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Nitridation of Al-Mg-Si Alloys Through Dynamic Heating

(Penitridaan Aloi Al-Mg-Si Secara Pemanasan Dinamik)

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ABSTRACT

Nitridation behaviour of Al-Mg-Si alloys was studied as a function of temperature by means of thermogravimetry method. A reactive gas, N_2-4%H_2 at a rate of 10 ml/min was purged into the thermogravimetry analyser chamber. The Al alloys were heated from 25°C to 625°C at the heating rate of 15°C/min and then reduced to 3°C/min until it reached 1500°C. It was found that by varying the amount of Mg and Si in Al-Mg-Si alloys significantly influenced the growth of the composites. A differential thermogravimetric curve shows the Mg containing alloys experienced many steps of chemical reactions. This indicates that besides AlN presence as a major phase, other compounds also exist in the final product. The X-ray diffraction results confirmed the existence of oxide phases such as α-Al_2O_3, $MgAl_2O_4$ and MgO in addition to residual Si and Al metal. The presence of oxide compounds is believed to be due to the reaction between the alloying elements and residual oxygen gas left in the reaction atmosphere. It was also found that Si could play a role in promoting the weight gain of the composite produced. The heating rate has also a profound effect on the weight gain, whereby higher heating rate resulted in low yielded of AlN during the nitridation reaction of the Al-Mg-Si alloys.

Keywords: Thermogravitmetry; nitridation; dynamic heating; AlN

ABSTRAK

Kelakuan penitridaan aloi Al-Mg-Si dikaji sebagai fungsi suhu menggunakan kaedah termogravimetri. Gas reaktif $N_2$4%H dimasukkan ke dalam kebuk analisis termogravimetri pada kadar 10 ml/min. Aloi Al dipanaskan daripada suhu 25°C hingga 625°C pada kadar 15°C/min dan kadar tersebut kemudian dikurangkan kepada 3°C/min sehingga suhu mencapai 1500°C. Didapati dengan mempelbagaikan amaun Mg dan Si dalam aloi Al-Mg-Si, mempengaruhi pertumbuhan komposit dengan signifikan. Lengkung perbedaan termogravimetri mempamerkan aloi yang mengandungi Mg mengalami langkah tindakbalas kimia yang banyak. Ini menunjukkan selain AlN wujud sebagai fasa dominan, komponen lain turut hadir dalam produk akhir. Keputusan pembelauan sinar-X mengesahkan kehadiran fasa oksida seperti α-Al_2O_3, $MgAl_2O_4$ dan MgO sebagai tambahan kepada logam Al dan Si. Kehadiran sebatian oksida dipercayai disebabkan oleh tindakbalas antara unsur pengaloian dan gas oksigen tersisa yang masih tinggal dalam atmosfera tindak balas. Si juga didapati memainkan peranan dalam mempromosi pertambahan berat komposit yang dihasilkan. Kadar pemanasan juga mempengaruhi pertambahan berat dimana kadar pemanasan yang tinggi mengakibatkan penghasilan AlN yang rendah semasa tindak balas penitridaan aloi Al-Mg-Si.

Kata kunci: Termogravimetri; penitridaan; pemanasan secara dinamik; AlN

INTRODUCTION

The directed nitridation of molten Al alloys by vapour phase nitridants can be used to produce AlN ceramic matrix composites. Under appropriate alloy compositions, processing temperature and nitrogen pressure, a rapid reaction of the molten alloy occurs with the reaction products grow outward from the original metal surface (Daniel & Murthy 1995).

A protective nitride layer immediately forms on the surface of aluminium when it is exposed to nitriding atmosphere, even at low temperatures, which prevents further nitridation of Al in the liquid state. It is now recognised that the presence of volatile elements from group I and II in the Periodic Table will be able to hinder the formation of the protective layer and thus allow continuous nitridation of the alloys (Yuan et al. 1994). For example, Mg can acts as initiator to starts the reaction and also to maintain the oxygen gas level below a threshold value in nitriding atmosphere. Additional elements such as Si, Ge, Sn or Pb are also added to act as surface-active dopants to improve the wettability of the liquid alloy which will facilitate the transport of Al atoms through the reaction product to the reaction front (Scholz & Greil 1991). LeHuy and Dallaire (1989) reported that no significant growth of AlN/Al composite was observed in binary Al alloy systems (Al-Mg and Al-Si alloys) for temperatures below 1450°C at the heating rate of 4°C/min. However, for ternary alloys such as Al-Mg-Si exhibited accelerated weight gain for temperature beyond 1200°C. Scholz and Greil (1991) reported that the increase of Mg/Si ratio and decrease of oxygen pressure in the nitridating atmosphere, lead to four reaction domains; (i) passivating surface nitridation, (ii) diffusion-controlled volume nitridation, (iii) volume nitridation involving outward growth of AlN-Al and (iv) a break-away nitridation with complete conversion of Al to AlN.

The alloy compositions will influence the above-mentioned processes and make the identification of their individual roles in the overall process complicated. Nevertheless, such effort has been done to identify their individual roles in the directed nitridation of Al alloys. Mg for instant was added into the alloys not only to improve its wettability but also to act as a gettering agent in maintaining the oxygen partial pressure below a critical level. In this paper the effects of Mg and Si on nitridation of Al-Mg-Si alloys are reported.

Materials and Methods

Alloys were prepared from aluminium, magnesium and silicon of high purity (>99.9%) by conventional casting technique. Metals were melted in graphite crucibles at 800°C under argon gas to reduce any contamination. The alloys were cast into cylindrical rods. These rods were machined to smaller billets of 4 mm in diameter with about ~135 mg in weight for nitridation experiment to be carried out in the thermogravimetry analyser chamber. XRF analysis was carried out on the cast Al alloys in order to determine the actual composition of the alloys (Table 1).

Simultaneous thermogravimetric analyses (TGA) were carried out using a thermogravimetry analyser, TGA/SDTA851^e/LF 1600, Mettler Toledo. Sintered high-density alumina crucibles (70 ml) serve as alloy container for the operation at high temperatures. Before commencing the experiment, air in the furnace chamber was removed and purged with N_2-4%H_2 gas until it reached one atmospheric pressure. Subsequently a steady flow of the mixed gases at ~10 ml/min was supplied. All the measurements were performed under dynamic heating conditions at two stages programmed heating rate, namely 15°C/min from 25°C to 625°C and 3°C/min from 625°C-1500°C. An X-ray diffractometer, Siemens 5000 with Cu K_α was used for phase analysis of the resultant reaction products.

Results and Discussion

The results of the nitridation experiments carried out in the TGA chamber are shown in Table 2. The data were obtained after the experiments were completed at 1500°C. The presence of Mg and Si was found to affect the weight gain significantly. Figure 1a shows the weight gain curve of Al-7Mg-(1-4)Si alloys heated in nitriding atmosphere. At the beginning of the nitridation (<700°C), Al-7Mg-(1-4) Si alloys did not exhibit any significant changes in weight. Above 700°C the alloys gained weight significantly and all had a similar increase in weight gain until about 1180°C. As the temperature increased more than 1180°C, the amount of Si incorporated in the alloys influenced the weight gain. Al-7Mg alloys with low percentage of Si (1%) appeared to gain the highest weight during the nitridation compared to the one with higher amount of Si (4%). It shows that Si affected the nitridation reaction with the lower amount of Si increased the nitridation reaction.

Derivative weights gain curves (DTG) (Figure 1b) indicated that the Al-7Mg-(1-4)Si alloys had gone through a few steps of reaction according to the nitriding temperature. At the temperature between 700° and 1000°C, the increase in weight occurred at various reaction steps and each alloy has distinct reaction rate even though not very much different. According to Scholz & Greil (1991), these situations arose from the vaporization of Mg and also reaction to form oxide (α-Al_2O_3, $MgAl_2O_4$) and nitride (Mg_3N_2) phases. The results were confirmed from the XRD analysis (Figure 2) that shows the existence of several phases after nitridation namely AlN, α-Al_2O_3, $MgAl_2O_4$, MgO, Al and Si. The formations of oxide phases were due to the reaction between the metals and residual O_2 gas present in the reaction atmosphere. However no Mg_3N_2 phase was detected in the final product as it is not stable at 1500°C (LeHuy & Dallaire 1989).

TABLE 1. Composition of Al alloys

Alloys	(wt %)		
	Al	Mg	Si
Al-7Mg	92.66	7.34	-
Al-7Si	92.75	-	7.25
Al-7Mg-1Si	91.77	7.11	1.12
Al-7Mg-2Si	90.76	7.13	2.11
Al-7Mg-3Si	89.75	7.12	3.13
Al-7Mg-4Si	88.76	7.1	4.14
Al-6Mg-1Si	92.79	6.1	1.11
Al-5Mg-1Si	93.78	5.13	1.09
Al-4Mg-1Si	94.76	4.13	1.11
Al-3Mg-1Si	95.79	3.13	1.08

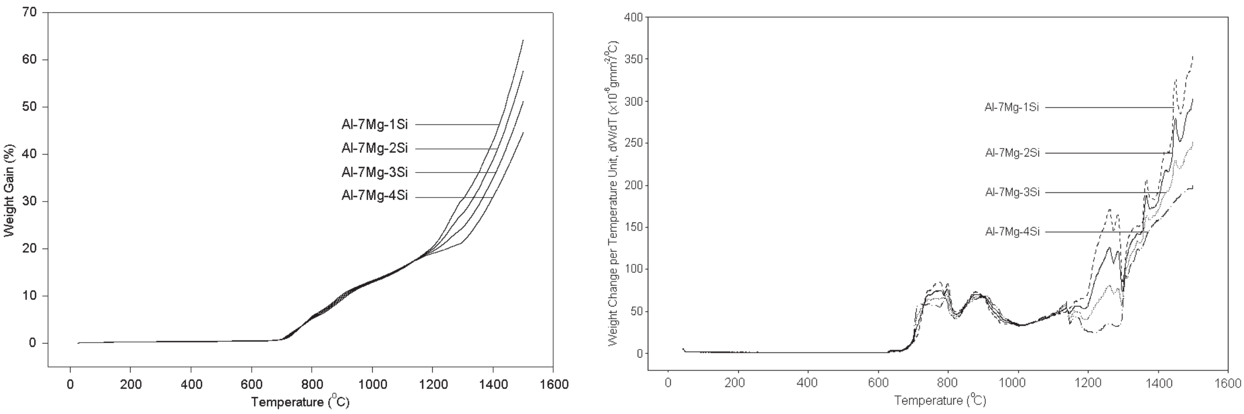
TABLE 2. TGA data of the Al-alloys after heating up to 1500°C in nitriding atmosphere

Sample	Initial weight (mg)	Weight gain (mg)
Pure Al	134.21	5.88
Al-7Mg	134.41	32.29
Al-7Si	134.32	2.01
Al-7Mg-1Si	134.48	86.31
Al-7Mg-2Si	134.46	77.51
Al-7Mg-3Si	134.44	68.70
Al-7Mg-4Si	134.42	59.90
Al-6Mg-1Si	134.50	74.71
Al-5Mg-1Si	134.50	67.28
Al-4Mg-1Si	134.56	57.91
Al-3Mg-1Si	134.59	51.66

As the temperature was increased from 1000° to 1137°C, the DTG curves were almost flat and like previously each alloy shows different reaction rate according to their composition. It was found that at this stage, both vaporization of Mg and alloy reaction to form either oxide or nitride phase have the same rate. The drastically increase in weight of DTG curves for the temperature between 1137°C until 1295°C was due to the occurrence of volume nitridation (Scholz & Greil 1991). At the final stage, a huge increment in weight was observed from 1295°C till the end of the nitridation experiment at 1500°C was believed to be due to the breakaway nitridation (Scholz & Greil 1991).

The nitridation reaction of Al-7Mg-(1-4)Si alloys occurred by continuous supply of molten Al to the alloy surface. Therefore, Si concentration increased especially near the reaction front leading in an additional increase in viscosity of molten Al near the surface. The different features of weight increment for ternary Al-Mg-Si alloy are attributed by the viscosity of the melt (Kagawa et al. 1993). As flow rate of molten Al-Mg-Si alloy to surface was getting less, lesser amount of Al reacted with N_2 gas and resulted in low nitride growth rate. Higher Si concentration in the initial alloy increased the viscosity of the melt and also the thickness of Si rich layer thus the diffusion flux of Al to the reaction zone decreased. This, therefore led to the decreased in weight gain. High viscosity of the melt resulted slow infiltration of atoms to the surface (Kagawa et al. 1993) and lead to the decreasing of reaction between the atoms of alloy and N_2-4%H_2 (Moller et al. 2001).

Figure 3 shows the thermogravimetric curves of Al-(3-7)Mg-1Si alloys where all samples started to gain weight at a temperature around ~ 680°C. The alloys experienced various steps of reactions during nitridation and were dependent on the percentage of Mg added into the alloys. The presence of high amount of Mg encouraged the nitridation process and increased weight gain tremendously. As in the experiment of Al-7Mg-(1-4)Si alloys, the reaction began with the vaporization of Mg at the temperature of 700° to 900°C. The slow vaporization of Mg led to the formation of tiny pores at the surface and made a way for the diffusion of molten Al through capillary action and formed a reaction front. Initially, the rate of vaporization was almost proportional to the amount of Mg in the alloy. The low amount of Mg in the alloys resulted in low vaporization of Mg and decreased the infiltration of molten Al to the surface and vice versa. Therefore, weight gain decreased with Mg content present in the Al alloys. From 900°C to 1090°C, the DTG curves were found to be almost flat because the amount of Mg vaporized and the amount of reaction products produced were equal. A drastic increment in weight occurred between 1090° and 1300°C due to volume nitridation (Figure 4), which involved the outward growth of the Al/AlN composite as also reported by Scholz and Greil (1991). Further increase in temperatures until the end of the experiment, the weight



(a) (b)

FIGURE 1. (a) TGA and (b) DTG curves of Al-7Mg-(1-4)Si alloys heated until 1500°C in nitriding atmosphere

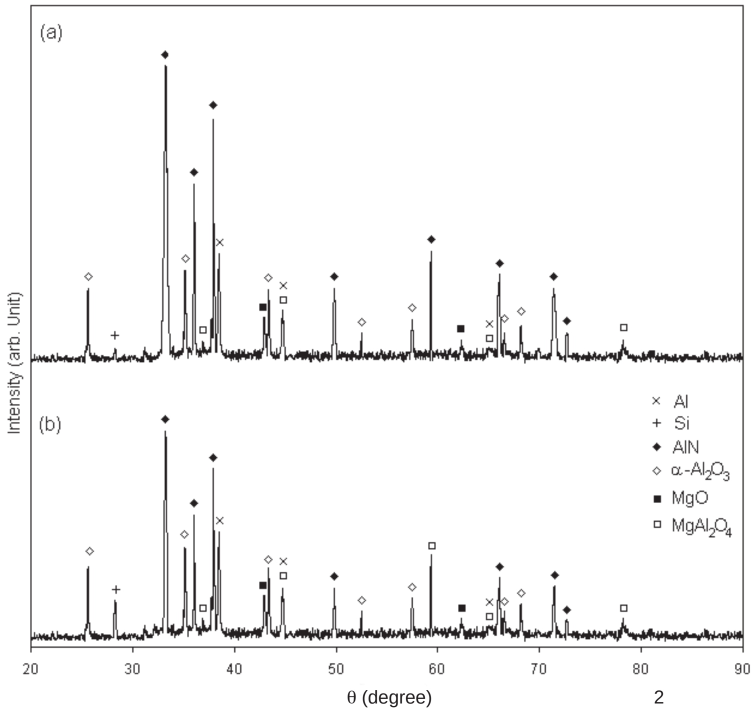
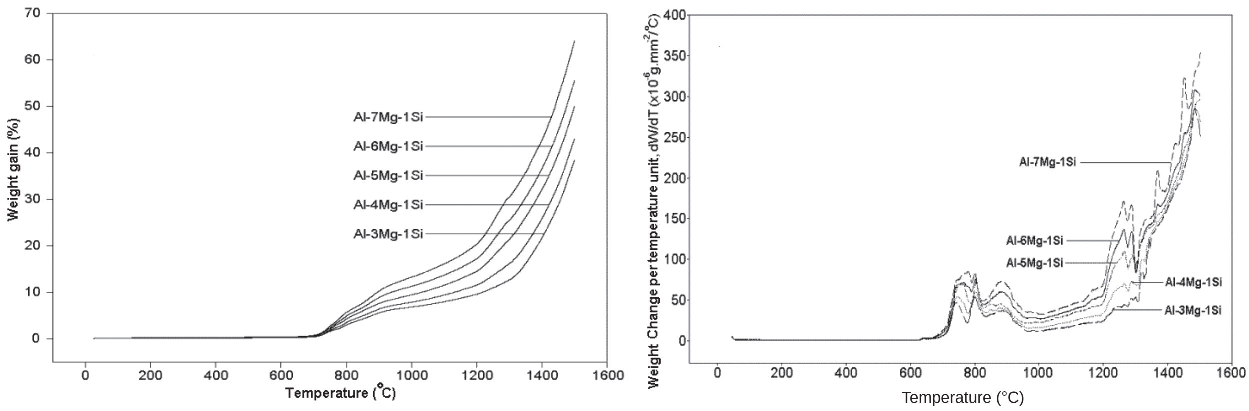


FIGURE 2. XRD diffractograms of (a) Al-7Mg-1Si and (b) Al-7Mg-4Si alloy heated until 1500°C in nitriding atmosphere

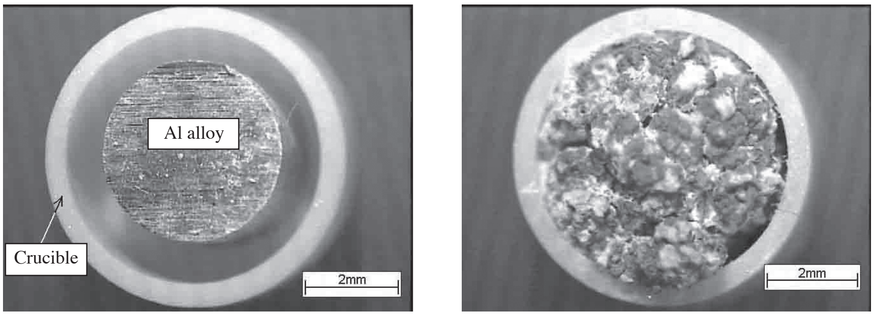


(a) (b)

FIGURE 3. (a) TGA and (b) DTG curves of Al-(3-7)Mg-1Si alloy heated until 1500°C in nitriding atmosphere

gain seemed to be linearly proportional to temperature. It was believed that the breakaway nitridation reaction occurred whereby Al in the alloy was completely converted into AlN (Scholz & Greil 1991).

Four different heating rates were also studied in the nitridation process of Al-7Mg-1Si alloy, namely 3°C/min, 4°C/min, 5°C/min and 6°C/min. The TGA curves (Figure 5) show that the Al-7Mg-1Si alloy had similar weight gain for all heating rates for temperature up to 1000°C before a significant different in weight gain was observed. During the heating, infiltration of molten metal through the pores at the molten surface did not occur in a short time. Reaction between the Al alloy and gas phase also required a long time to take place. A long period of process gave ample time for the molten metal to infiltrate toward the surface and allowed a complete conversion of metal phase (Al) to ceramic (AlN). This is in agreement with Hou et al. (1995), who reported that a long period of the nitridation process yielded higher AlN.



(a) (b)

FIGURE 4. Al-Mg-Si alloy (a) before heating and (b) after heating at 1000°C in nitriding atmosphere shows the outward growth of the AlN/Al composite

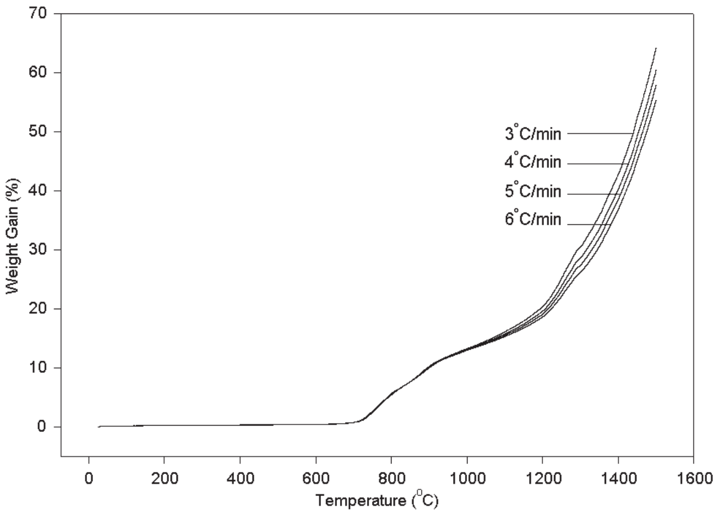


FIGURE 5. TGA curves of Al-7Mg-1Si alloy with different heating rate in nitriding atmosphere

CONCLUSION

The low Si but high Mg concentration in the Al-Mg alloys improved the nitridation reaction, which resulted in a high nitride growth rate. AlN is the major phase existed in the final product besides MgO, α-Al_2O_3, $MgAl_2O_4$, Si and residual Al. The presence of the oxide phases indicated the existence of threshold O_2 content in the nitriding atmosphere. A lower heating rate means a longer reaction period is required, thus allowed more conversion of Al to AlN to form Al/AlN composite.

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REFERENCES

Daniel, B.S.S. & Murthy V.S.R. 1995. Directed melt oxidation and nitridation of aluminium alloys: a comparison. *Materials & Design* 16(3): 155-161.

Hou, Q., Mutharasan, R & Koczak, M. 1995. Feasibility of aluminium nitride formation in aluminium alloys. *Materials Science and Engineering A* 195: 121-129.

Kagawa, Y., Khatri, S.C. & Koczak, M.J. 1993. Directed nitridation of liquid aluminium alloys: growth process and modelling. *Ceramics Engineering & Science Proceeding* 14: 776-781.

LeHuy, H. & Dallaire, S. 1989. Effect of Si and Mg dopants on the kinetics of aluminium alloys nitridation. *Proceeding of the International Symposium on Ceramics and Metal Matrix Composites CIM*. 17: 302-311.

Moller, W., Parascandola, S., Telbizova, T., Gunzel, R. & Richter. 2001. Surface processes and diffusion mechanisms of ion nitriding of stainless steel and aluminium. *Surface and Coating Technology* 136: 73-79.

Scholz, H. & Greil, P. 1991. Nitridation reaction of molten Al-(Mg,Si)-alloys. *Journal of Materials Science* 26: 669-677.
Yuan, D.W., Chengn, V.S., Yan, R.F. & Simkovich, G. 1994. Reaction formed processes for AlN/Al ceramic composites. *Ceram. Eng. Sci. Proc.* 15(4): 85-94.

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