Journal of Alloys and Compounds 566 (2013) 191–195

Contents lists available at SciVerse ScienceDirect

Journal of Alloys and Compounds

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

Kinetics and microstructure evolution of Ti_2SC during in situ synthesis process

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ARTICLE INFO

Article history:
Received 14 January 2013
Received in revised form 4 March 2013
Accepted 9 March 2013
Available online 19 March 2013

Keywords:
Ti_2SC
Reaction synthesis
Activation energy
Densification

ABSTRACT

Using in situ reaction method, we have studied the sinter process of the layered ternary Ti_2SC with Ti, TiS_2 and C powders as initial materials. By XRD and thermodynamic calculations we know that Ti_2SC is the final result of the reaction between TiS and TiC. TiS is an important intermediate which is more possible the result of TiS_2 and Ti rather than the decomposition of TiS_2. DSC curves are used to investigate the reaction kinetics of the whole sintering process. By Kissinger and Ozawa method the activation energy are separately calculated to be 125.4 kJ/mol and 134.9 kJ/mol. We also have observed the grain growth and densification process of bulk sample by SEM.

1. Introduction

A series of nanolaminated ternary carbides and nitrides, widely referred to as so called $M_{n+1}AX_n$ phase ($n = 1$, 2 or 3), where M is a transition metal, A is an element from column 13 to 16 in the periodic table, and X represents either carbon or nitrogen, has attracted much attention due to its unique structural characteristics [1,2]. The crystal structure of this kind of MAX phases can be described as a stacking of near-close-packed transition metal carbide/nitride layers interleaved with layers of pure A-group elements. It is the presence of this structure that endows these solids with a unique combination of metallic and ceramic properties. They are readily machinable but elastic stiffness, are good thermal and electrical conductors, and are the only known polycrystalline compounds that deform by a combination of kink bands within individual grains and shear bands which are crucial for its potential application [3–9].

Ti_2SC as a member of S-containing MAX phases has the lowest c/a ratio of M_2AX compounds [2,10]. So it is reasonable to believe this compound exhibits unusual properties. Based on the first-principles calculation, Ti_2SC has high bulk modulus and hardness ascribed to the strong Ti–S hybridization, which is an extraordinary example in the MAX phases studied so far [11–13]. Experiments confirm that Young's modulus of Ti_2SC is one of the highest reported for a M_2AX phase and its Vickers hardness is at 8 ± 2 GPa [14] higher than the vast majority of MAX phases for which the hardness is more in the range of 2–4 GPa [3,5,15,16]. Other research identify that Ti_2SC has the highest room temperature thermal conductivity (60 W/mK) [17] up to date measured and its structural is stable with no phase transformation even under nearly 50 GPa [18], similar to other MAX phases [19–23].

However, unlike other MAX phases, there are seldom reports about synthesis details of Ti_2SC. All the bulk sample are obtained by hot pressing Ti_2SC powder [14,17,18,24–26]. As we known, one of the most important fabrication methods for bulk MAX phases is hot pressing from a powder mixture. To the best knowledge of the authors, we first fabricate bulk Ti_2SC with in situ/hot press method. In addition, it is important to understand the formation of MAX-phase microstructures because MAX-phases frequently coexist with phases such as M–A intermetallic compound, M–X or A–X binary compounds which are intermediate products of their synthesis [27,28]. The existing of these phases largely influences the application of compounds. For Ti_2SC, when heated in Ar atmosphere, it dissociates into TiS_2 which is an MA compound [25], not like other MAX phases to be MC and the A-rich liquid [2]. So in this paper, we tried to use TiS_2 as a main raw material to investigate the reaction path of Ti_2SC formation. DSC behavior of raw material had also been used to investigate the reaction kinetics of the whole sintering process. In addition, as Ti_2SC was expected to its mechanical behavior, and microstructure did play a significant role in determining it, so we finally observed the densification process of bulk Ti_2SC by SEM.

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http://dx.doi.org/10.1016/j.jallcom.2013.03.032

2. Experimental

Commercial powders of Ti (Alfa Aesar, 99.5% purity, 100–300 m), S (Sigma–Aldrich, 5–20 m), and C (Alfa Aesar, graphite, 5–10 m) were used as starting materials. First, TiS_2 powder was obtained by mixed Ti and S powder with molar ratio of 2:1 which was pressed into thin disks, heated to 650 °C and maintained for 10 h in the vacuous quartz tubes. Then the as-received Ti, TiS_2, C power with molar ratio of 3:1:2 were weighed and ball-milled for 24 h. The green compacts were separately sintered pressureless and hot pressed under 30 MPa at different temperatures in the range 1000–1600 °C for 2 h in a flowing Ar atmosphere.

The synthesis samples were examined by X-ray diffractometer (Bruker D8 Advance, Germany) with Cu $K\alpha$ radiation. The TG–DSC was performed with a NETZSCH DSC thermogravimetric analyser (TA449c/3/G, Germany) to analyze the reaction kinetics. About 10 mg Ti/TiS_2/C mixed powder was used for testing and the heating temperature range was from room temperature to 1500 °C at heating rates of 10, 20 and 30 °C/min under flowing Ar. The measurement was carried out in argon flow at the rate of 10 ml/min. The microstructures of synthesized bulk Ti_2SC were observed by a scanning electron microscopy (JSM, 5610LV, Japan).

3. Results and discussions

3.1. Reaction synthesis of Ti_2SC

Fig. 1 showed X-ray patterns of samples synthesized in the temperature range of 1000–1600 °C. By XRD, we could analysis the phase changes in the studied Ti–TiS_2–C system. For the first sample sintered at 1000 °C, Ti was the main phase and little TiS_2 existed. Moreover, we could observe the presence of the peak of TiS and TiC. The reaction between Ti and C lead to the formation of TiC:

$$Ti + C \rightarrow TiC \tag{1}$$

However, there were two possible reaction paths to form TiS, as expressed below:

$$TiS_2 \rightarrow TiS + S \tag{2}$$

$$TiS_2 + Ti \rightarrow 2TiS \tag{3}$$

As temperature was increased to 1200–1400 °C, a small amount of Ti_2SC was detected, whereas the content approximately constant, indicating that no more external drive force to make Ti_2SC formation. In this temperature range, TiS was determined as the predominant phase, together with the increase of TiC content. Ti and TiS_2 phases were no more detected which were possibly consumed to produce TiC and TiS. When the temperature increased up to 1600 °C, the main crystalline phase was Ti_2SC. Little TiC and TiS existed as the impurity. We noted that Ti_2SC formation was accompanied by the decline of TiS and TiC. So it was reasonable to propose that TiS and TiC were the intermediate phases intimately involved in the formation of Ti_2SC. The Ti_2SC formation could be expressed by the following reaction:

$$TiS + TiC \rightarrow Ti_2SC \tag{4}$$

As we known, intermetallic MA is crucial to the MAX formation, so was the situation of Ti_2SC based on above analysis. The only problem was which reaction was the path of TiS formation.

By calculating changes in Gibbs free energy with thermochemical data we can determine the feasibility of reaction. As a first approximation, the standard free of formation of the Ti_2SC is two times those of the TiC [2]. The thermodynamic data of the other compounds can be obtained from [29,30]. So we plotted the free energy of formation changed of corresponding above four reactions by temperature, as showed in Fig. 2.

From Fig. 2, we could see that the calculation supported the proposed TiC formation reaction ($\Delta G < 0$). For the key TiS formation path, the reaction Eq. (3) was thermodynamically favorable ($\Delta G < 0$), confirming the feasibility of proposed reaction, just the opposite of reaction Eq. (2). So Ti and TiS_2 was more possible be responsible for the generation of TiS. This judgment was in good agreement with the other research. Thermal stability study of Ti_2SC in Ar atmosphere showed that they dissociated into TiS_2 starting at ≈400 °C. On further heating, above ≈650 °C, the amount of Ti_2SC was found to increase again [25]. No TiS phase was found, thus confirming that TiS_2 was not easy to dissociate to TiS. Finally, we noted that Eq. (4) was also thermodynamically unfavorable. But as the curve showed, ΔG decreased significantly with the rise of temperature, and near to zero at 1600 °C. Apparently temperature was important for the Ti_2SC formation. Considering the value of Ti_2SC thermochemical data was estimated, it somehow affected the calculation accuracy. Besides, the mixed powder was pressed at 30 MPa to the green compact before sintering, internal pressure may be the extra driving force to the reaction. Based on these, we thought the reaction (4) was the path to Ti_2SC formation, as showed in XRD.

3.2. Non-isothermal kinetics

In order to investigate the reaction dynamics during the whole sintering, differential scanning calorimetry curves were used. Kissinger [31,32] and Ozawa [33,34] methods were adopted to calculate the activation energy of the reaction.

The three formulas listed below were basic principles:

$$\text{The mass action law}: \ d\alpha/dt = k(1-\alpha)^n \tag{5}$$

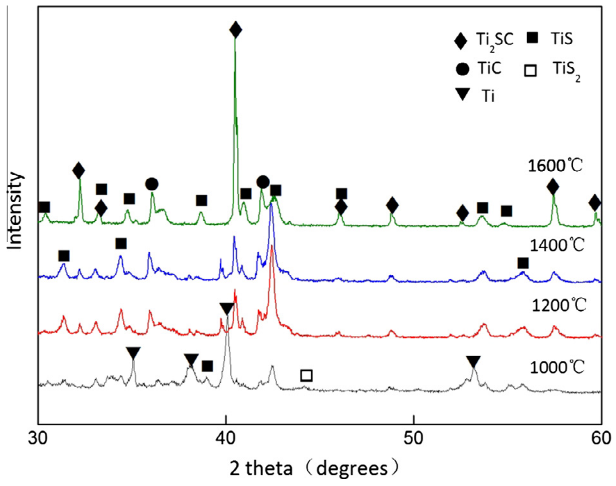

Fig. 1. X-ray patterns of $3Ti/TiS_2/2C$ mixed powders pressureless sintered at 1000 °C, 1200 °C, 1400 °C and 1600 °C.

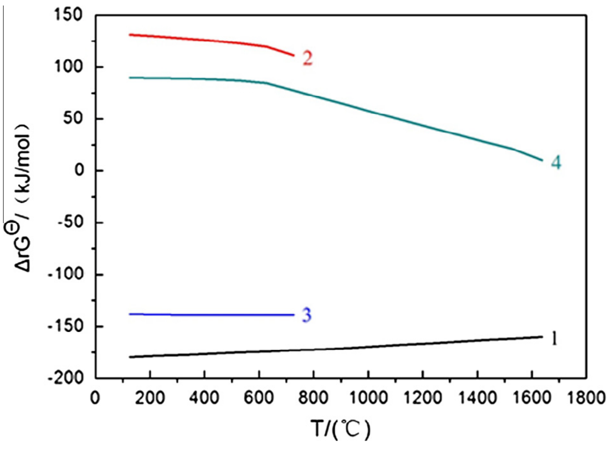

Fig. 2. Free energy of formation changed by temperature.