterns after 3 h milling the peaks are broadened and weakened significantly, due to reduction of crystallites size, and increasing the non-uniform lattice strain that is applied by mechanically impact. Further milling up to 6 h resulted to formation of small amounts of Ti_5Si_3 in milling stage. Indeed increasing milling time

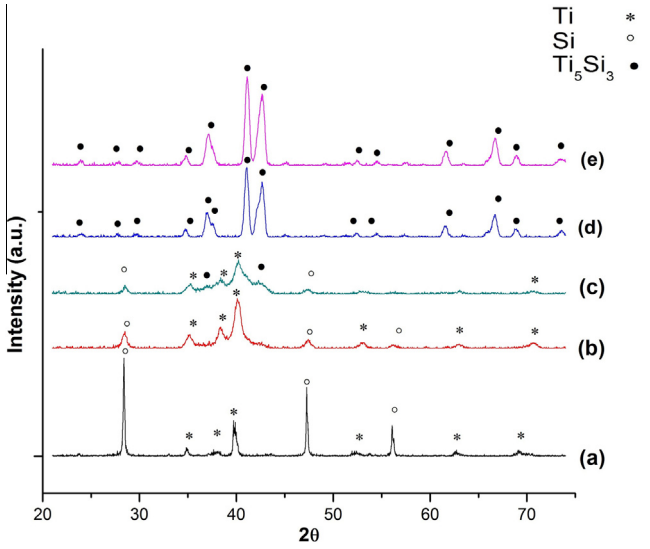

Fig. 1. XRD patterns of the X = 0 sample, (a) as-received powder, (b) 3 h milled, (c) 6 h milled, (d) synthesized after 3 h activation and (e) synthesized after 6 h activation.

caused a decreasing in crystallites size, enhancing the imperfections in the lattice and raising the temperature in the system, therefore diffusion is increased and formation of Ti_5Si_3 is accelerated. In the XRD pattern of synthesized samples after 3 and 6 h activation only Ti_5Si_3 peaks are identified. Fig. 2 shows XRD patterns of milled and synthesized powders with composition of $Ti_{62.5}Si_{30}Al_{7.5}$ (X = 0.2). As can be seen the Ti_5S_3 phase is not synthesized in milling stage even after 6 h. Indeed, Al is present in the mixture as a ductile phase while Si is present in the mixture as a brittle phase. In ductile–brittle components initially, ductile particles get flattened by the ball- powder- ball collisions, while the brittle particles get comminuted. These fragmented brittle particles tend to become occluded by the ductile constituents and trapped in the ductile particles, With further milling, the ductile powder particles get work hardened and refined [22]. In fact, Al can prevent of effective collisions between Ti and Si. In addition, still just Ti_5Si_3 peaks are identified in the diffraction pattern of

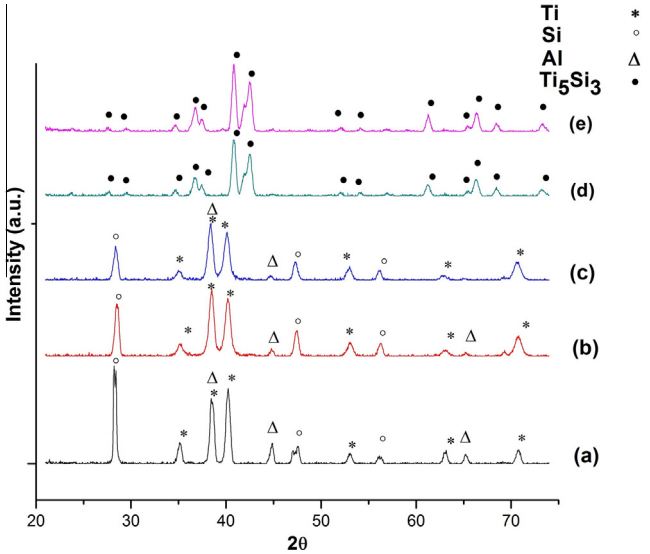

Fig. 2. XRD patterns of the X = 0.2 sample, (a) as-received powder, (b) 3 h milled, (c) 6 h milled, (d) synthesized after 3 h activation and (e) synthesized after 6 h activation.