Synthesis of FeAl/Al₂O₃ Composites by Thermite Reaction†

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FeAl/Al₂O₃ composites were synthesized by using *in-situ* thermite reaction of iron oxide and aluminum powder mixtures. The phase, microstructure of the composites were investigated by X-ray diffractometry, scanning electron microscopy combined with differential scanning calorimetry. The results show that a chemical reaction in Fe₂O₃/Al system is possible and the FeAl/Al₂O₃ composites with the interpenetrating network structure are obtained calcined at 900 °C for 60 min.

Key Words: FeAl/Al₂O₃ composites, Microstructure, Thermite reaction.

INTRODUCTION

Alumina, as an excellent construction ceramics, possesses the attractive properties of good hardness, chemical stability, refractory character and low density. However, it is brittle at low temperature for the lack of fundamental dislocation mobility and insufficient slip systems¹. From the standpoint of material design, it is undoubtedly a good method to develop ceramic-matrix composite with metal or alloy dispersion because of their high strength and multi-functional properties^{2,3}. Among the metal or alloy, the intermetallic compound FeAl possesses a high melting temperature (1250 °C), good oxidation resistance, relatively low density (5.56 g·cm⁻³) and high thermal conductivity. These properties make FeAl alloy a promising candidate for high temperature structural applications^{4,5}. In addition, FeAl alloy has also been identified that its thermodynamics is compatible with alumina⁶.

Recently, the alumina-metal composites were synthesized by many techniques, such as reactive milling⁷, reactive metal infiltration⁸, directed metal oxidation⁹, reactive sintering¹⁰, thermomechanical powder consolidation processes¹¹, thermite reaction synthesis¹²⁻¹⁴. Among these techniques, the thermite reaction method is an attractive technique, which utilizes the exothermicity of solid-state reaction to produce advanced materials. It shows many advantages of relatively simple equipment, low energy and possibility to form intermediate phase. In the present paper, FeAl/Al₂O₃ composites were synthesized by using *in situ* thermite reaction method. Their microstructure of FeAl/Al₂O₃ composites were investigated.

EXPERIMENTAL

Reagent grade aluminum powders (*ca.* 74 μm) and iron oxide powders were weighed according to 4-6 molar ratio. The powders were thoroughly mixed by a planetary mill for 15 h and then the mixtures were pressed to pellets with a diameter of 32 mm under a uniaxial pressure of 60 MPa. The green compacts were calcined at 700, 850, 900 °C for 1 h, respectively.

The phase of samples were identified by the X-ray diffraction spectrometer using CuK_α radiation (XRD-6000, Shimadzu). Its microstructure was observed through the scanning electron microscope (SEM, JSM-5900). The main constituent elements were determined by energy dispersive X-ray spectroscopy equipped in SEM. Thermal analyses were carried out by differential scanning calorimetry (SDT 2960, TA Co.).

RESULTS AND DISCUSSION

Phase of FeAl/Al₂O₃ composites: Fig. 1 shows XRD patterns of the samples obtained at different temperatures. It is found that the major phase of sample calcined at 700 °C are Fe₂O₃ and Al. Diffraction peaks referred to Al₂O₃, Fe and/or FeAl are observed as it was calcined at 850 °C for 1 h, which means that the chemical reaction in Fe₂O₃/Al system was initiated. It can be seen that all diffraction peaks are identified to be Al₂O₃ and FeAl as it was calcined at 900 °C for 1 h. No other impurity peak is detected in the samples.

Microstructure of FeAl/Al₂O₃ composites: Fig. 2 shows SEM images of samples calcined at different temperatures.

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Fig. 2. SEM images of samples calcined at different temperatures. a) 700 °C, b) 850 °C, c) 900 °C

Firstly, aluminium begins to melt and spread on the surface of Fe₂O₃ particles at 700 °C [Fig. 2 (a)]. According to compositions of the samples (Table-1), it is verified that the gray region A is Al₂O₃ particles and white region B is FeAl particles in Fig. 2(b). The microstructure of Fe₂O₃/Al system becomes dense for the chemical reaction of Fe₂O₃/Al system was initiated at 850 °C. Fig. 2(c) shows a typical image of a sample calcined at 900 °C for 1 h and one can see that FeAl/Al₂O₃ composites with interpenetrating networks structure can be obtained.

Fig. 1. XRD patterns of samples calcined at different temperatures for 1 h

TABLE-1
COMPOSITIONS OF THE REGIONS IN Fig. 2 (Wt %)

Region	Al	Fe	Other element	Total content
A	90.31	7.50	2.19	100
B	49.66	47.66	2.37	100
C	44.00	53.79	2.21	100

Differential scanning calorimetry analyses: Fig.3 shows the differential scanning calorimetry curve of the green compact at heating rate of 10 °C/min. There are one endothermic peak (P_{Endo}) and one exothermic peak (P_{Exo}) in the curve. The observed endothermic peak locating at 660 °C can be reasonably ascribed to the melting of aluminium, the exothermic peak can be ascribed to the thermite reaction of Fe₂O₃/Al system.

The standard free energy of formation¹⁵ can be given by:

$$\Delta G_f^0 = -RT \ln k_T \quad (1)$$

Fig. 3. Differential scanning calorimetry curves of Fe₂O₃/Al powder mixture at heating rates of 10 °C/min

where T is temperature, k_T is equilibrium constant, for α -Al₂O₃, $\Delta G_f^0 = -1120500 + 214.2 T$, while for Fe₂O₃, $\Delta G_f^0 = -540600 + 170.3 T$. The standard free energy of the formation (ΔG_f^0) of α -Al₂O₃ and Fe₂O₃ versus temperature is calculated and shown in Fig. 4.

The following equation is employed to predict strictly if the chemical reaction occurs:

$$\Delta G_f = \Delta G_f^0 + RT \ln \frac{a_{\text{Fe}}}{a_{\text{Al}}^2} \quad (2)$$

and a_{Fe} and a_{Al} are the activities of iron and aluminum in the system. Generally, it is reasonable to predict from ΔG_f^0 if the

Fig. 4. Standard free energy of the formation of α -Al₂O₃ and Fe₂O₃ conclusions

reaction occurs, when ΔG_f^0 is negative and its absolute value is large enough. Fig. 4 shows the possibility of the chemical reaction in $\text{Fe}_2\text{O}_3/\text{Al}$ system.

$\text{Fe}_2\text{O}_3/\text{Al}$ system is well known by the exothermic reaction, as it is submitted to thermal treatments. The thermite reaction equation is:

and the enthalpy is:

$$\Delta H_T = \Delta H_0 + \int \Delta C_p dT \quad (4)$$

where ΔH_0 is the enthalpy at standard state. The ΔH_0 is - 847.63 $\text{kJ}\cdot\text{mol}^{-1}$ Al_2O_3 for eqn. 3. ΔC_p is the difference of the heat capacity between the products and the reactants and for reaction eqn. 3. $\Delta C_p = a + b\cdot 10^{-3}T + c\cdot 10^5T^{-2}$. Table-2 gives the values of ΔH_T for difference temperatures. It is also verified that there are strong exothermic effect in $\text{Fe}_2\text{O}_3/\text{Al}$ system. Actually, the $\text{FeAl}/\text{Al}_2\text{O}_3$ composites are obtained, which is attributed to the thermite reaction of $\text{Fe}_2\text{O}_3/\text{Al}$ system.

TABLE-2
EXOTHERMIC VALUES OF REACTION Eq. (3)
AT DIFFERENT TEMPERATURES

Temperature T (K)	933	1000	1100	1200	1300
ΔH ($\text{kJ}\cdot\text{mol}^{-1}\text{Al}_2\text{O}_3$)	-911.91	-900.56	-916.96	-935.32	-955.13

Conclusion

Aluminum and iron oxide powders were used to prepare $\text{FeAl}/\text{Al}_2\text{O}_3$ composites by *in situ* thermite reaction. The chemical reaction is feasible thermodynamically in $\text{Fe}_2\text{O}_3/\text{Al}$ system. Thermite reaction in $\text{Fe}_2\text{O}_3/\text{Al}$ system is ignited as the temperature is above 850 °C. $\text{FeAl}/\text{Al}_2\text{O}_3$ composites with interpenetrating network structure are obtained at temperature of 900 °C for 1 h.

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