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Original Research Paper

Mechanochemical synthesis mechanism of Ti_3AlC_2 MAX phase from elemental powders of Ti, Al and C

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ABSTRACT

In this study, the synthesis of Ti_3AlC_2 MAX phase in Ti–Al–C system was investigated by high-energy ball milling. To this aim, mixtures of Ti, Al and C with stoichiometric ratios were milled by a planetary ball mill for different milling times up to 10 h. The structural evaluation of powder particles, after different milling times, was studied by X-ray diffraction (XRD), scanning electron microscopy (SEM) equipped with energy-dispersive spectroscopy (EDS) and measurement of vial temperature. Thermodynamic investigations showed that direct reactions among elemental powders of titanium, aluminum, and carbon were strongly exothermic and the product phases were formed in a self-sustaining regime. The experimental result showed that after 10 h milling the elemental powders reacted together through a rapid combustion reaction process resulting in the formation of Ti_3AlC_2 and TiC. It was proved that mechanically induced self-propagating reaction (MSR) is dominant mechanism.

1. Introduction

Recently, a class of ternary layered compounds $M_{n+1}AX_n$ phases or MAX for short, where $n = 1, 2$ or 3, M is early transition metal, A is an A-group element (mostly groups 13 and 14), and X is C or N) has attracted much attention because of the unique combination of both metal- and ceramic-like properties such as high fracture toughness, high Young's moduli, high thermal and electrical conductivities, easy machinability, excellent thermal shock resistance, high damage tolerance, and microscale ductility [1]. Titanium aluminum carbide (Ti_3AlC_2) is a member of this family that possesses an unusual combination of properties. It combines the merits of both metals and ceramics. Like metals, Ti_3AlC_2 is thermal and electrical conductive, easy to machine with conventional tools, and resistant to thermal shock; like ceramics, it has high strength, high melting point and thermal stability. Those properties make Ti_3AlC_2 useful in many fields; for example, it can be used as a high-temperature structural material instead of expensive high-temperature alloys [2].

Over the past decades, several methods have been used to synthesize these materials. At first Pietzka and Schuster [3] synthesized Ti_3AlC_2 powders by sintering of cold-compacted powder mixture of TiAl, Al_4C_3 and carbon in pure hydrogen for 20 h. After that, different routes have been developed to fabricate these materials; namely, hot isostatic pressing (HIP) [4], self-propagation high-temperature synthesis (SHS) [5], hot pressing (HP) [6], combustion synthesis (CS) [7] and spark plasma sintering (SPS) [2]. All these methods required rigorous conditions such as high pressure, high temperature and long time.

Mechanochemical synthesis, chemical reactions induced by high-energy ball milling, is one of the promising routes for the synthesis of different classes of materials [8]. The mechanochemical reactions fall into two categories [9]; namely, (a) those which occur during the mechanical activation process and the reaction enthalpy is highly negative in them, and (b) those which occur during subsequent thermal treatment and the reaction enthalpy is only moderate in them. Whenever a reaction is highly exothermic, it can occur abruptly after a certain time of milling and, once started, it proceeds in a self-sustained way. In this case, the reaction requires a given time to begin. This time is called ignition time, and due to the exothermic reaction, it can be determined by an increase of temperature. This route also called mechanically induced self-propagating reaction (MSR) [9].

Jin et al. [10] used ball milling to synthesize Ti_3SiC_2 MAX phases. Yang et al. [11], Shi et al. [12], Zhu et al. [13] and Sadeghi et al. [14] synthesized successfully MAX phase in Ti–Al–C system by high energy ball milling. The main objective of this study is in

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detailed investigation of mechanochemical synthesis of Ti_3AlC_2 from elemental powders in high energy planetary ball milling.

2. Materials and methods

Commercially available powders of Ti (particle size <100 μm, 99.7% purity), Al (particle size <200 μm, 99.7% purity), and graphite C (particle size <200 μm, 99.7% purity) were used as raw materials to synthesize Ti_3AlC_2 MAX phases. These powders were weighed in a mole ratio according to the stoichiometric composition of Ti_3AlC_2 with Ti:Al:C = 3:1:2. Ball milling was performed in a planetary type ball mill using hardened chromium steel vial and balls under argon atmosphere. The milling was carried out with a ball-powder mass ratio of 10:1 and rotation speed of 450 rpm. The volume of cups was 250 cc and the diameter of balls were 10 mm. The phase analysis of the powders after milling was identified by X-ray diffraction (XRD, Philips PW-1800, Cu target, Kα radiation (40 kV and 30 mA)), a scanning step of 0.05° and time per step 1sec were also used. The particle size and morphology of samples were investigated by scanning electron microscope (SEM, JEOL JSM8A, japan) equipped with energy dispersive spectroscopy (EDS). The direct temperature measuring of the powders during ball milling was impossible. Therefore, during the ball milling, the mill was stopped at different milling times in order to measure vial temperature using a thermocouple.

3. Results and discussion

Since MAX-phase materials are relatively new, there is limited data in terms of the enthalpy of formation and specific heat capacities as a function of temperature, which is one of the reasons thermodynamic analysis of these materials has been limited to date. Barsoum [15] showed that the relationship below is a good approximation of Gibbs free energy change of formation of the ternary carbides. There is similar relationship for heat capacity.

$$\Delta G_f^{\circ}(M_{n+1}AX_n) = (n+1) \times \Delta G_f^{\circ}(MX) \quad (1)$$

Thus, for Ti_3AlC_2 Gibbs free energy change of formation is equal to three times of TiC Gibbs free energies of formation, which is given in the literature [16]. Ti, Al and C with stoichiometric composition react to give Ti_3AlC_2 according to the reaction (1).

$$3Ti + Al + 2C \rightarrow Ti_3AlC_2 \quad \Delta G_f^{\circ}(Ti_3AlC_2) = -549150 + 30.25T \quad (j) \quad (2)$$

$$\Delta G_{298}^{\circ} = -540135.5\ \mathrm{J/mol} \quad \Delta H_{298}^{\circ} = -549150\ \mathrm{J/mol}$$

This reaction can thermodynamically occur during milling in room temperature due to its negative free energy change. ΔH°_{298} value for the reaction indicates that this reaction is highly exothermic.

For a reaction to be self-propagating, Merzhanov [17] has shown an empirical relation stating that the combustion wave can be self-sustaining if adiabatic temperature (T_{ad}) $T_{ad} > 1800$ K, which also corresponds to the condition $\Delta G_r^{298\ K}/c_p^{298\ K} \geqslant 2000$ K in which c_p is heat capacity [18]. In addition, Schaffer and McCormick [9] showed that if $T_{ad} > 1300$–1800 K, the reaction will be self-sustained during milling and in MSR mode. In this study, the authors considered a self-sustained reaction between solid reactants of titanium, aluminum and carbon to form Ti_3AlC_2 according to Eq. (2). The value of T_{ad} is calculated by assuming that the exothermic enthalpy of the reaction is used to heat up the products with the assumption of no loss of heat to the surrounding environment although in reality some heat will always be lost.

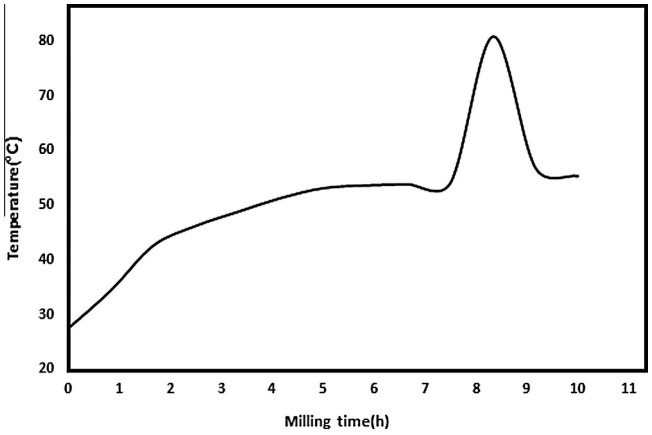

Fig. 1. Temperature variation of vial as a function of milling time.

From the thermodynamic calculation, the adiabatic temperature, T_{ad}, is 3643 K and, therefore, greater than 1800 K. Thus, the reaction expected to undergo self-sustaining self-propagating high temperature synthesis reaction. Fig. 1 shows the vial temperature variation with milling time. The variation of temperature of vial during ball milling can provide a future insight into the reaction mode. As seen, after 8.33 h of milling time, the temperature of vial increased rapidly suggesting a combustion reaction between Ti, Al and graphite. This can be expected from the adiabatic temperature, T_{ad}, for the reaction. The combustion reaction is promoted by dynamically maintained high Ti/Al/C interface areas, as well as the short-circuit diffusion path provided by increasing number of defects such as dislocations and grain boundaries induced during ball milling [19].

Fig. 2 shows the XRD pattern of Ti, Al and C powder mixture at different milling times. The diffraction peak of as-received powder mixture without milling or 0 h milling includes the peaks of initial powder elements. After 3 h milling the peaks of C disappear. The disappearance of graphite peaks could indicate that graphite particles were heavily deformed and fractured into fine slices. The brittle behavior of graphite after 3 h of milling may make the grain size decrease significantly. After 5 h milling, there is no significant reaction between the reactant elements and almost no new phase appearing except a decrease of Ti and Al peaks intensity. Broadening and decreasing the intensity of diffraction peaks of Ti and Al phases resulted in the reduction of the average crystallite size, buildup of defects and formation of internal strains. Finally, after 10 h milling the peaks of initial powders disappeared, those of Ti_3AlC_2 and TiC were observed, and Ti_3AlC_2 was the main phase. In fact, in addition to Ti_3AlC_2 some TiC phase was formed, which was reported in the previous works [11,13]. When the mechanical alloying carried out for a certain activation time, particle size was reduced and components were mixed thoroughly with increasing the number of chemically active defect sites, the MSR may be induced and completed quickly. As the milled powders reached a defined critical size, the diffusion distance decreased and a large surface area was formed, which contributed to the occurrence of a combustion reaction. The practical reactions in MSR may be very complicated, and once the reaction is ignited, the reacting time only maintained for several seconds. In fact, in spite of reaction (2), some parallel reactions could occur as reaction (3)

$$Ti + C \rightarrow TiC \quad (3)$$