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НАЦИОНАЛЬНАЯ АКАДЕМИЯ НАУК РЕСПУБЛИКИ
АРМЕНИЯ

Հայաստանի քիմիական հանդես 66, №1, 2013 Химический журнал Армении

ОБЩАЯ И ФИЗИЧЕСКАЯ ХИМИЯ

THE EFFECT OF AL EXCESS ON SHS/ PHIP OF CERAMIC COMPOSITES USING ILMENITE CONCENTRATE

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In order to increase the hardness and other mechanical characteristics of the composites produced through the SHS/PHIP process using ilmenite and Al as precursors, and the conversion of Fe to FeAl in the product, additional Al, in comparison to the stoichiometric amount, was used. After performing a number of experiments, the green mixture with a 50% addition of Al to the stoichiometric amount was chosen as optimal. The results of XRD and microstructural analyses with SEM and EDS methods show that the product is a composite consisting of TiC, TiB_2, FeAl, Al_2O_3, as well as metastable $Al_{86}Fe_{14}$ phase. Hardness and fracture toughness of this composite measured by the Vickers indenter method, as well as density measured by the ASTM C GO7 method show that the product is a lightweight composite with very high hardness and toughness, in comparison to conventional ceramics. Moreover, no sign of rusting and oxidation was observed on the surface of the product in an aquatic environment.

Fig. 6, tabl. 1, ref. 8.

Introduction

Ceramic composites containing aluminium oxide, boron carbide, and titanium diboride can produce unique mechanical properties which make them appropriate for different applications of high wear resistance, high toughness, high melting point, high thermal shock resistance, and relatively low density. Some of the applications of this type of composite are cutting tools, drawing dies, hardface mechanical sealing, military light weight ceramics (armor), and other wear-resistance components [1-2]. Production of these ceramics and composites using hot isostatic pressing (HIP), hot pressing and conventional sintering is costly because of the facility intensive and time intensive nature of these processes [3]. Moreover, the low fracture toughness (K_{IC}) of these materials can limit their use in specific applications alone. One of the most effective methods for increasing fracture toughness (KIC) is the process, in which a binder with appropriate toughness is used for connecting other components [4]. Ilmenite concentrate ($FeTiO_3$) has the potential of being the main raw material for producing of multi-ceramic composite with high toughness, fracture toughness and low price. As a result of aluminathermic reduction Ti can cause the formation of titanium diboride (TiB_2) and titanium carbide (TiC). Moreover, and Fe, alone or as an intermetallic component FeAl, can act as a binder appropriate for high fracture toughness [5]. In the present study ilmenite concentrate powder (Kohnoj mines, Iran), as well as Al powder and a low percentage of B_4C powders were used as raw materials. Moreover, for the production of a dense multi-ceramic composite, self-propagating high-temperature synthesis (SHS) or combustion synthesis (CS), combined with the pseudo hot isostatic pressing (PHIP) were used. The latter have certain benefits, such as high energy efficiency, reduction of production time, high purity of products due to evaporation of volatile impurities during high temperature reaction, and the relative simplicity of the process and equipment used [1-3].

The main reaction of this process is:

$$3\,FeTiO_3 + B_4C + 6Al \rightarrow 3Al_2O_3 + 2TiB_2 + TiC + 3Fe \qquad (1)$$
$$P=1\text{-}10\text{ atm}\quad T_{ad} = 2500\text{ K}$$

To change Fe into FeAl, Al was increased by 50%, more than the Al of the above reaction, and it is expected that the following reaction be gained:

$$3\,FeTiO_3 + B_4C + 9Al \rightarrow 3Al_2O_3 + 2TiB_2 + TiC + 3FeAl \qquad (2)$$
$$P=1\text{-}10\text{ atm}\quad T_{ad} = 2325\text{ K}$$

The abovementioned values of adiabatic combustion temperature were calculated using ISMAN-THERMO software [6].

Experimental

In the current study the following raw materials were used:

Ilmenite concentrate with 81% content of $FeTiO_3$ (considering the XRF analysis in table 1) and mean particle size of 15 *µm*;

B_4C powder with 95% purity and particle size of less than 10 *µm*;

Aluminium powder with 99% purity and mean particle size of 20 *µm*.

Considering reaction 2 and the purity of the used ilmenite, the necessary quantities of the above powders were prepared and were completely dried in an oven in 80 ± 5^oC for 20 *hours*. Then the prepared powder mixture was milled for 7 *hours* under rotation speed of 60 *rpm* in a ball mill with a 200 *mm* diameter and 150 *mm* length. The ball to powder weight ratio was 25 and ball with diameter 5-15 *mm* [7]. 60 *grams* of the milled powder were compacted into disc-shaped tablets of 50 *mm* diameter and 14mm height, with a hydraulic press at 5 *MPa* pressure. This weight and pressure were gained by a number of experiments in order to achieve a portable tablet without cracks or other apparent defects [7]. The produced tablet was transferred to a SHS/PHIP system like a schematic figure (1). This system is designed in a way that the dust and gases resulting from combustion and inclusions can easily exit from the sand surrounding the tablet during combustion and compression. During compression the sand plays the role of isostatic transmission of power to the tablet [7]. By adjusting pressure, delay time, and the time of compression, a number of samples were produced, the best result of which, for an intact sample without cracks and sufficient strength, was gained with 100 *MPa* pressure, 10 *seconds* delay time, and 10 *seconds* time of compression. In order to avoid thermal shock to the synthesized samples, these samples were transferred to a furnace with 1000^{o}C temperature after synthesis and then were cooled with 2^{o}C /*min* speed [7].

Table 1: ***XRF chemical analysis of ilmenite***

compound	Wt.%
Al_2O_3	1.38
MgO	0.37
CaO	2.16
Fe_2O_3	47.64
TiO_2	42.59
SiO_2	5.61
Na_2O	0.02
K_2O	0.04
SO_3	<0.05

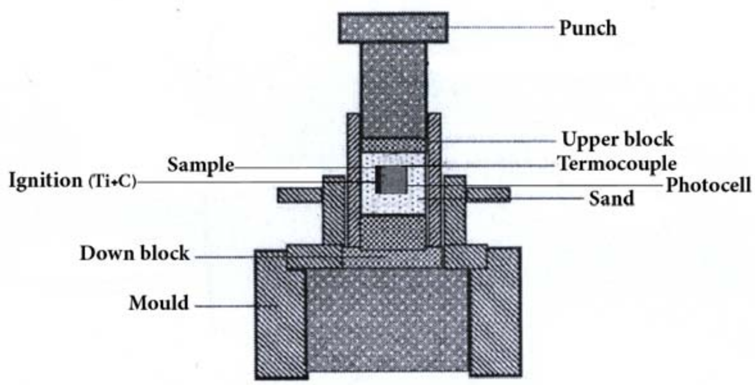


Figure 1. The scheme of the SHS/PHIP experimental set up.

Results and discussion

1. Phase constituents of combustion synthesized product.

Figure 2 shows the X-ray diffraction pattern of synthesized sample, in which FeAl, Al_2O_3, TiB_2, TiC phases are clearly visible. Note that the semi-stable $Al_{86}Fe_{14}$ phase is present in the products too. Furthermore, there are no characteristic peaks of the initial reactants, namely ilmenite, B_4C, and Al, in the product. It should be taken into consideration that since ilmenite used in this synthesis has a 81% purity, a certain additional amount of ilmenite has been added to the stoichiometric amount of reaction 2 [7].

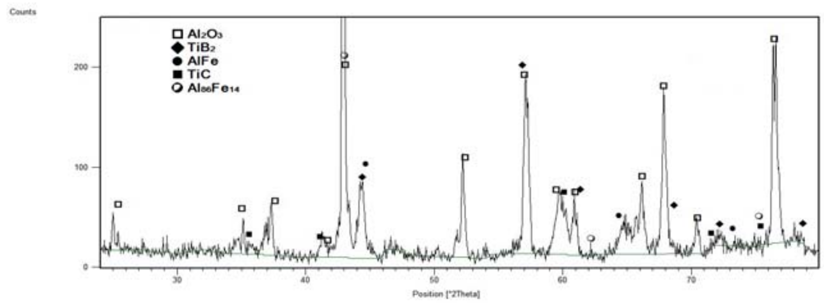


Figure 2. XRD pattern of the synthesized product.

2. Microstructure of combustion synthesized $Al_2O_3/TiB_2/TiC/AlFe$ composite.

The study of microstructure by scanning electron microscopy (SEM) equipped with an EDS (energy disperse spectrometry) detector confirms the results of the formation of the TiB_2, TiC, Al_2O_3, and FeAl compounds (figures 3, 4 and 5).

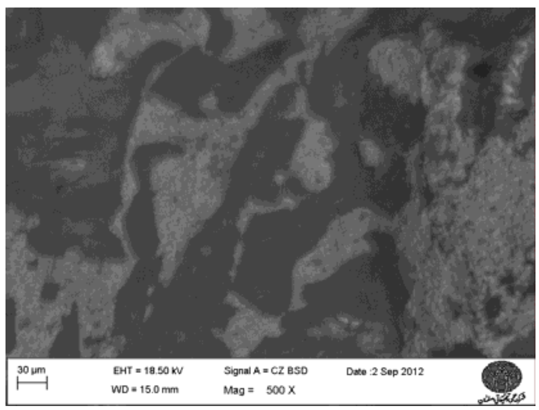
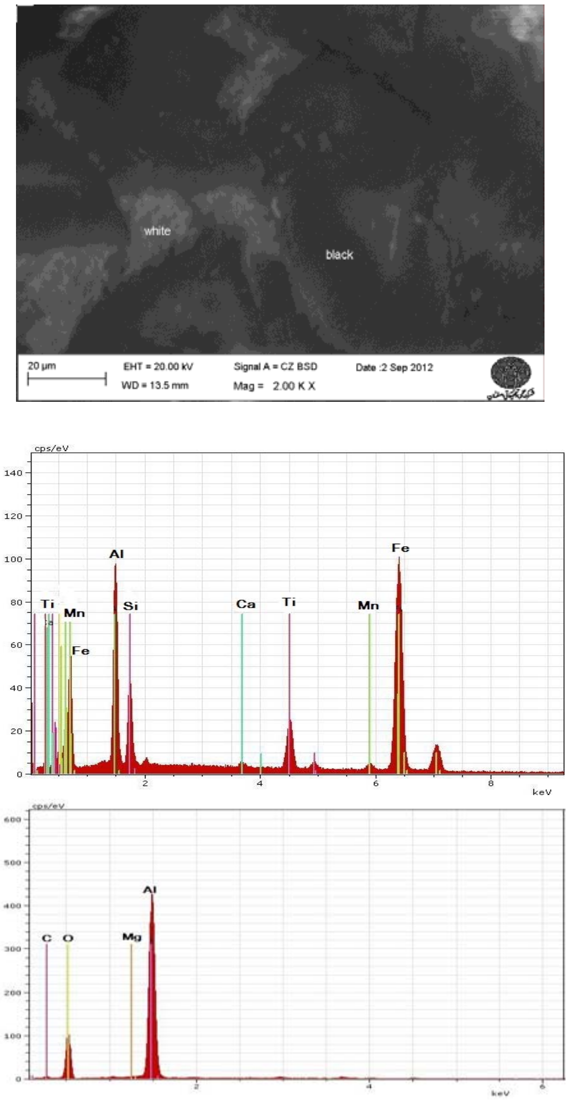


Figure 3. The overall distribution of phases.



White area Black area

Figure 4. EDS analysis results for regions containing Al_2O_3 (black) and FeAl (white).

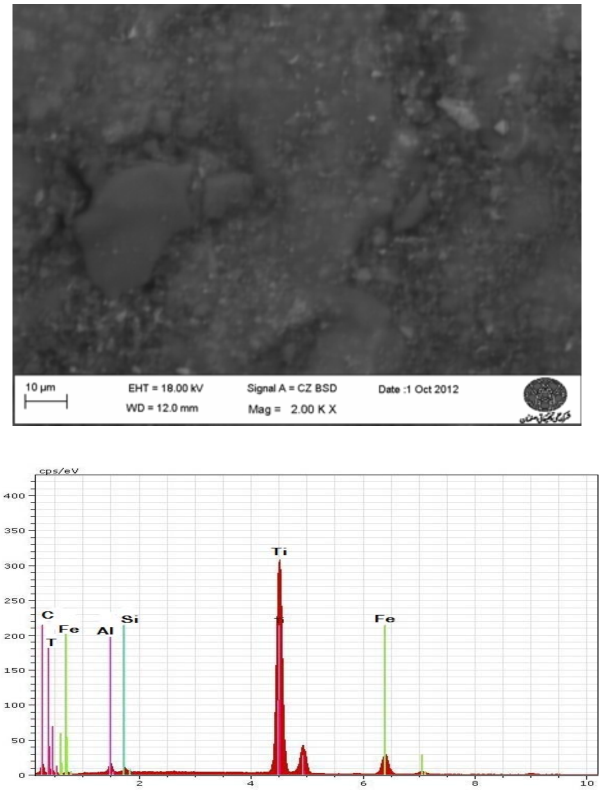


Figure 5. EDS analysis result for regions containing Ti compounds.

3. Hardness and density.

The density of samples prepared by SHS/PHIP process, after grinding and cutting was measured by the ASTM C GO7 method and the 3.9 gr/cm^3 density was obtained. Moreover, hardness of samples was measured through the Vickers method and various forces were 3-60 *Kg*, and the mean hardness was 1650 HV (for material obtained with stoichiometric amount of Al, hardness was 1500 HV). It should be noted that we tried to measure the fracture toughness of the samples too using the Vickers indentation fracture toughness test [8]. But there was no detectable crack produced using different forces in Vickers test [7].

4. Resistance to rusting in the aquatic environment.

In order to ensure the transformation of Fe into FeAl and full removal of Fe in the microstructure, in addition to previous tests, the samples were immersed for 10 days in a normal aquatic environment at a mean temperature of 30^{o}C. After 10 days no sign of rusting was observed on the surface of samples. However, on the samples containing Fe, with a similar test, rusting was clearly visible (figure 6 a).

(a) (b)

Figure 6. (a) Sample with Fe binder after immersion in tap water; (b) Sample with FeAl binder after immersion in tap water.

Conclusion

Combustion synthesis coupled with PHIP method, and use of ilmenite concentrate with additional Al, produced a multi-ceramic composite of Al_2O_3/TiC/TiB_2/FeAl. This composite has very high toughness, appropriate fracture toughness, and resistance to oxidation in aquatic and humid environments. As a result, this composite is suitable for use as wear resistant and high strength parts. Furthermore, the relatively low density of this composite, and the above mentioned properties can make it suitable for uses such as armors.

ԱԼՅՈՒՄԻՆԻ ԱՎԵԼՑՈՒԿԻ ԱԶԴԵՑՈՒԹՅՈՒՆԸ ԲԻՍ-ՄԱՄԼՄԱՆ ԵՂԱՆԱԿՈՎ ԻԼՄԵՆԻՏԻ ԽՏԱՆՅՈՒԹԻ ՕԳՏԱԳՈՐԾՄԱՄԲ ԿԵՐԱՄԻԿԱԿԱՆ ԿՈՄՊՈԶԻՏՆԵՐԻ ՍՏԱՑՄԱՆ ՎՐԱ

Մ. ԽՈԼՂԻ, Հ. ԷԴՐԻՍ և Ս. ԽԱՌԱՏՅԱՆ

Իլմենիտի և ալյումինի օգտագործմամբ ԲԻՍ մամլման եղանակով ստացված կոմպոզիցիոն նյութերի ամրության և այլ մեխանիկական բնութագրերի բարելավման նպատակով, ինչպես նաև ռեակցիայի արդյունքում ստացվող Fe-ը FeAl-ի փոխարկելու համար, ելային բովախառնուրդին տրվել է Al-ի ավելցուկ: Ստուգողական փորձերի արդյունքում որպես օպտիմալ է ընտրվել ռեակցիայի ստեխիոմետրիայի նկատմամբ Al-ի 50% ավելցուկը:

ՌՖԱ, ԷՄ և միկրոանալիզի արդյունքները ցույց են տվել, որ ռեակցիայի արգասիքն իրենից ներկայացնում է կոմպոզիտ՝ բաղկացած TiC, TiB_2, FeAl, Al_2O_3, ինչպես նաև $Al_{86}Fe_{14}$ մետաստաբիլ ֆազից: Վիկերսի եղանակով կատարված չափումների, ինչպես նաև խտության չափումների արդյունքներից եզրակացություն է արվել որ ստացված կոմպոզիտն ավանդական կերամիկայի նկատմամբ աչքի է ընկնում առավել ամրությամբ և թեթևությամբ: Բացի այդ, ստացված կոմպոզիտը ջրային միջավայրում կոռոզիայի չի ենթարկվում:

ВЛИЯНИЕ ИЗБЫТКА АЛЮМИНИЯ НА ПОЛУЧЕНИЕ КЕРАМИЧЕСКИХ КОМПОЗИТОВ МЕТОДОМ СВС-ПРЕССОВАНИЯ С ИСПОЛЬЗОВАНИЕМ КОНЦЕНТРАТА ИЛЬМЕНИТА

М. ХОЛГИ, Г. ЭДРИС и С. Л. ХАРАТЯН

Для повышения твердости и других механических характеристик композитов, полученных методом СВС-прессования с использованием ильменита и Al в качестве прекурсоров, а также превращения Fe в FeAl в продукте был использован избыток Al по сравнению со стехиометрическим количеством. После проведения ряда экспериментов в качестве оптимальной была выбрана исходная смесь с 50% избытком Al. Результаты РФА и микроструктурных анализов с помощью СЭМ и микроанализа показали, что продуктом реакции является композит, состоящий из TiC, TiB_2, FeAl, Al_2O_3, а также метастабильной фазы $Al_{86}Fe_{14}$. Плотность, твердость и вязкость разрушения этого композита, измеренные по методу Виккерса, показали, что продукт представляет собой легкий композит с очень высокой твердостью и прочностью по сравнению с традиционной керамикой. Кроме того, никаких признаков коррозии не наблюдалось на поверхности продукта в водной среде.

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