Exothermic Synthesis of the Composites $\alpha$-Al$_2$O$_3$/NiAl from Al-Ni$_2$O$_3$-Ni System

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Abstract. Nickel aluminum matrix composites material reinforced with 10% volume fraction of $\alpha$-Al$_2$O$_3$ is prepared by exothermic sintering process. The reaction process and microstructures are analyzed by using differential scanning calorimetry (DSC), X-ray diffraction (XRD), scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS). The results show that the activation energy of the sample with a volume fraction of 10% is 439kJ/mol. The reinforcements are $\alpha$-Al$_2$O$_3$ uniformly distributed in the NiAl matrix. The reaction occurs spontaneously at 1100K and emits a lot of heat.

Introduction

In recent years, the NiAl intermetallic composites [1, 2, 3] reinforced by Al$_2$O$_3$ has been widespread concerned due to many the excellent properties such as: high hardness, excellent wear resistance and good thermal stability, it also has low density, superior oxidation, corrosion resistance, excellent heat treatment capability and flexible preparation technology etc. Commonly preparation methods of NiAl composites include: powder metallurgy, liquid metal infiltration, stirring casting and in situ composites [4] etc. According to the different reinforcement, NiAl matrix composites can be divided into fiber reinforced and particulate reinforced NiAl matrix composites. But the particle reinforced NiAl matrix composites is one of the most mature metal matrix composites. The matrix usually is NiAl alloy, and the reinforcing body is a dispersion of hard particles. The interface of the obtained by in situ reaction is clean and pollution-free, and the comprehensive performance is better than that obtained by other methods, for example, Rathod S[5] has obtained TiC reinforced Cu matrix composites by in-situ synthesis and the properties of the composite is excellent. The in situ reaction usually adopts self-propagation high-temperature synthesis (SHS)[6], vapor liquid method (VLS), reflecting the direct melt oxidation method (DIMOX), contact reaction method(CR), mechanical alloying method (MA), microwave synthesis method (MS) and exothermic synthesis method (ES). Among them, the exothermic synthesis method[7] has the advantages of simple operation, environmental protection, low energy consumption, good compactness, small particle size and excellent mechanical property etc. In this study, exothermic synthesis method[8,9] is used, then NiAl matrix composites reinforced by $\alpha$-Al$_2$O$_3$ particles are obtained, and the sintering process is analyzed by using high temperature DSC analyzer, then calculating the reaction activation energy, and the microstructure of the samples is analyzed by X-ray diffraction and scanning electron microscopy.

Experiment

The Al(3-50$\mu$m,99.8% purity), Ni$_2$O$_3$(3-50$\mu$m,99.7% purity), Ni(10~30$\mu$m,99% purity) powders are used as raw materials in the present study. Preparation of NiAl matrix composites reinforced with 10% volume fraction of Al$_2$O$_3$. First, the mass ratio of various components is calculated as follows: Al:Ni$_2$O$_3$:Ni=1:0.342:1.689 (10% reinforcement). According to the proportion of the mass
of the powder, put into the ball mill for mixing in a stainless steel vacuum jar for 6 hours, in which the mass ratio of ball to powder is 5:1. After the ball mill is completed, it is transferred to the drying box at 130 °C for 2 hours. The prepared powder is made into a cylindrical sample with a diameter of 20 mm and a length of about 3~5mm, under a pressure of 180 MPa. And then it was placed in the electromagnetic induction furnace under argon atmosphere. Setting power is 3kW, the reaction peak is recorded by temperature measuring device. After reaction, the furnace was turned off and then cooled down to room temperature. The reaction process was analyzed by high temperature DSC and the samples were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS).

Results and Discussion

Thermodynamic Analysis

In order to obtain the DSC curves, the compact sample was heated in argon atmosphere in the furnace of STA449C thermal analyzer. The reactions occurring in the Al-Ni$_2$O$_3$-Ni system during the heating process were analyzed. In this system, the following reaction may occur:

$$4\text{Al} + \text{Ni}_2\text{O}_3 \rightarrow \text{Al}_2\text{O}_3 + 2\text{NiAl}$$

$$\Delta G^\circ_T = -1434694 - 12.9T \text{J/mol}$$  \hspace{1cm} (1)

It can be seen that the value of the Gibbs free energy in this equation (1) is negative in the experimental temperature range, from the thermodynamic point of view, this reaction can be carried out spontaneously. The Gibbs free energy of NiAl is more negative compared with other NiAl intermetallic compounds, Such as Ni$_2$Al$_3$, Ni$_3$Al, NiAl$_3$ etc. So the synthesis of NiAl intermetallic is stable in this composite.

DSC Analysis

Fig.1 show the DSC curves of NiAl-Al$_2$O$_3$ system with 10% volume fraction at different heating rates of 10K/min, 15K/min and 25K/min. There are three exothermic peaks: A, B and C in this figure, peak A is the endothermic melting peak of Al. As shown in Fig.1 the peak A occurs around 933K is endothermic melting peak of Al, because of the melting point of Al is 933K approximately. Peak B is exothermic peak in the formation of NiAl intermetallic. In these figure, it can be observed that the B peak occurs around 942K which is the reaction between Ni and Al. The ignition temperatures of Ni+Al= NiAl is 900K approximately and the conclusion has been proved by H Zhang and HG Zhu [10].Since Ni and Al are relatively easy to react, some NiAl intermetallic are preferentially formed. The peak C is exothermic peak of the reaction of equation (1). Peak C sharp due to the reaction of a large number of reactants at the same time to achieve the reaction conditions, the reaction occurs in a moment, a large amount of heat release. Therefore, the exothermic peak will be sharp, it mainly due to instantaneous thermal explosion, emit heat. Because of the formation of some solid solution in the reaction process, there will be a low temperature secondary peak in the exothermic process sometime.

As can be seen from the figure with the increase of heating rate, this exothermic peak is continuously shifted: peak A from 933K to 936K; peak B from 942K to 952K; peak C from 1115K to 1136K. This is due to the lag of heat transfer. The higher the heating rate is, the easier it is for the surface of the particles to obtain the energy of the reaction, and the transfer of heat takes time, which leads to the formation of the temperature difference between the inside and outside of the particles, and the diffusion of the reactants also takes time. Therefore, when the surface of the sample reaches the reaction temperature, the heat stored in the sample is not enough to support the reaction because of the large temperature gradient, as the heat continues to pass lead to the furnace body temperature continues to rise, reaching the reaction temperature. In addition, with the increase of the heating rate, the exothermic peak area of the DSC curve increases, the peak becomes sharp.
Figure 1. DSC curves of Al-Ni$_2$O$_3$-Ni powder mixtures to different heating rates: (a) 10 K/min, (b) 15 K/min and (c) 25 K/min.

**Activation Energy**

Based on the dynamic model proposed by Kissinger [11]:

\[
\ln \frac{\beta}{T^2} = -\frac{E_a}{RT} + C
\]

we can gain the activation energy of equation (1).

In the formula:  
- $\beta$-Heating rate, K/ min;  
- $E_a$-Phase change activation energy, kJ / mol;  
- $R$-Gas constant, J / mol·K;  
- $T$-The peak temperature of exothermic peak, K;  
- $C$-constant;

We use obtained $K$ value at various temperatures, then the $\ln(\beta/ T^2)$ to $1/T$ mapping, fit a straight line. The slope of the line is $E_a/R$, so the $E_a$ value can be obtained. Due to the peak C is exothermic peak of the main reaction (1). The DSC measurements peak temperature at three different heating rates of peak C in Fig.1 are used to fit the straight line by Origin, and the slope of the straight line is obtained and the activation energy of main reaction could be calculated.

Respectively, the corresponding temperature value of the peak C in Fig.1: 1115K, 1126K, 1136K. It can be seen that with the increase of heating rate, the peak temperature of the system increases with the other conditions being unchanged, this is consistent with the trend of Kissinger equation. And with the increase of heating rate, the thermal effect (dH/ d T) produced by unit time also increases.

Figure 2. Plots of $\ln(\beta/T_m)$ versus $1/T_m$. 

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Error</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>35.63213</td>
<td>4.86495</td>
</tr>
<tr>
<td>B</td>
<td>-52837.04129</td>
<td>5475.63261</td>
</tr>
</tbody>
</table>
Data generated automatically by the Origin, the slope of the straight line is $-E_a/R = -52837$, Constant $R=8.314\text{J} / \text{mol} \cdot \text{K}$, calculated $E_a=439\text{kJ} / \text{mol}$.

**Microstructure Characterization**

Fig.3 is NiAl-Al$_2$O$_3$ composite’s XRD spectra, it can be seen in the composite material mainly containing two phase: NiAl and $\alpha$-Al$_2$O$_3$. The organization is consistent with the previous thermodynamic analysis.

![Figure 3. XRD pattern of the reaction sample.](image)

Fig.4 is the results of scanning electron micrographs (SEM) and energy dispersive spectroscopy (EDS) spectra of the composites. From the Fig.4a, it can be clearly observed that there are uniformly distributed fine particles in the matrix. Fig.4b is the EDS spectrum analysis of the gray A point of Fig.4a. The results show that the gray reinforcement main component is $\alpha$-Al$_2$O$_3$. Fig.4c shows the EDS energy spectrum analysis of B point of Fig.4a, which shows that the main composition of the matrix is NiAl intermetallic, so the main reaction in Al-Ni$_2$O$_3$-Ni system is the equation (1). The results are the same as those of thermodynamic analysis.

![Figure 4. SEM image of the composite and the EDS pattern of particle A and B.](image)
Conclusions

1) Al-Ni$_2$O$_3$-Ni systems NiAl/Al$_2$O$_3$ composites can be successfully prepared by exothermic synthesis method. The thermodynamic analysis shows that the reaction can proceed spontaneously; the corresponding $\alpha$-Al$_2$O$_3$ particle reinforcements and NiAl intermetallic matrix are formed. With the increase of the heating rate, the exothermic peak area of the DSC curve increases, the peak becomes sharp, and moves toward the high temperature.

2) The gray reinforcement particles Al$_2$O$_3$ are uniformly distributed in the NiAl matrix, the activation energy of the NiAl-Al$_2$O$_3$ system with the volume fraction of 10% is 439kJ / mol.

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Reference


