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Study of the kinetics of the nitridation reaction on Al–(Mg,Si) alloys by TG ☆

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Abstract

The thermal behaviour of metal Al and Al–(Mg,Si) alloys in N_2 has been examined by TG. Above 700°C, the Al–(Mg,Si) alloys in N_2 can be directly converted to AlN/Al matrix composite. The reaction rate of the nitridation of Al–(Mg,Si) alloys is greatly influenced by the dopants Mg and Si. The reaction mechanism of nitridation established from the regression of $g(\alpha)$ under various conditions versus t seems to be one-dimensional diffusion.

Keywords: Alloy; Aluminium; Kinetics; Magnesium; Silicon; TG

1. Introduction

A reaction self-composing (RSC) process is involved in the direct nitridation reaction of molten Al–(Mg,Si) alloys in N_2 to yield AlN/Al matrix material. It is a processing technique with industrial applications for fabricating ceramic matrix composites. In order to characterize the growth process of the ceramic matrix composite, TG can be used to investigate the nitridation reaction of Al–(Mg,Si) alloys in N_2.

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In this paper, the thermal behaviour of Al and Al–(Mg,Si) alloys in N_2 and the influence of the dopants Mg and Si on the reaction rate of nitridation are examined. At the same time, the rate equation of nitridation and the reaction mechanism for Al–(Mg,Si) alloys have been established from isothermal TG data.

2. Experimental

2.1. Metal and alloys

Aluminium metal and alloys 1, Al–(5% Mg, 2–8% Si) and 2, Al–(4% Si, 3–9% Mg) were employed.

2.2. Experimental equipment and conditions

All experiments were performed on a Shimatzu DT-20B thermal analyser; sample weight, 5 mg; heating rate, 10°C min^{-1}; chart speed, 1.25 mm min^{-1}; N_2 atmosphere.

2.3. Experimental procedure

The alloys were placed in a small basket made of alundum which was suspended at the centre of the reaction tube, and then balanced with weights. Then nitrogen was introduced.

At first the alloy was heated in programmed temperature mode to the reaction temperature. This temperature was maintained for 1.5 h in order to carry forward the reaction. The temperature and weight gain in the process of nitridation were recorded.

3. Results and discussion

3.1. Thermal behaviour of Al and Al–(Mg,Si) alloys

In order to investigate the nitridation reaction of Al–(Mg,Si) alloys, TG was used to follow the nitridation process of Al and Al–(Mg,Si) alloys. Fig. 1 shows the TG curves of Al and Al–(Mg,Si) alloys in N_2. Data from these curves are summarized in Table 1.

It can be seen from Fig. 1 that only one weight gain step (from 710°C) appears on TG curve 1 up to 1080°C. The weight gain step can be attributed to the conversion of Al to AlN, the conversion per unit being 34.18% after 4.3 h at 1080°C. It can also be seen from Fig. 1 that there are two weight gain steps (560–750–1080°C) on TG curve 2. The first weight gain step is probably related to the conversion of (Mg,Si), and the second weight gain step obviously corresponds to the conversion of Al in the alloy to AlN, but both the initial temperature of

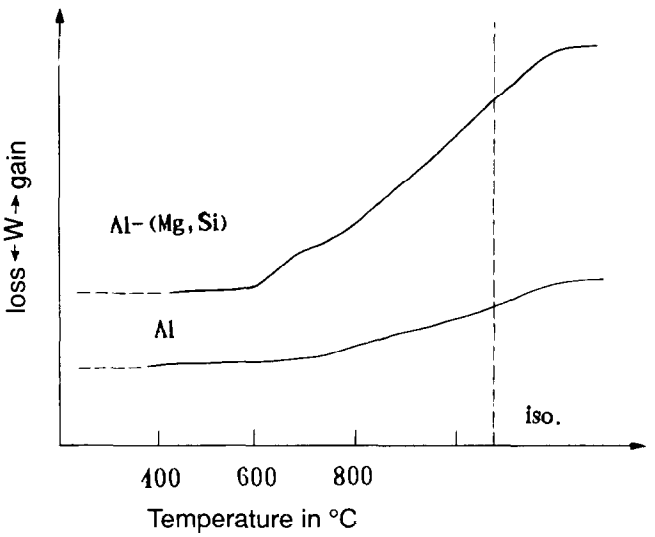

Fig. 1. TG curves of Al and Al–(Mg,Si) alloys in N_2.

Table 1
Results from TG of Al and Al-(Mg,Si) alloys in N_2

Sample	Sample weight/mg	Temperature range/°C	Isothermal time/h	Theoretical weight gain/mg	Actual weight gain/mg	Conversion/ %
Al	2.55	710–1080	4.3	1.17	0.43	34.18
Al-(Mg,Si)	2.60	750–1080	4.5	1.19	0.96	80.69

reaction and the reaction rate are higher than those for pure Al. The conversion per unit can reach 80% after 4.5 h at 1080°C. This may be related to the coordination effect of Mg and Si.

3.2. Influence of dopants Mg and Si on the reaction rate of nitridation

In order to examine the influence of Mg and Si on the reaction rate of nitridation of Al–(Mg,Si) alloys, TG was also used to follow the nitridation process of Al–(x% Mg,4% Si) and Al–(5% Mg,x% Si) alloys.

Fig. 2 shows the TG curves of Al–(x% Mg,4% Si) alloys in N_2. Table 2 gives the results of the TG measurement. Fig. 3 is a plot of reaction rate versus percentage of Mg.

All the TG curves of the Al–(x% Mg,4% Si) alloys in N_2 are similar, i.e. there are two weight gain steps. As above, the second weight gain step corresponds to the conversion of Al in the alloys. One can see from Table 2 that the weight gain increases with the increase in Mg content and reaction temperature. The average conversion per unit at 1100°C is 22% higher than that at 1000°C. When the Mg

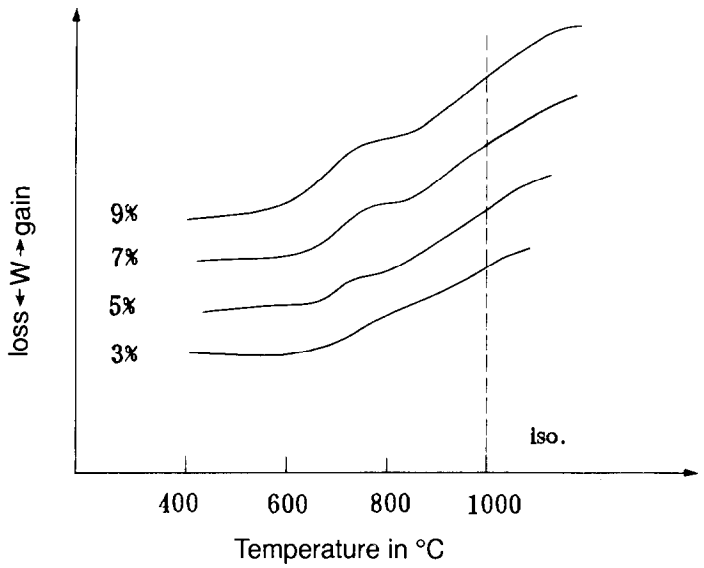

Fig. 2. TG curves of Al–(x% Mg,4% Si) in N_2.

Table 2
TG results of Al–(x% Mg,4% Si) in N_2 at 1000 and 1100°C for 1.5 h

Reaction temperature/°C	Sample weight/mg	Mg content/%	Theoretical weight gain/mg	Actual weight gain/mg	Reaction rate/ ($g\ min^{-1}\ g^{-1}$)	Conversion/ %
1000	2.36	3	1.108	0.246	1.158×10^{-3}	21.61
	2.40	5	1.133	0.290	1.343×10^{-3}	25.59
	2.40	7	1.108	0.310	1.435×10^{-3}	27.98
	2.45	9	1.106	0.350	1.587×10^{-3}	31.64
1100	2.40	5	1.133	0.420	1.944×10^{-3}	37.06
	2.37	7	1.108	0.580	2.719×10^{-3}	52.34
	2.40	9	1.106	0.640	2.963×10^{-3}	57.86

content is in the 3–9% range, the average reaction rate at 1100°C is nearly one third faster than that at 1000°C.

TG curves of Al–(5% Mg,x% Si) alloys in N_2 are similar to those of Al–(x% Mg,4% Si) alloys. The TG results of Al–(5% Mg,x% Si) alloys in N_2 at 1000 and 1100°C for 1.5 h are listed in Table 3. A plot of reaction rate versus percentage of Si is shown in Fig. 4. One can see from Table 3 that the weight gain caused by nitridation of Al increases with reaction temperature, and seems to increase with the Si content. The average conversion per unit at 1100°C is 14% higher than that at 1000°C. And the former average reaction rate is slightly higher than the latter.

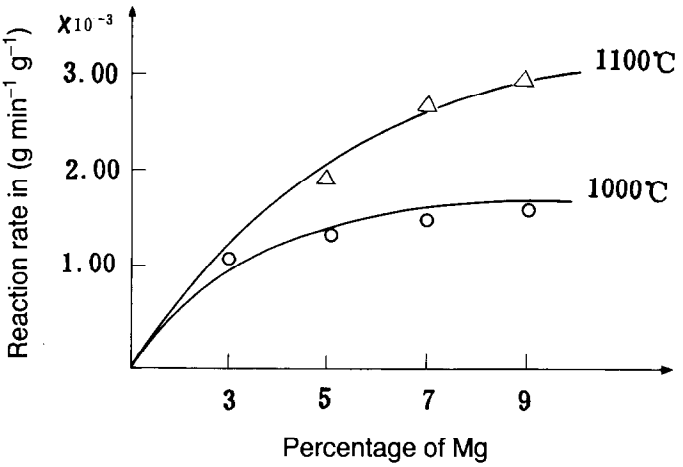

Fig. 3. Plot of reaction rate versus %Mg.

Table 3
TG results of Al(5% Mg,x% Si) in N_2 at 1000 and 1100° C for 1.5 h

Reaction temperature/°C	Sample weight/mg	Si content/%	Theoretical weight gain/mg	Actual weight gain/mg	Reaction rate/ ($g\ min^{-1}\ g^{-1}$)	Conversion/ %
1000	2.40	2	1.138	0.250	1.157×10^{-3}	21.96
	2.40	4	1.133	0.310	1.435×10^{-3}	27.36
	2.40	6	1.108	0.280	1.296×10^{-3}	25.27
	2.45	8	1.106	0.290	1.315×10^{-3}	26-22
1100	2.40	4	1.133	0.420	1.944×10^{-3}	37.07
	2.40	6	1.108	0.480	2.130×10^{-3}	43.32
	2.30	8	1.106	0.400	1.932×10^{-3}	36.16

3.3. Establishment of the rate equation of nitridation for Al–(Mg,Si) alloys

The nitridation reaction of Al–(Mg,Si) alloys can be represented stoichiometrically by the equation

$$2Al\text{–}(Mg,Si) + N_2 \rightarrow 2AlN(Mg,Si)$$

As 90% of the alloys is aluminium and the nitrogen does not need to be diluted, we can regard Al and N_2 as constant. Thus the reaction rate of nitridation of Al–(Mg,Si) is greatly influenced by the dopant (Mg,Si) and by the temperature.

We can designate the isothermal rate equation as follows

$$dc/dt = KC_{Mg}^{n} C_{Si}^{m} \quad (1)$$

$$K = Ae^{-E/RT} \quad (2)$$

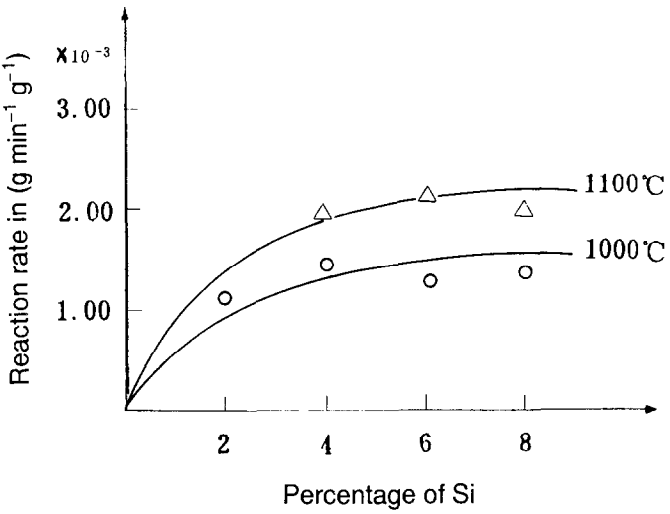

Fig. 4. Plot of reaction rate versus %Si.

where K is the rate constant, C_{Mg} and C_{Si} the Mg and Si contents, n and m the reaction orders, A the pre-exponential factor, E the activation energy, R the gas constant and T the absolute temperature.

The natural logarithm form of Eq. (1) can be expressed as

$$\ln(dc/dt) = \ln K + n \ln C_{Mg} + m \ln C_{Si} \tag{3}$$

If the contents of Mg and Si are fixed, Eq. (3) becomes

$$\ln(dc/dt) = q_1 + n \ln C_{Mg} \tag{4}$$

$$\ln(dc/dt) = q_2 + m \ln C_{Si} \tag{5}$$

In order to obtain the reaction orders n and m, TG determinations of Al–(Mg,Si) alloys with various contents of Mg and Si were performed at various temperatures. Their respective reaction rates can be evaluated from TG data. The reaction orders n and m can be obtained from the regression of $\ln(dc/dt)$ versus $\ln C_{Mg}$ or $\ln C_{Si}$. The results are shown in Table 4.

Table 4
Evaluated values of reaction orders n and m

Reaction order	Temperature/°C			
	950	1000	1050	1100
n	0.045	0.276	0.505	0.732
m	0.115	0.082	0.043	0.006

Table 5
TG results of Al–(7% Mg,4% Si) in N_2 at various temperatures for 1.5 h

Temperature/°C	Sample weight/mg	Actual weight gain/mg	Reaction rate/ ($g\ min^{-1}\ g^{-1}$)	Conversion/%
950	2.40	0.290	1.342×10^{-3}	26.17
1000	2.40	0.310	1.435×10^{-3}	27.98
1050	2.50	0.420	1.866×10^{-3}	37.90
1100	2.37	0.580	2.719×10^{-3}	52.34

Table 6
Calculated values of K and ln K

Temperature/°C	$1/T$	K	ln K	ln K
950	0.817×10^{-3}	2.190×10^{-3}	−6.1237	−6.20
1000	0.785×10^{-3}	3.892×10^{-3}	−5.5486	−5.42
1050	0.755×10^{-3}	8.208×10^{-3}	−4.4026	−4.68
1100	0.728×10^{-3}	19.427×10^{-3}	−3.9411	−4.03

The natural logarithm form of Eq. (2) can be rewritten as

$$\ln K = \ln A\left(\frac{E}{R}\frac{1}{T}\right) \tag{6}$$

TG determinations on the Al–(7% Mg,4% Si) alloy at various temperatures were performed for evaluating the activation energy E and pre-exponential factor A. The TG results of Al–(7% Mg,4% Si) alloy in N_2 at various temperatures for 1.5 h are given in Table 5.

According to Eq. (1), the rate constants K at various temperatures were calculated from the corresponding reaction rates. The results and smoothed ln K values from plots of ln K versus $1/T$ are summarized in Table 6.

According to Eq. (6), an activation energy E of 195.8 kJ mol^{-1}, and a pre-exponential factor A of 472220 are obtained from the regression of ln K versus $1/T$. Thus, the rate constant can be represented by the equation

$$K = 472220 \exp(-195.82/RT) \tag{7}$$

The values of the reaction constant K calculated from Eq. (7) are compared with the values found in Table 7. The comparison shows that the values of the rate constant calculated are basically in agreement with the values found. The error is less than 8.3%. Thus the rate equation of nitridation of Al–(Mg,Si) can be written as

$$1000°C \quad dc/dt = 472220 \exp(-195.82/RT) C_{Mg}^{0.276} C_{Si}^{0.08} \tag{8}$$

$$1100°C \quad dc/dt = 472220 \exp(-195.82/RT) C_{Mg}^{0.732} C_{Si}^{0.06} \tag{9}$$

Table 7
Comparison of values of rate constant K

Temperature/°C	Rate constant K		Error/%
	Calculated	Found	
950	1.8889×10^{-3}	2.0294×10^{-3}	6.9
1000	4.249×10^{-3}	4.4271×10^{-3}	4.0
1050	8.499×10^{-3}	9.2790×10^{-3}	8.3
1100	16.5277×10^{-3}	17.7743×10^{-3}	7.0

3.4. Confirmation of the reaction mechanism of nitridation for Al–(Mg,Si) alloys

The isothermal rate equations can also be expressed as

$$d\alpha/dt = Kf(\alpha) \tag{10}$$

where α is the reaction fraction, t the time, and $f(\alpha)$ a function of α.

The integral form of Eq. (10) can be expressed as

$$g(\alpha) = \int d\alpha/f(\alpha)\, dt = Kt \tag{11}$$

If $f(\alpha)$ is properly chosen the plot of $g(\alpha)$ vs. t would be linear and the reaction mechanism can be confirmed from $g(\alpha)$. Values of $g(\alpha)$ derived by Šesták for different solid state reaction mechanisms are given in Table 8.

The regressions of $g(\alpha)$ at various temperatures vs. t for different reaction mechanisms were performed. The values of the correlation coefficient obtained and of the activation energy calculated according to Eq. (6) are shown in Table 9. One can see from Table 9 that the R values for all the D models are higher than those of the other models; the values of R corresponding to D_1 at 1000 and 1050°C are the highest. The value of E corresponding to D_1 is 201.67 kJ mol^{-1}, which is near

Table 8
Values of $g(\alpha)$ for different solid state reaction mechanisms

Model	$g(\alpha)$	Reaction mechanism
R_1	α	Power law
R_2	$1-(1-\alpha)^{1/2}$	Contracting sphere
R_3	$1-(1-\alpha)^{1/3}$	Contracting cylinder
D_1	α^2	Power law, one-dimensional diffusion
D_2	$\alpha+(1-\alpha)\ln(1-\alpha)$	Valensi, two-dimensional diffusion
D_3	$(1-2/3\alpha)-(1-\alpha)^{2/3}$	Brounshtein–Ginstling, three-dimensional diffusion
F_1	$-\ln(1-\alpha)$	Manple unimolecular law
F_2	$[-\ln(1-\alpha)]^{1/2}$	Avrami–Erofeev, two-dimensional nuclei growth
F_3	$[-\ln(1-\alpha)]^{1/3}$	Avrami-Erofeev, three-dimensional nuclei growth

Key: R, phase boundary controlled; D, diffusion controlled; F, nucleation and nuclei growth controlled.

Table 9
The values of the correlation coefficient R and of the activation energy E

Model	r				E/(J mol^{-1})
	950°C	1000°C	1050°C	1100°C	
R_1	0.9482	0.99108	0.98984	0.97067	98.69
R_2	0.95470	0.99385	0.99316	0.99216	113.53
R_3	0.95626	0.99440	0.99694	0.99623	119.44
D_1	0.98144	0.99912	0.99916	0.99407	201.92
D_2	0.98390	0.99831	0.99774	0.99793	224.25
D_3	0.98471	0.99794	0.99665	0.99695	232.96
F_1	0.95932	0.99573	0.99877	0.99874	132.50
F_2	0.93433	0.98238	0.98934	0.99103	62.79
F_3	0.92436	0.97557	0.98373	0.98348	41.18

to the actual measured value of 195.82 kJ mol^{-1}. This explains why the controlling step of the nitridation reaction of Al–(Mg,Si) alloys seems to be one-dimensional-diffusion controlled.

4. Conclusions

There are two weight gain steps in the TG curve of Al–(Mg,Si) alloys in N_2. The first (560–750°C) is related to the conversion of Mg and Si and the second (750–1080°C) is due to the conversion of Al in the alloys to AlN.

Both the dopants, Mg and Si, enhance the nitridation reaction of Al in the alloys, but the action of Mg is obviously greater than that of Si.

The reaction rate equation of the nitridation of Al in the alloys can be expressed as the equation

$$dc/dt = KC_{Mg}^{n} C_{Si}^{m}$$

The calculated values of the rate constant are basically in agreement with the values found experimentally: the error is less than 8.3%.

The reaction mechanism of nitridation is found to be one-dimensional diffusion from the regression of $g(\alpha)$ vs. t. The value of the activation energy corresponding to the mechanism approaches the value found. Thus, the reaction mechanism of nitridation of Al–(Mg,Si) alloys is one-dimensional diffusion.

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