JOURNALOF

Ceramic Processing Research

Developing Al₂O₃-TiC in-situ nanocomposite by SHS and analyzingtheeffects of Al content and mechanical activation on microstructure

A. Masoudian^a, M. Karbasi^b, F. SharifianJazi^{a,*} and A. Saidi^b

^{*a*} Mining and Metallurgical Engineering Department, Amirkabir University of Technology, P. O. Box 15875 4413, Tehran, Iran ^{*b*} Materials Engineering Department, Isfahan University of Technology, Isfahan 84154-83111, Iran

 Al_2O_3 -TiC in-situ nanocomposite was developed by self propagating high temperature synthesis (SHS) process using TiO₂, Al and C powders as starting materials. The effects of mechanical activation and Al content on the reaction mechanisms and microstructures of products were investigated and thermodynamic and kinetic aspects of reactions were evaluated. Samples were characterized by X-Ray diffraction (XRD), scanning electron microscopy, (SEM)and Energy Dispersive Spectroscopy (EDS). According to the findings, increasing Al content of reactants led to enhancing the heat transfer and avoiding heat outlet by omitting CO as gas product. Also, mechanical activation resulted in better distribution of the initial materials, a decrease in the diffusion distance, and in better kinetics of the combustion synthesis reaction at lower temperature. Consequently, ceramic matrix nanocomposites (CMNC) with phase size less than 800 nm and crystalline size less than 65 nm were developed.

Key words: Self propagating high temperature synthesis (SHS), Ceramic matrix nanocomposite (CMNC), Mechanical activation (MA), Thermodynamic, Kinetic.

Introduction

Ceramics have intrinsic characteristics like high melting point, high hardness, excellent wear resistanceand no chemical reactivity which have resulted in their wide applications as functional materialsat elevated temperatures [1]. Today, advanced ceramics are used in various fields including cutting tools, extrusion molds and many high-temperature engine parts [1-3]. On the contrary, because of their low fracture toughness, mono-phase ceramics are less used in those applications 6Ceramic composites are ofincreasing interest with oxide matrices, particularly Al₂O₃being dominant. Al₂O₃containing ceramic composites are potential substitutes for more traditional materials due to their highhardness, excellent chemical and mechanical stability undera broad range of temperatures, and high specific stiffness. Some of these composites, e.g. Al₂O₃/TiC, Al₂O₃/TiB₂, and Al₂O₃/SiC, have been used invarious engineering applications and offer advantages withrespect to friction and wear behavior [6, 7].

In order to overcome the limitationson fracture toughness, much emphasis has been laid on the processing methods involved in the ceramic composite production. Many methods and their variants have been suggested as means to enhance fracture toughness in ceramic materials [8, 9]. These include control of grain size, porosity, or other microstructural features [10, 11]. Although the first publication of ceramics with nanoscale constituents date back to the late 1980s, the concept of ceramic nanocomposites as a self-contained class of ceramic materialswas first introduced by Niihara [12]. An excellent review of the potential of nanoceramics including structural and functionalaspects was given by Cain and Morell [13]. They pointed outhat the most important benefits from the nanoscale approach were the reduction of firing temperature, improvement of optical properties, reduction in microcracking and the ability to obtain better surface finish. Viswanathan et al. [14] have reviewedthe state of the art of nanocomposite processing [15].

In recent years numerous methods have been introduced to produce ceramic matrix composites (CMCs) such as sintering, hot pressing, spark plasma sintering [16-19] but main problemsof theseprocesses are high energy consumption and cost, difficult treatment and poor interfaces, and heterogeneous phase distribution of products [17-19]. Combustion synthesis is an interesting method to produce a wide range of materials including ceramic matrix composites [20]. The basic principle of this method is application of generated heat from reactions of pre-heat materials to provide a self-sufficient process in other parts of the specimen [20-22]. Industrializing combustion synthesis is easy, due to simple needed equipment, low cost, and high production rates achieved [21, 22].

Most of available researches in the field of Al₂O₃-

^{*}Corresponding author:

Tel : +98-21-64542955 Fax: +98-21-66405846

E-mail: jazi sharifian@yahoo.com

Sample code	X in reaction1	Activation Time (hr)	TiO ₂ (gr)) C(gr)	Al(gr)
1	1	0	5.308	1.596	1.196
2	2	0	5.06	0.760	2.280
3	2	24	5.06	0.760	2.280

Table 1. Specifications of specimens.

TiC ceramic matrix composite have focused more on synthesis method and the resulting mechanical properties, and less on the mechanisms of the reactions. In this study, in-situ production of Al₂O₃-TiC ceramic matrix nanocomposite using self-propagating high-temperature synthesis (SHS) method was investigated. Also, the effects of mechanical activation and Al content in reactants on the reactionmechanisms and microstructures of products were studied and thermodynamic and kinetic aspects of reactions were examined.

Experimental

Commercial aluminum (98.7%, < 75 μ m), titanium oxide(99.3%, < 60 μ m) and graphite (98.5%, < 10 μ m) were used as starting materials. To study the effect of aluminum content on reaction mechanisms and product microstructures, reaction1 was considered with different amounts of aluminum:

$$2xA1+3TiO_2 + (9-3x)C = 3TicC + xA_2O_3 + (6-3x)CO$$
(1)

The specifications of samples are summarized in Table 1. After weighing, physical mixing (with a few steel shots and a few drops of acetone in a plastic bag using a 3-axis electric motor, 15 min, 90 rpm) and drying in air wereperformed. It must be noted that, to activate specimen 3, a planetary ball mill with ball to powder ratio of 50 and rotating speed of 400 rpm was used for 24-hrs for mechanical activation of starting materials instead of mixing. For preparation of compacted samples, 8grams of each mixture was poured into a 12mm diameter metal mold and pressed with 100 MPa stress. One side of pressed samples was heated to the burning temperature. X-Ray Diffraction (Cuka-1.5406 A °) was used to investigate phase changes during SHS process. To observe the sample's microstructures, a Philips XL 30 scanning electron microscope with EDAX energy dispersive spectrometer was employed. Crystallite size of products was calculated from the broadening of XRD peaks using the Williamson-Hall method [23].

Results and discussion

In order to examine the effect of Al content of reactant, first samples were prepared according to substitution of X = 1 in equation 1. The reaction that could occur under this condition is shown below:



Fig. 1. XRD patterns of samples: (a) sample 1 before heating, (b) sample 1 after heating, (c) sample 2 before heating, (d) sample2 after heating, (e) sample 3 after milling and (f) sample3 after heating.

Table	2.	Gibbs	free	energy	as	а	function	of	temperature	for
reactio	n2.									

T(K)	298	300	400	500	600	700	800	900	1000	1100	1200
ΔG (KJ)	0.1	-1.7	-93.2	-186	-278	-371	-464	-556	-647	-737	-827



Fig. 2. Thermal profiles of reactions.

$$2A1 + 3TiO_2 + 6C = 3TiC + 2A1_2O_2 + 3CO$$
 (2)

XRD patterns of sample 1 are shown in Fig. 1(a) (before SHS) and Fig. 1(b) (after SHS). As can be seen, peaks of initial materials (Al, TiO₂) and also peaks of products (Al_2O_3 ,TiC) are present in Fig. 1(b).

It can be concluded that synthesis reaction 2 occurred in this specimen, although it did not progress well, and there remainsome incomplete reacted regions. Using thermodynamicdata [24], changes in Gibbs free energy of reaction 2, as a function of temperature, can be



Fig. 3. (a) SEM-BS micrograph of unreacted end of the specimen 1(X = 1) with heterogeneous distribution of the initial materials and EDS analysis of different regions of micrograph, (b) darkest phase, (c) brightest phase and (d) matrix.

derived from equations 3 and 4 (two equations were usedbecause of Al melting at $933 \times K$).

 $\Delta G(J) = 253623.85 - 433.6 \text{ T} - 76.25 \text{ T} \ln \text{ T} + 0.058 \text{ T}^2$ T(K) < 933 for solid Al phase (3)

$$\Delta G(J) = 232623.85 - 411.68 \text{ T} - 76.25 \text{ T} \ln \text{T} + 0.058 \text{T}^2$$

T(K) > 933 for liquid Al Phase (4)

Table 2 shows the Gibbs free energy of reaction2 as a function of temperature. As can be seen, Gibbs free energy is effectively negative at temperatures above 500 K. However, the maximum temperature measured during reaction was $1550 \,^{\circ}$ C (Fig.2,x = 1). Based on this consideration, reaction 2 could happen from thermodynamic point of view, but according to XRD results (Fig. 1(b)) it was not completed for other reasons.

To have a better understanding of mechanism of reaction 2, SEM examination was started from the end of the specimen toward the point of heat source contact. SEM back scattered (BS) micrograph of sample 1 is shown in Fig. 3(a). Since back scattered signals are correlated to the atomic number of elements, different colors in SEM-BS images could correspond to the presence of different phases in the sample's microstructure. As it is already known, higher atomic numbers cause brighter appearance of phases in



Fig. 4. SEM-BS micrographs of middle section of sample1: (a) semi- reacted zones with some reaction sites over the unreacted core, (b-c) formation of reaction sites involving reactants (black zones are mount)



Fig. 5. SEM-BE micrograph of nearest region to heat source in sample 1: (a) two phases could be seen in completely reacted regions, (b) EDS analysis of dark grey region, (c) EDS analysis of bright grey region, (d- f) different morphology of products (black zones are mount)

SEM-BS micrographs. In addition, the EDS results are presented in Fig. 3(b-d). EDS results confirm that different regions of Fig. 3(a) correspond to the presence of C (darkest phase), Al (brightest phase), and TiO₂ phase (matrix). As can be seen, distribution of the starting materials in physically mixed sample is not homogeneous, thus leading to lack of effective contacts of reactant and incomplete progress of reaction 2 as kinetic barriers.

SEM-BS micrographs of middle section of sample are shown in Fig. 4(a-c). In these micrographs, the brightest area could refer to Al phase (Fig. 4(a)), as established before. Progress of reaction 2and formation of some reaction sites involving products could be observed in this region (Fig. 4(b, c)), but several unreacted zones, consisting of reactants, are clearly visible (Fig. 4(a)). In other words, unreacted cores are visibledue to the lack of important kinematic requirements such as ineffective contacts of reactant resulting from heterogeneous distribution of reactants. Therefore, growth and development of product's phases were discontinued and semi-reacted regions remained intact.

Nearest part of sample1 to heat source is shown in SEM-BS micrographs of Fig. 5. Two different regions (dark and bright grey) could be observed generally in the reacted parts of micrographs (Fig. 5(a)). EDS results (Fig. 5(b-c)) could be good evidence for the presence of Al₂O₃in dark grey and TiC in bright grey. As could be seen, reaction2progressedmore at this region in comparison with middle part of the sample (Fig. 4). However, initial materials are visible in the middle of the micrograph. The morphologies of product phases are different (Fig. 5(d-e)). Difference in morphologies could have resulted from different heat conduction conditions [25-28] of regions during selfpropagation of high temperature synthesis. As a consequence of sufficientheat during SHS, Al could be melted and act as a heat transfer agent and therefore could affect the nucleation and growth of products'phases. Hence, due to heterogeneous distribution of Al, different thermal profiles were obtained across regions and different morphologies of phases were formed.

As mentioned before, Al could be melted and act as heat transfer agent and so could affect the progress of reaction. Thus, forbetter heat transfer and more chance of TiC and Al_2O_3 production, Al content of reactant was increased by two times (X = 2 in reaction1). In this condition, the following reaction could occur:

$$4A1 + 3TiO_2 + 3C = 3TiC + 2A1_2O_3$$
(5)

Apparently, reaction 5 could have two advantages: more Al content with stronger probability of heat transfer and omission of gas product (CO) that could be suitable for reduction of heat exit and better energy saving. On the other hand, the disadvantage of this reaction is positive Gibbs energy at temperatures higher than 298 °K; this behavior is described in detail in the following paragraphs.

Gibbs free energy of reaction5 was calculated using thermodynamic data [24]. As described before, due to the melting of Al at 933 °K,the equations (6) and (7) couldbederived:

$$\Delta G(J) = -1081834.93 + 3761 \text{ T} - 21.5 \text{ T} \ln \text{ T} - 0.0286 \text{ T}^2$$

T(K) < 933 K for solid A1 (6)

$$\Delta G(J) = -1123834.93 + 3805.1 \text{ T} + 21.49 \text{ T} \ln \text{ T} - 0.0313 \text{ T}^2$$

T(K) > 933 for liquid Al (7)

Table 3 shows the Gibbs free energy of reaction as a function of temperature. As can be seen, G is positive

above 300 °K. Therefore, reaction progress is possible at temperatures precisely less than 298 °K.

However, the temperature of laboratory was about 290 °K ($\Delta G = -28.9$ KJ)and activation energy was provided by heating the top of sample.

The XRD patterns before and after the combustion synthesis of sample2 are shown in Fig. 1(c-d). These XRD patterns show peaks of initial materials. There are no visible peaks showing any signs of products. Temperature profile (Fig. 2, X = 2) also confirmed that no reaction has occurred in specimen 2. In Fig. 6(a) SEM-BS micrograph of specimen 2 is shown. Three grey levels observed, as described before, could be related to Al, TiO₂ and C. Hence, initial materials remained intact and no products were formed. In addition, reactants were distributed heterogeneously. Though Al was introduced to reactions in the solid state, it must be noted thatdistribution of Al phase in reactants is more important than the amount of Alas iteffectively determines the heat transfer procedure.

As described before, more Al content of reactant was not worked because of thermodynamic (not enough negative Gibbs energy) and kinetic (heterogeneous distribution of reactants) barriers. So, the third specimen with the same chemical composition as sample 2 (X = 2), was pre-activated mechanically for 24 hrs by ball milling and then exposed to heat. All peaks of XRD pattern of mechanically activated sample3 were related to reactants after milling (Fig.

Table 3. Gibbs free energy as a function of temperature for reaction2.

T(K)	298	300	400	500	600	700	800	900	1000	0110	01200
ΔG (KJ)	-0.1	7.1	366.4	724.7	71081.	.91438	1793	2148	250	1285	83214

Fig. 6. SEM-BS micrograph of specimen 2.



Fig. 7. SEM-BS micrographs of sample 3: (a) homogeneous distribution of productions in mechanically activated sample 3 with increasing Al content, (b) ultrafine phase size due to lower reaction temperature.



Fig. 8. (a) and(b): SEM-SE micrograph of ultrafine phase size of mechanically activated sample with increased Al amount in reactants.

1(e) but there were no peaks visible that could be related to the initial materials in the XRD pattern of the mechanically activated (MA) specimen 3 after heating, and all revealed peaks resulted from the presence of products (Fig. 1(f)).

According to the Gibbs-Hemholtz equation (equation 9),

the Gibbs free energy between activated and nonactivated solid state depends on changes in the difference in enthalpy (Δ H) and entropy (Δ S):

$$\Delta G = \Delta H - T \Delta S \tag{9}$$

The values of DS are very small and negligible if the crystal disordering is low. In contrast, inhighly deformed and disordered crystals, the values of DS can be significant and could shift the Gibbs free energy tomore negative amounts. In other words, ball milling could increase the entropy effectively, and shift the G tothe more negative quantities. On the other hand, it can be concluded that it was due to the ball milling that difference in energy level of the initial materials and products increased, and G became more negative [30, 31].

In addition, kinematic barriersdictated by heterogeneous distribution of initial materials were overcomeby ball milling. Consequently, thermodynamic and kinetic efficiency wasachieved.

Fig. 1(f) shows that all the revealed peaks are related to the product phase and Fig. 2 shows that the maximum temperature of about 1189 °C is obtained during reaction2. This temperature is approximately 400 °K lower than maximum temperature of reaction1. The SE-BSE micrographs of the microstructure of activated sample after synthesis are shown in Fig. 7(a). As described before, darkphase is Al₂O₃ and bright phase is TiC. Size of some Al₂O₃ phases in the TiC matrix is less than 3 micrometer (Fig. 7(b)). The phase size ofinactivated specimen was5-10 micron (Fig. 5(de)) while in Fig. 8a and Fig. 8(b) product needles with a diameter of 200 nm can be seen. So, it could be concluded that products in the activated specimen3 are much smaller in size than non-activated samples. This decrease in size of the products phase is due to lower synthesis temperature (Fig. 2), and to decrease in diffusion distance. Better reaction kinetic aspectsresulted from fine and homogeneous distribution of reactants after ball milling.

Using Williamson-Hall method on XRD patterns, crystalline size of TiC and Al₂O₃ phases were calculated as 43 and 65 nm, respectively. Lower synthesis temperature and fine distribution of raw materials and shorter diffusion distance during pre-activated reaction5 led to lower growth chance of products and development of a ceramic matrix nanocomposite (CMNC). This could be very useful to improve properties of CMCs as described in introduction [12, 13].

Conclusions

Increasing Al content of reactant could lead to better heat transfer, an increase in TiC and Al_2O_3 production, and better energy saving due to decreasing CO as gas product if kinematic barriers are overcome. Mechanical activation of the specimen resulted in increasing entropyand more negative ΔG , better distribution of the initial materials, a decrease in diffusion distance, and better kinetics of the synthesis reactions. Also, all the materials could be changed to products. Finer structure resulted in activated sample phasesize about5-10 μ m without activation and less than 3 μ m with activation. Phase size less than 200 nm is visible in the activated specimen. This is because the reaction was completed at lower temperature (400 °K) with less growth chance. Crystalline sizes of the produced TiC and Al₂O₃ phases were calculated as 43 and 65 nm, respectively

References

- 1. B. John, J.R. Watchman, "Structural Ceramics", Academic Press, London (1989).
- C.B. Carter, M.G. Norton, "Ceramic Materials", Science and Engineering (2007).
- D. Jianxin, C. Tongkun, S.Junlong, J.Ceram.Int. 31 (2005) 249-256.
- S. Rattanachan, Y. Miyashita, Y. Mutoh, J. Eur.Ceram. Soc. 23 (2003) 1269-1276.
- D.Jianxin, C.Tongkun, D. Zeliang, L.Jianhun, S.Junlong, Z. Jinlang, J.Eur. Ceram. Soc. 26 (2006) 1317-1323.
- B.Liu, C. Huang, M.Gu, H. Zhu, H. Liu, Journal of Materials Science and Engineering A. 460 (2007) 146-148.
- 7. L.P. Huang, J. Li, Journal of Composites Part A. 30 (1999) 615-618.
- A.G. Evans, Journal of Materials Science and Engineering 71 (1985) 3-21.
- 9. R.W. Rice, Journal of Physics and Chemistry of Solids 45 (1984) 1033-1050.
- 10. R. Rice, Journal of Material Science19 (1984) 1267-1271.
- J.J. Mechosks, R.C. Rradt, A.G. Evans, D.P. Hasselman, F.F. Lange, "Fracture mechanics of ceramics", Plenum, New York (1983) 165.
- 12. K. Niihara, Journal of Ceramic Society of Japan 99 (1991) 974-982.
- M. Cain, R. Morell, Journal of Applied Organometallic Chemistry 15 (2001) 321-330.

- V. Viswanathan, T. Laha, K. Balani, A. Agrwal, S. Seal, Journal of Materials Science and Engineering R54 (2006) 121-285.
- R. Gadow, F. Kern, A. Killinger, Journal of Materials Science and Engineering B148 (2008) 58-64.
- E.M.Sharifi, F. Karimazdeh, M.H. Enayati, Journal of Alloys and Compounds 491 (2010) 411-415.
- 17. T.D. Xia, T.Z. Liu, W.J. Zhao, B.Y. Ma, T.M. Wang, Journal of Materials Science 36 (year 2001) 5581-5584.
- Y. Zhang, L. Wang, W. Jiang, L. Chen, G. Bai, J. Eur.Ceram. Soc.26 (2006) 3393-3397.
- N. Liu, M. Shi, Y.D. Xu, X.Q. You, P.P. Ren, J.P. Feng, International Journal of Refractory Metals & Hard Materials22 (2004) 265-269.
- J.H. Lee, CY. An, C.W. Won, S.S. Cho, B.S. Chun, Materials Research Bulletin 35 (2000) 945-954.
- 21. Y. Yang, K. Yang, Z.M. Lin, J.T. Z.M., (Name of Journal Materials letters) 61 (2007) 671-676.
- J.W. McCauley, "An Historical and Technical Perspective on SHS". The 14th Annual Conference on Composites and Advanced Ceramic Materials11 (1990) 1137-1181.
- 23. K. Williamson, W.H. Hall, Journal of ActaMetallurgica 1 (1953) 22-31.
- 24. D.R. Gaskell, "Introduction to Thermodynamic of Materials", the 3rdedition (1995).
- L.P. Wang, K.Y. Fu, X.B. Tian, B.Y. Tang, P.K. Chu, Journal of Materials Science and Engineering A 336 (2002) 75-80.
- R.P. Liu, D.M. Heriach, M. Vandyoussefi, A.L. Greer, Journal of Metallurgical and Materials Transaction A 35 (2004) 1067-1073.
- 27. Z. Amjad, R.W. Zunl, NACE-International Corrosion Conference Series (2006) 63851.
- J.C. Roio, C. Marin, J.J. Derby, E. Dieguez, Journal of Crystal Growth183 (1998) 604-613.
- 29. P. Pourghahramani, "Phd Thesis", Lulea University of Technology (2007).
- C. Gras, D. Vrel, E. Gaffet, F. Bernard, Journal of Alloys and Compounds314 (2001) 240-250.
- L. Jianlin, L. Fei, H. Keao, Journal of Materials Processing Technology 147 (2004) 236-240.