Synthesis and Characterization of In Situ (Al₂O₃–Si)/Al Composites by Reaction Hot Pressing

El Oualid Mokhnache · Guisong Wang · Lin Geng · Balasubramaniam Kaveendran · Lujun Huang

Received: 26 June 2014 / Revised: 29 August 2014 / Published online: 10 October 2014
© The Chinese Society for Metals and Springer-Verlag Berlin Heidelberg 2014

Abstract In situ (Al₂O₃–Si)/Al composites with a reinforcement volume fraction of 10% were synthesized from the Al–SiO₂ system using low energy ball milling and reaction hot pressing. Differential thermal analysis was used to investigate the reaction mechanisms between SiO₂ and Al. X-ray diffraction results revealed that the reaction between Al and SiO₂ took place completely at 900 °C with a holding time of 2 h, thereby forming Al₂O₃ and Si. Scanning electron microscopic, energy dispersive X-ray spectroscopic, and transmission electron microscopic (TEM) results showed that the in situ synthesized Al₂O₃ and Si particles, whose sizes are less than 2 μm, were polygonal in shape and dispersed uniformly in the matrix. Moreover, Al₂O₃ particle size showed a tendency to increase from ~2 to ~6 μm when the synthesis temperature was increased. Furthermore, TEM observation showed that the interface between the reinforcements and Al matrix is clean. The yield strength, ultimate tensile strength, and Brinell hardness of the in situ (Al₂O₃–Si)/Al composite was significantly higher than the aluminum matrix. Mechanisms governing the tensile fracture process are discussed.

KEY WORDS: Al composites; Microstructure; Al₂O₃; Silicon

1 Introduction

Research on metal matrix composites (MMCs) has dramatically advanced in the last two decades due to their distinct advantages such as excellent strength, high specific modulus, light weight, wear resistance, and high temperature applications [1–7]. Among these MMCs, aluminum matrix composites (AMCs) are expected to play an important role in various advanced applications such as automobile, aerospace, and some military applications owing to their unique high properties, the easiness of fabrication and processing, and relatively low cost [8–11].

Good understanding of exothermic reaction processes has proved to be effective in the fabrication of in situ AMCs. In addition, these exothermic reaction processes are known under a variety of names: reactive synthesis, self-propagating high-temperature synthesis (SHS), combustion synthesis, and XDTM. Moreover, the reactive synthesis has the important advantage that the reinforcements are formed in situ in the matrix, thereby forming a strong interface bonding and clean interface between the reinforcements and the matrix [12, 13]. However, the major limitation of synthesis reactive process is the formation of high concentration of pores [14]. In order to overcome this limitation, the RHP has been proposed where the in situ reinforcements are synthesized by an exothermic conversion of the reactants, followed by the hot compaction of the porous composite product. For example, various in situ composites have been fabricated by RHP, where the pressure plays an important role in decreasing the porosity and obtaining a fully dense composite. Hence, the mechanical properties can be improved significantly [15–17].

Available online at <http://link.springer.com/journal/40195>

E. Mokhnache · G. Wang (✉) · L. Geng · B. Kaveendran · L. Huang
School of Materials Science and Engineering, Harbin Institute of Technology, Harbin 150001, China
e-mail: wangguisong@hit.edu.cn

Very recently, the use of oxides such as SiO₂, TiO₂, CuO₂, ZnO, and CeO₂ to synthesize Al₂O₃ particles is thermodynamically feasible and found to be beneficial in terms of cost and wettability compared to the direct incorporation of Al₂O₃ in Al matrix [18–22]. Brestlin *et al.* [18] produced an Al₂O₃/Al co-continuous ceramic composite from Al–SiO₂ system via solid/liquid displacement reactions, and they reported that the reaction between Al and SiO₂ can occur as follows:

However, no research has been reported to clarify the effect of the sintering parameters (temperature and pressure) on the microstructures and mechanical properties of the fabricated composites in the Al–SiO₂ system. Accordingly, in this study, RHP was used to synthesize the in situ (Al₂O₃–Si)/Al composite, with the main focus being to determine the synthesis temperature and holding time for the complete reaction between Al and SiO₂. Moreover, the effect of the synthesis temperature and pressure on the microstructures and mechanical properties of the fabricated composites was investigated.

2 Experimental Procedures

Commercial pure aluminum (Al) powder (99.6% purity) and silica (SiO₂) powder (99.2% purity), with an average size of 30 μm and 2 μm, respectively, were used as raw materials. To produce the composites with a total 10 vol% of reinforcements (i.e. 7.1 vol% Al₂O₃ + 2.9 vol% Si + 90 vol% Al), the stoichiometric starting materials (i.e. 92.54 wt% Al + 7.46 wt% SiO₂) were weighed according to the hypothetical reaction (1). The mixture of powders were ball milled using low energy at 160 r/min for 4 h in a planetary ball mill under argon atmosphere with a ball to powder ratio of 4:1. The milled powders were transferred into the graphic mould pre-coated with boron nitride to avoid the reaction between the mould and the reactants. In a vacuum of 4.5×10^{-2} Pa, the powders were heated to 600 °C and compacted with 25 MPa for 1 h to produce the as-sintered SiO₂/Al billet 60 mm in diameter and 17 mm in height.

To determine the synthesis temperature of the Al–SiO₂ system, the as-sintered SiO₂/Al billet was cut to small samples. Each sample was placed into a quartz container, which was filled with a vacuum atmosphere to avoid oxidation of the samples. Subsequently, all samples were heated in conventional furnace at 800, 900, and 1,050 °C to produce the composites namely C1, C2, and C3, respectively. After the synthesis temperature was selected, the in situ (Al₂O₃–Si)/Al composite was cooled down from

Table 1 Composites nomenclature and their processing fabrication steps

Composite	Step 1	Step 2	Step 3
As sintered SiO ₂ /Al	600 °C, 1 h, 25 MPa	–	–
C1	600 °C, 1 h, 25 MPa	800 °C, 2 h, 0 MPa	–
C2	600 °C, 1 h, 25 MPa	900 °C, 2 h, 0 MPa	–
C3	600 °C, 1 h, 25 MPa	1050 °C, 2 h, 0 MPa	–
C4	600 °C, 1 h, 25 MPa	900 °C, 2 h, 0 MPa	580 °C, 1 h, 25 MPa

900 to 580 °C and re-compacted with 25 MPa for 1 h to produce a dense composite named C4. All the processing steps to fabricate the as-sintered SiO₂/Al, C1, C2, C3, and C4 composites are shown in Table 1.

The samples made from the fabricated composites were mechanically polished and investigated using XRD (Philips'Xpert) to identify and quantify the composites phases. SEM (Quanta 200FEG) and TEM (TECNAIF30) along with EDX were used to investigate the microstructure and morphology of the composites. A sample 2 mm in diameter and 1 mm in height cut from the as-sintered SiO₂/Al billet was used to perform the DTA test. The sample was heated in an argon atmosphere in the TGA/SDTA85 IE thermal analyzer, where the temperature varied from the room temperature (25 °C) to 1100 °C at heating rate of 10 °C/min. Hydrostatic weighing method was used to measure the relative density of the samples.

Brinell hardness measurements were carried out using HB-3000B-1 machine with an indenter with a ball diameter of 5 mm under a load of 9807 N for a dwell time of 30 s. Room temperature tensile tests, according to the metal materials testing standards of ISO 6892: 1998 [23], were carried out using an Instron-5569 universal testing machine at a constant crosshead speed of 0.5 mm/min. A total of three tensile samples with dimensions of 15 mm × 5 mm × 2 mm were tested for each material.

3 Results and Discussion

3.1 Thermal Analysis

The main reaction between Al and SiO₂ can be expressed in Eq. (1). Moreover, according to the thermodynamic data [24], the variation of Gibbs free energy for reaction (1) can be expressed by,

$$\Delta G_T^0 = 2\Delta G_{\text{Al}_2\text{O}_3}^0 + 3\Delta G_{\text{Si}}^0 - 4\Delta G_{\text{Al}}^0 - 3\Delta G_{\text{SiO}_2}^0, \quad (2)$$

$$\Delta G_T^0 = -668.1 + 0.139T. \quad (3)$$

By calculating the Gibbs free energy variation within the temperature range of 25–1,100 °C including the operating temperatures in the present work, it was found that all the values of ΔG_T^0 are negative (i.e., $\Delta G_{25}^0 = -665$ kJ/mol, $\Delta G_{1100}^0 = -515.5$ kJ/mol), indicating that Eq. (3) is spontaneous and reaction (1) is thermodynamically feasible.

From the Al–Si phase diagram [25], using a reinforcement volume fraction of 10 vol%, a mass of around 3.1 wt% of Si is expected to form, which means that the reduced Si has two possibilities, either present as precipitates in the Al matrix or being dissolved in Al to form Al–Si solid solution.

DTA analysis of the as-sintered SiO₂/Al composite is shown in Fig. 1. It can be seen that a large endothermic peak at 664 °C was observed, which corresponds to the melting temperature of aluminum. After the aluminum melts, the reduction of SiO₂ by molten Al becomes more favorable due to the increase of the elemental diffusion in Al–Si–O system owing to the increment in temperature. Therefore, an

Fig. 1 DTA curve of as-sintered SiO₂/Al as heated at 10 °C/min

Fig. 2 XRD patterns of the composites

exothermic peak at 785 °C was observed. Hence, the Gibbs free energy of reaction (1) is negative at 785 °C (i.e., $\Delta G_{785}^0 = -551$ kJ/mol); consequently, the exothermic peak might correspond to the aluminothermic reduction of silica by molten aluminum forming Al₂O₃ and Si.

3.2 XRD Analysis and Microstructures

Figure 2 shows the XRD patterns of the as-sintered SiO₂/Al, C1, C2, C3, and C4 composites. In the case of the as-sintered SiO₂/Al, XRD analysis revealed that only SiO₂ and Al phases exist like those in starting powders.

As seen in Fig. 3a and b, SEM along with EDX (result of point A) comprised of Si (42.51 wt%) and O (57.49 wt%) further confirmed the presence of only SiO₂ particles dispersed in Al matrix. This indicates that no reaction products existed at a temperature of 600 °C which is lower than the melting temperature of Al.

As mentioned above, the first stage of the sintering process involved the compaction of the powders in order to increase the surface contact between the Al and SiO₂ powders, thereby decreasing the diffusion length between Al and SiO₂. Lokesh *et al.* [26] reported that the poor contact between particles could lead to bad reactivity in Al–SiO₂–C system and no exothermic reaction can occur above the melting temperature of aluminum. That means that the first compaction step is crucial in increasing the reactivity of the selected Al–SiO₂ system which determines the initiation temperature of the reaction (Eq. 1).

After heating the sample at 800 °C for 2 h, the XRD pattern of composite C1 shows newly produced phases, in situ synthesized Al₂O₃ and Si, as a result of the aluminothermic reaction between SiO₂ and Al according to the hypothetical reaction in Eq. (1). Moreover, SEM photographs of composite C1 shown in Fig. 3c showed that the newly produced phases were dispersed uniformly as particles in the Al matrix, and their sizes were less than 2 μm. EDX results which are shown in Fig. 3d and e suggest that these new phases are Si precipitates with light gray color, Al₂O₃ particles with dark gray color, and Al. That is to say, reaction (1) takes place forming Al₂O₃ and Si particles.

However, some unreacted SiO₂ also was detected in the XRD pattern of the composite C1 as shown in Fig. 2, which indicates that the reduction of SiO₂ did not occur completely due to the insufficiency of combustion energy. Therefore, in order to increase the combustion energy, the temperature of the system was increased at a constant holding time. As a result, the XRD pattern of composite C2 revealed that at 900 °C for 2 h, the reaction between SiO₂ and Al takes place completely with Al₂O₃, Si, and Al as final phases (Fig. 2). Furthermore, the XRD pattern of composite C3 showed that using a synthesis temperature of

Fig. 3 SEM images and EDX results of the composites: (a) SEM image of as-sintered SiO₂/Al; (b) EDX result of point A in a; (c) SEM image composite C1; (d) EDX result of point B in c; (e) EDX result of point C in c; (f) SEM image of composite C2; (g), (h) SEM images of composite C3; (i) SEM image of composite C4

1050 °C had no effect on the composition of the final products, and the contents of Al₂O₃ and Si remain unchanged compared to composite C2 (Fig. 2).

From Fig. 3f and g, it can be seen that with increasing the synthesis temperature from 900 to 1050 °C, Al₂O₃ particle size showed an increase from ~2 to ~6 μm. Al₂O₃ coarsening can be attributed to the high energy due to the increment in temperature of the system. Coarsening of the in situ particles with increasing synthesis temperature and holding time has been reported by many researchers [27, 28], where synthesis temperature and holding time drastically affect the size of TiC particles [27]. Moreover, due to the sharp temperature gradient during cooling, many pores and shrinkage defects between the coarse Al₂O₃ particles and Al matrix were observed in Fig. 3h. In the case of composite C4, the final compaction

step with 25 MPa pressure for 1 h was applied. As a result, some coarse Al₂O₃ particles were broken, as seen in Fig. 3i. In general, the formation of fine particles is more advantageous than that of the coarse particles for the enhancement of the strength of the composites [1].

Figure 4 shows the TEM images, SAED patterns and EDX results of composite C4. It is clearly shown that Al₂O₃ (rhombohedral) and Si (cubic) were dispersed in Al forming a clean interface. Polygonal-shaped Al₂O₃ and Si with a size of around 1 and 0.3 μm, respectively, were observed.

3.3 Mechanical Properties

The mechanical properties of the in situ composites (hardness, relative density, UTS, YS and elongation)

Fig. 4 TEM images, diffraction patterns, and EDX results of composite C4 showing (a) the in situ synthesized Al_2O_3 (b) Si particle

compared with those of as-sintered SiO_2/Al and pure Al matrix are presented in Table 2.

3.3.1 Hardness and Relative Density

From Table 2, it can be observed that the as-sintered SiO_2/Al composite shows a slight increase of hardness (30 HB) compared to that of pure aluminum (27 HB), which is attributed to the combined effect of low relative density and the uniform dispersion of SiO_2 particles in the Al matrix as seen in Fig. 3a. Moreover, compared with the as-sintered SiO_2/Al , the composites C1 and C2 show a decrease of relative density from 93.1 to 90.2 and 88.3%, respectively. However, the formation of the in situ synthesized Al_2O_3 and Si significantly improved the hardness of the composites C1 and C2, where their hardness values are 39.4 and 39 HB, respectively. It is noted that compared the composite C3 with C2, despite the occurrence of a complete reaction in composite C3, as revealed by XRD patterns, a further decrease of hardness and relative density was observed due to the formation of many pores and the coarsening of Al_2O_3 particles, resulting from the high

synthesis temperature. Furthermore, composite C4 shows the highest hardness (45 HB) due to its high relative density (98.9%), attributed to the final pressing stage as well as the complete synthesis of 10 vol% Al_2O_3 and Si.

3.3.2 Tensile Properties

From Table 2, it can be seen that the composites C1, C2, and C3 fabricated without the final pressing step showed mediocre tensile properties due to the existence of a large amount of pores. However, composite C4 depicts an improvement in ultimate tensile strength, yield strength, and elongation compared with the as-sintered SiO_2/Al and pure aluminum, where UTS, YS, and elongation are 121, 59 MPa, and 12.4%, respectively.

Figure 5 shows the fracture surfaces of the as-sintered SiO_2/Al and composite C4, respectively. It can be observed that the fracture surface of the as-sintered SiO_2/Al was composed of a large concentration of SiO_2 , as source of voids and nucleation, in the Al matrix, which eventually led to the fracture of the as-sintered SiO_2/Al . This explains the limited strength of the as-sintered SiO_2/Al .

Table 2 Mechanical properties of fabricated composites under various processing conditions

Material	YS (MPa)	UTS (MPa)	Hardness (HB)	Elongation (%)	Relative density (%)
Pure Al	15 ± 3	40 ± 2	20 ± 0.3	20 ± 0.3	99.1
As sintered SiO ₂ /Al	44 ± 2	69 ± 2	30.1 ± 0.2	4.2 ± 0.1	93.1
C1	45 ± 2	87 ± 2	39.4 ± 0.2	3.3 ± 0.15	90.2
C2	50 ± 2	85 ± 3	39 ± 0.3	3.1 ± 0.2	88.3
C3	42 ± 3	83 ± 2	32.2 ± 0.1	2.9 ± 0.1	85.4
C4	59 ± 2	121 ± 2	45 ± 0.1	12.4 ± 0.15	98.9

Fig. 5 Tensile fracture surfaces of (a, b) as sintered SiO₂/Al (c, d) composite C4

It can be seen that the formation of fine dimples with some pulled out Al₂O₃ particles indicates that the strength of the composite can be mainly attributed to the existence of Al₂O₃ particles by means of dispersion strengthening mechanism [29, 30]. Furthermore, in Al–Si alloys, the tensile properties are mainly affected by the size and morphology of the hard and brittle Si precipitates [31], suggesting that the composite C4 would undergo brittle fracture. However, since the content of the reduced Si precipitates is relatively low (around 3.1 wt%) and the size is small in composite C4, the Si precipitates did not significantly affect the fracture of the composite. Consequently, the composite C4 showed a good ductility (~12.4%) depicting that the composite C4 underwent ductile fracture.

4 Conclusions

- (1) In situ (Al₂O₃–Si)/Al composite with a reinforcement content of 10 vol% was fabricated successfully using the Al–SiO₂ system by low energy ball milling and reaction hot pressing. Hence, the dense in situ (Al₂O₃–Si)/Al composite exhibits superior mechanical properties

compared to the as-sintered SiO₂/Al and pure aluminum, due to the formation of Al₂O₃ and Si as strengthening phases.

- (2) Investigation of the reaction mechanisms showed that after the melting temperature of aluminum, the reduction of silica took place to form Al₂O₃ and Si as reinforcements. High synthesis temperature is required for the completion of the reaction.
- (3) Synthesis temperature clearly affects the microstructure and the morphology of the in situ (Al₂O₃–Si)/Al, where the size of Al₂O₃ particles tends to increase with increasing synthesis temperature. Hence, some coarse Al₂O₃ particles were broken due to the final compaction pressure. Therefore, application of pressure after the synthesis of Al₂O₃ and Si plays a key role in avoiding pores and determining the final microstructure.
- (4) The strengthening of (Al₂O₃–Si)/Al composite can be attributed to the formation of Al₂O₃ and Si as reinforcements by means of dispersion strengthening mechanism. Moreover, the presence low content of Si plays a dominant role in determining the fracture mechanism of the composite.

Acknowledgments This work was financially supported by the National Natural Foundation of China (No. 51201047) and National Basic Research Program of China (No. 2012CB619600).

References

- [1] S.C. Tjong, Z.Y. Ma, *Mater. Sci. Eng. R* **29**, 49 (2000)
- [2] Y. Du, P. Zhang, Y. Wang, J. Zhang, S. Yao, C. Li, *Acta Metall. Sin. (Engl. Lett.)* **26**, 69 (2013)
- [3] V.C. Srivastava, A. Schneider, V. Uhlenwinkel, K. Bauckhage, *Mater. Sci. Eng. A* **412**, 19 (2005)
- [4] A. Mortensen, J.A. Cornie, M.C. Flemings, *J. Met.* **40**, 12 (1988)
- [5] J. Wang, X. Guo, L. Xiao, L. Wang, W. Lu, B. Li, Z. Li, D. Zhang, *Acta Metall. Sin. (Engl. Lett.)* **27**, 205 (2014)
- [6] A. Mortensen, M.N. Gugor, J.A. Cornie, M.C. Flemings, *J. Met.* **38**, 30 (1986)
- [7] I. Sulima, P. Klimczyk, P. Malczewski, *Acta Metall. Sin. (Engl. Lett.)* **27**, 12 (2014)
- [8] S.V. Prasad, R. Asthana, *Tribol. Lett.* **17**, 445 (2004)
- [9] W. Speer, O.S. Es-Said, *Eng. Fail. Anal.* **118**, 95 (2004)
- [10] S. Ernest, C. Chin, *Mater. Sci. Eng. A* **259**, 155 (1999)
- [11] H. Kurita, E. Feuillet, T. Guillemet, J.M. Heintz, A. Kawasaki, J.F. Silvain, *Acta Metall. Sin. (Engl. Lett.)* **27**, 714 (2014)
- [12] M.J. Koczak, M.K. Pekumar, *Emerg. J. Met.* **44**, 44 (1993)
- [13] Z.Y. Ma, J.H. Li, S.X. Li, X.G. Ning, Y.X. Lu, J. Bi, *J. Mater. Sci.* **31**, 741 (1996)
- [14] J.J. Moore, H.J. Feng, *Prog. Mater. Sci.* **39**, 243 (1995)
- [15] L.J. Huang, S. Wang, L. Geng, B. Kaveendran, H.X. Peng, *Compos. Sci. Technol.* **82**, 23 (2013)
- [16] L. Geng, D.R. Ni, J. Zhang, Z.Z. Zheng, *J. Alloys Compd.* **463**, 488 (2008)
- [17] D. Roy, S. Ghosh, A. Basumallick, B. Basu, *J. Alloys Compd.* **436**, 107 (2007)
- [18] M.C. Breslin, J. Ringlanda, J. Segeer, A.L. Marasco, G.S. Daehn, H.L. Fraser, *Ceram. Eng. Sci. Proc.* **15**, 104 (1994)
- [19] M. Rafiei, M.H. Enayati, F. Karimzadeh, *J. Alloys Compd.* **488**, 144 (2009)
- [20] C. Gang, G. Sun, Z. Zhu, *Mater. Sci. Eng. A* **251**, 226 (1998)
- [21] T.G. Durai, K. Das, S. Das, *Mater. Sci. Eng. A* **445**, 100 (2007)
- [22] W. Hongming, L. Guirong, Z. Yutao, C. Gang, *Mater. Sci. Eng. A* **527**, 2881 (2010)
- [23] ISO 6892. Metallic materials-tensile testing at ambient temperature, 1998
- [24] M.W. Chase, *JANAF Thermochemical Tables*, 3rd edn. (American chemical Society and the American Institute of Physics for the National Bureau of Standards, 1985)
- [25] J.L. Murray, A.J. McAlister, *ASM Handbook*, vol. 3 (ASM International, 1992), p. 312
- [26] L.C. Pathak, D. Bandyopadhyay, S. Srikanth, S.K. Das, P. Ramachandrarao, *J. Am. Ceram. Soc.* **84**, 915 (2001)
- [27] T. Nukami, M.C. Dlemings, *Metall. Mater. Trans. A* **26**, 1877 (1995)
- [28] T. Nukami, *J. Mater. Sci. Lett.* **17**, 267 (1998)
- [29] F. Tanga, I.E. Andersona, T.G. Heroldb, H. Prask, *Mater. Sci. Eng. A* **383**, 362 (2004)
- [30] E. Orowan, in *Symposium on Internal Stress in Metals and Alloys* (Institute of Metals, 1948), p. 451
- [31] M. Gupta, S. Ling, *J. Alloys Compd.* **287**, 284 (1999)