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Synthesis of Ti_3AlC_2 MAX-Phase with Different Content of B_2O_3 Additives

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The MAX-phase Ti_3AlC_2 has been fabricated by sintering of the preliminary cold-pressed mixtures of elemental powders of Ti, Al and C with different contents of B_2O_3 under pressure of 320 and 640 MPa, respectively. Identification and quantification of the phases have been performed by X-ray diffraction. It has been shown when we increase concentration of boron oxide up to 5% wt. in the initial $\text{Ti}_3\text{Al}_{1.1}\text{C}_2$ powder mixture cold-pressed at 320 MPa the percentage of the MAX-phase Ti_3AlC_2 in the pellets after sintering rises up to ~98.5% wt. It has been found that at the high compacting pressure of 640 MPa, the fraction of the MAX-phase Ti_3AlC_2 in the sintered pellets also abruptly increases up to ~98% wt. In this instance the boron oxide amount added to the initial powder mixture before pressing was low as 1% wt. Thus, it has been found that there is a clear relationship between the percentage of boron oxide in the initial powder mixture, pressing pressure and percentage of the MAX-phase after sintering, *i.e.* the higher compacting pressure the less amount of the boron oxide should be added to the initial powder mixture to achieve high yield of MAX-phase.

Key words: MAX-phase, ball-milling, XRD, Ti_3AlC_2 , boron oxide.

MAX-фаза Ti_3AlC_2 синтезована в результаті спікання попередньо скомпактованої суміші елементарних порошків Ti, Al і C з різним вмістом B_2O_3 при тисках 320 і 640 МПа. Показано, що для синтезу практично чистої MAX-фази при тиску компактування 320 МПа вихідних порошків опти-

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мальний вміст окису бору в композиті становить 5% ваг. Для отримання фази Ti_3AlC_2 при збільшенні тиску до 640 МПа достатньо 1% ваг. оксиду бору. Встановлено, що існує чітка залежність між відсотком оксиду бору у вихідній порошковій суміші, тиском компактування та вмістом МАХ-фази в отриманих компактах після спікання — чим вищий тиск компактування, тим меншу кількість оксиду бора необхідно додати до вихідної порошкової суміші для досягнення високого вмісту МАХ-фази в композиті.

Ключові слова: МАХ-фаза, механоактиваційна обробка, рентгеноструктурний аналіз, Ti_3AlC_2 , оксид бору.

МАХ-фаза Ti_3AlC_2 синтезована в результаті спекання суміси елементарних порошків Ti, Al і С з різним вмістом B_2O_3 , попередньо скомпактированої при тисках 320 і 640 МПа. Показано, що в результаті попереднього компактирования вихідних порошків при тиску 320 МПа для синтезу практично чистої МАХ-фази оптимальне масове вміст оксиду бора становить 5% мас. Для отримання фази Ti_3AlC_2 при збільшенні тиску до 640 МПа достатньо 1% мас. оксиду бора. Встановлено, що існує чітке співвідношення між процентним вмістом оксиду бора в вихідній порошковій суміші, тиском пресування і вмістом МАХ-фази в отриманих компактах після спекання — чим вище тиск компактирования, тим менше кількість оксиду бора необхідно додати до вихідної порошкової суміші для досягнення високого вмісту МАХ-фази в композиті.

Ключевые слова: МАХ-фаза, механоактивационная обработка, рентгеноструктурный анализ, Ti_3AlC_2 , оксид бора.

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1. INTRODUCTION

Nowadays, ternary carbides/nitrides with general formula $M_{n+1}AX_n$, where $n = 1, 2$ or 3 , M is an early transition metal, A is an A-group element, and X is C and/or N [1, 2], known as MAX-phases, have received considerable interest due to their unique set of chemical, physical, electrical, and mechanical properties. The MAX-phases crystallize in hexagonal structures with space group of $P63/mmc$ [3]. These phases combine of both ceramics and metals properties. On the one hand, like to metals, MAX-phases have high thermal and electrical conductivities, are easily machined by conventional tools without lubrication, are fatigue-resistant and are resistant to thermal shock. On other hand, like ceramics, they present a high strength, high melting point and thermal stability, and good oxidation resistance. Due to these unique properties mentioned above, MAX-phases could be applied in various fields of industry: catalyst for improving the reversible hydrogen storage properties of MgH_2 [4], protective coatings [5–7], high-

temperature materials [8], materials for lead-cooled fast reactors [9] and electrical contact materials [10, 11].

MAX-phases could be fabricated through a variety of processing techniques: hot isostatic pressing (HIP), slip casting (SC), spark plasma sintering (SPS) [12], hot pressing (HP), self-propagating high-temperature synthesis (SHS), mechanical alloying (MA) [13]. The most promising approach to obtain MAX-phases consists in sequential applying HP method [14, 15]. However, this method includes complex technological processes such as high pressure and high temperature. The some methods of synthesis are characterized by multiple stages. Typically, a relatively small amount of Al_3Ti , TiAl , and Ti_3Al phases always are formed simultaneously with MAX-phase [16].

In the work of Peng and all [17] proposed a new method to synthesize high-purity Ti_3AlC_2 bulk material by hot-pressing through adding a little amount of B_2O_3 as a low-temperature aid. It was found that additive of B_2O_3 weakens the reaction between the powders of Ti, Al, and C. It results in increase of the amount of Ti_3AlC_2 phase in the sample. In their later work, the authors argue that the proposed method is not stable and does not lead to repeatability of the results [18].

In our paper we investigated effect of the B_2O_3 percentage and variety of compacting pressure on the formation of the MAX-phase Ti_3AlC_2 during sintering of preliminary mechanically activated elemental powders.

2. MATERIALS AND METHODS

Two types of samples were prepared for the study. In the first case, the samples were prepared from a commercially available spectroscopic graphite powder, aluminium and titanium ones. The raw powders were mixed by Ti:Al:C atomic ratio of 3:1.1:2. In another case to the above mentioned powder mixture 1, 3 and 5% wt. of boron oxide (B_2O_3) was added, respectively. Powders have been homogenized by planetary ball milling (Fritsch Pulverisette P-6) during 1 hour. The rotational speed of the vial (200 rpm) and the ball-to-powder ratio (10:1) were kept constantly in the all experiments. To prevent the powders from oxidation after ball milling all samples were handled in the glove box filled by purified argon (99.998%) and stored in the argon filled small containers. The preliminary homogenized powder blends were compacted at two values of pressure: 320 and 640 MPa, respectively. The pressed pellets were sintered in an argon gas atmosphere at 1400°C during 1 hour.

The phase analysis of the sintered samples was performed by XRD. X-ray diffraction patterns were recorded using a powder diffractometer (HZG-4A) in the Bragg–Brentano geometry with CoK_α radiation. Data were collected in the 2θ range of 5°–90° with a step interval of

0.05° and a count time 5 s per step. Rietveld refinement of the XRD patterns was performed by the MAUD software [19]. Scanning electron microscopy studies of bulk materials were performed on a JEOL JSEM IT-300 microscope with EDS attachment.

3. RESULTS AND DISCUSSION

The powders $\text{Ti}_3\text{Al}_{1.1}\text{C}_2$ were homogenized, cold-pressed under 320 MPa and sintered at 1400°C during 1 hour. The XRD patterns of powder mixture $\text{Ti}_3\text{Al}_{1.1}\text{C}_2$ after homogenization and subsequent sintering are shown on Fig. 1. There are sharp peaks only on diffraction pattern of the initial mixture (Fig. 1, *a*).

These peaks are attributed to carbon, titanium and aluminium phases. We can see the more significant differences between the XRD patterns of initial mixture and bulk material (Fig. 1, *b*). The peak of carbon is at typical position but peaks associated with Al and Ti entirely disappeared. At the same time titanium carbide TiC phase and small amount of the Ti_3AlC_2 MAX-phase are formed. The Rietveld refinement shows that the synthesized material contains 45.1, 44.6 and 10.3% wt. of graphite, titanium carbide and Ti_3AlC_2 MAX-phase, respectively. Increasing the compaction pressure to 640 MPa does not causes to an increase in the MAX-phase content (Fig. 1, *c*). There are some impurity phases such as TiC, graphite, Ti_2AlC , Ti_3AlC , and Ti_3Al in the samples.

Fig. 1. XRD patterns of the homogenized mixture $\text{Ti}_3\text{Al}_{1.1}\text{C}_2$ (*a*), cold-compact material under 320 MPa (*b*), and 640 MPa (*c*) with following sintering at 1400°C for 1 hour.

The XRD patterns of $\text{Ti}_3\text{Al}_{1.1}\text{C}_2$ powder mixtures with a different percentage of boron oxide B_2O_3 cold-compacted at 320 MPa and sintered at 1400°C following 1 hour are shown on Fig. 2. It should be immediately noted that all sintered samples have diffraction peaks whose positions are very close to those of the Ti_3AlC_2 MAX-phase and TiC phase. The phase composition is strongly affected by the concentration of boron oxide added to the initial powder blend. Accordingly to Rietveld refinement, it was found that $\text{Ti}_3\text{Al}_{1.1}\text{C}_2 + 1\%$ wt. B_2O_3 sintered powder mixture contains 43.4% wt. of Ti_3AlC_2 MAX-phase and 56.6% wt. TiC (Fig. 2, *a*). The domains sizes are 34 and 162 nm, respectively. When the B_2O_3 percentage was increased up to 3% wt. (Fig. 2, *b*), the content of Ti_3AlC_2 phase after sintering also increased to 73.9% wt. At the same time the amount of TiC decreases to 26.1% wt. The crystalline domain sizes for Ti_3AlC_2 MAX-phase and titanium carbide TiC in this case are 54 and 218 nm, respectively. Further increase of boron oxide concentration up to 5% wt. promoted increasing the content of the MAX phase Ti_3AlC_2 (Fig. 2, *c*). There are 98.5% wt. Ti_3AlC_2 and 1.5% wt. TiC in the synthesized material. Therefore the amount of the MAX-phase in the preliminary compacted and sintered pellet under these technical conditions (pressure 320 MPa and sintering temperature 1400°C during 1 hour) is strongly affected by the content of B_2O_3 .

In this paper, consolidation pressure impacts on the MAX-phase Ti_3AlC_2 formation in the powder mixtures with different contents of

Fig. 2. XRD patterns of the mixture $\text{Ti}_3\text{Al}_{1.1}\text{C}_2 + 1\%$ wt. B_2O_3 (*a*), $\text{Ti}_3\text{Al}_{1.1}\text{C}_2 + 3\%$ wt. B_2O_3 (*b*), and $\text{Ti}_3\text{Al}_{1.1}\text{C}_2 + 5\%$ wt. B_2O_3 (*c*), cold-compacted under 320 MPa and sintered at 1400°C for 1 hour.

Fig. 3. XRD patterns of the mixture $\text{Ti}_3\text{Al}_{1.1}\text{C}_2 + 1\%$ wt. B_2O_3 (a), $\text{Ti}_3\text{Al}_{1.1}\text{C}_2 + 3\%$ wt. B_2O_3 (b), and $\text{Ti}_3\text{Al}_{1.1}\text{C}_2 + 1\%$ wt. B_2O_3 (c), cold-compacted under 640 MPa and sintered at 1400°C for 1 hour.

boron oxide were also studied. The XRD patterns of the compacted at 640 MPa and subsequently sintered samples are shown on Fig. 3. It could be seen from the XRD pattern, the higher pressure promotes to more amount of the MAX-phase Ti_3AlC_2 in the samples after consolidation and subsequent sintering. The regardless of the concentration of boron oxide, the resulting samples contain ~98% wt. of Ti_3AlC_2 phase and ~2% wt. TiC phase.

The key and important point of this work is the synthesis of the MAX-phase without the prior compacting of the homogeneous mixture $\text{Ti}_3\text{Al}_{1.1}\text{C}_2 + 5\%$ wt. B_2O_3 at high pressures. The non-compacted powder mixtures were put asleep in a graphite crucible and sintered at a temperature of 1400°C for 1 hour in argon gas atmosphere. There are ~95% wt. of Ti_3AlC_2 MAX-phase and ~5% wt. of TiC (Fig. 4, a) in the samples. Thus, at addition of 5% wt. boron oxide, the synthesis of the Ti_3AlC_2 MAX-phase occurs without high pressures impose. The sample obtained in the same conditions without the addition of boron oxide contains graphite, titanium carbide and Ti_3AlC (Fig. 4, b).

To get the distribution of the elements in the sintered samples, the EDS mapping of elements was carried out. Fig. 5 presents SEM image and elements distribution map. It is clear, the titanium and oxygen are uniformly distributed over cross section of the sample. At the same time, we can see the non-uniform distribution for boron, carbon and aluminium. Also, it can be observed the areas with a higher concentration of boron like a bright spots (see Fig. 5, b) on the EDS map.

Fig. 4. XRD pattern of the mixture $\text{Ti}_3\text{Al}_{1.1}\text{C}_2 + 5\% \text{ wt. B}_2\text{O}_3$ (a) and $\text{Ti}_3\text{Al}_{1.1}\text{C}_2$ (b) sintered at 1400°C for 1 hour.

In contrast to boron, there are the dark spots on the EDS maps for carbon and aluminium. These dark spots on the Fig. 5, c and Fig. 5, e mean lower concentration of carbon and aluminium. It is noteworthy that the bright spots on the boron EDS map (Fig. 5, b) and the dark spots on the EDS maps for the carbon and aluminium are overlapped. So, when we superimpose the EDS mapping results with the SEM image, we may most probably attribute the dark spots (Fig. 5, a) to the boron particle. Perhaps during the sintering process, a partial reduc-

Fig. 5. Typical SEM micrographs of composite $\text{Ti}_3\text{Al}_{1.1}\text{C}_2 + 5\% \text{ wt. B}_2\text{O}_3$ (a) and element distribution maps: B (b), C (c), O (d), Al (e), Ti (f).

tion of a small amount of the boron oxide to boron occurs.

4. CONCLUSION

The MAX-phase Ti_3AlC_2 has been synthesized by sintering of preliminary cold-compacted powder mixtures of $\text{Ti}_3\text{Al}_{1.1}\text{C}_2 + \text{B}_2\text{O}_3$. It was found that by varying the composition of the initial powder mixture $\text{Ti}_3\text{Al}_{1.1}\text{C}_2 + \text{B}_2\text{O}_3$ (where B_2O_3 content is 1, 3 or 5% wt.) and the compression pressure, it is possible to significantly increase the amount of MAX-phase in the sintered samples. It was also shown that at increase in the percentage of boron oxide in the initial powder mixture up to 5%, the amount of MAX phase in the sintered sample reaches 98% even without precompaction of the initial powder mixture. Thus, it can be assumed the maximal yielding of the MAX-phase in the sintered samples crucially depends from two factors—percentage of the boron oxide in the initial powder blend and compacting pressure. The higher compacting pressure, the less amount of the boron oxide should be added to the initial powder mixture to achieve high yield of MAX-phase.

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