DIRECT NITRIDATION OF ALUMINIUM UNDER FLOWING NITROGEN GAS: THE EFFECT OF OXYGEN PRESSURE

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Abstract- AlN has found applications in the automobile industry, aerospace, electronic industry, high temperature applications and other areas. Nitridation of aluminium in the forms of ingot and powder were carried out in a stainless steel tube furnace under flowing nitrogen gas at temperatures below the melting point of aluminium (550^0 – 630^0C). Magnesium powder and hydrogen gas were separately used to reduce the oxygen pressure of the furnace. The results showed that the use hydrogen gas successfully reduced oxygen pressure below the permissible value, which promoted nitridation process. XRD results gave AlN peaks with highest intensities (for both Al coupon and powder) at 630^0C after 4 hours of holding time when hydrogen gas was jointly flown with nitrogen gas into the furnace. The AlN peak intensities increased with temperature and holding time. XRD result did not revealed AlN peaks in the Al coupons nitrided in the absence of hydrogen gas.

Keywords- Aluminium, Aluminium Nitride, Direct Nitridation, Oxygen Pressure, XRD,

I. INTRODUCTION

Aluminium nitride has continued to attract researchers' attention in the last two decades. This is not unconnected with its desirable properties such as: wide band gap, which makes it useful in optoelectronic devices [1, 2]; good electrical and thermal properties which, makes it applicable as thermal interface for flexible electronics for quick dissipation of heat, in UV structure and photovoltaic devices [2-4]. Its good chemical stability makes it applicable in high temperature applications, while its good wear resistance makes it applicable as a thin layer coating to impart hardness and wear resistance on aluminium, steel and other metals [5-7]. Its high melting point of about 2800^0C makes it useful as refractories and other components for high temperature applications [8]. With such attractive qualities of AlN, many researchers have used different methods for its production: Direct nitrdidation of aluminium powder [9, 10]; infiltration technique [11-13], chemical vapour deposition methods, CVD [14-16], liquid-gas direct nitridation [17, 18], plasma nitridation [19, 20], self-propagation high temperature synthesis (SHS) [21, 22] and carbothermal reduction method to mention but a few [23-25].

In this paper, however, the effect of furnace atmosphere on nitridation of aluminium under flowing nitrogen below its melting point is being presented. The aluminium used was in the form of powder (99.0% purity) and ingot (A6066). The basis for nitridation of aluminium ingot in the form of coupons is to explore the possibility of forming a thin AlN coating on Al metal for the purpose of surface treatment to enhance its wear resistance and other electrical properties for use in the electronics industry and to explore the possibility of melting same to form Al-AlN composite.

II. MATERIALS AND METHODS

2.1 Materials and equipment

The following Materials were used for this research: aluminium ingot (A6066) sourced from Materials workshop Dragon, University of Malaysia Perlis; Magnesium and aluminium powder were sourced from Bumi Padu Solution, Kuala Lumpur, Malaysia; while oxygen free nitrogen (OFN) and hydrogen gases were sourced from Kangar in Perlis. The equipments used for this research include; stainless steel electric tube furnace, XRD and FESEM machines for phase/microstructural analyses, Arc Spark Machine model Q8 Magellan for chemical analysis, digital weighing balance and grinding machine for surface preparation.

2.2 Procedure

Prior to their use, the surfaces of the aluminium coupons of about 2.0g each and fairly equal sizes and shapes, which were cut from the aluminium ingot (A6066), were filed and ground on a grinding machine to remove any available oxide scales previously formed on them. The Al coupons and powders were heated inside the tube furnace at 20^0C/min and under normal pressure as follows: (i)The aluminium coupons were placed inside alumina crucible and charged into the stainless steel tube furnace and heated to temperatures of 550^0C, 575^0C, 600^0C and 630^0C under flowing nitrogen atmosphere and were held at each temperature for 1 through 4hours; (ii) Two of the Al coupons were heated at 600^0C and 630^0C for 4 hours under the same condition as the previous treatments, but with 3.0g magnesium powder placed side by side inside the furnace in order to reduce oxygen pressure; (iii) Step (ii) above was repeated but with magnesium powder removed while a mixture of nitrogen and hydrogen gases were jointly flown into the furnace in the ratio 4:1 respectively; (iv) 3.0g of Al powder was heated under the same condition of flowing nitrogen

at temperatures of 600^0C and 630^0C for 4 hours each in the absence and presence of flowing hydrogen in the ratio N_2:H_2; 4:1.

The weight gains were recorded in each case. The treated samples as well as the as-received samples were subjected to XRD and FESEM analyses to determine the effect of oxygen pressure in the furnace on the nitridation process and whether AlN was formed in the samples.

III. RESULTS AND DISCUSSION

The as-received as well as treated samples were characterized using XRD and FESEM as presented.

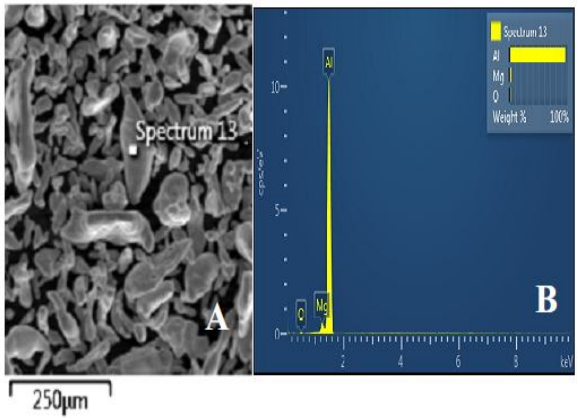


Figure 1(A) SEM image view of the as-received Al powder at 1000x (B) EDS of Al powder

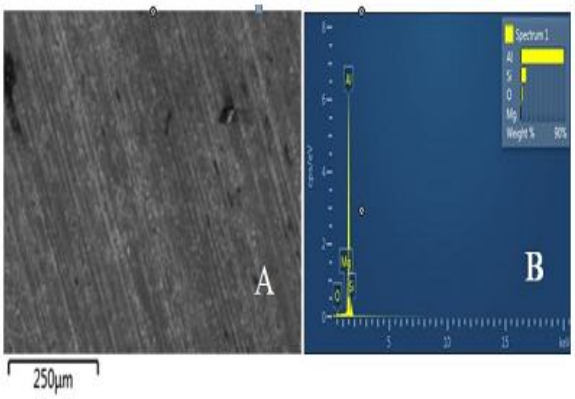


Figure 2 (A) SEM view of as-received Al ingot (B) EDS analysis of as-received Al ingot.

3.1 XRD and SEM Analyses

The SEM view and EDS of the as-received Al powder at 1000x magnification are presented in Fig.1(A & B). The EDS gave 0.26wt% O_2, 0.47wt%Mg and the balance is aluminium. For the as-received aluminium ingot (A6066), the SEM image view and EDS are presented in Figure 2 (A &B). The EDS gave 3.12wt% oxygen, 0.69wt% Mg, 10.58wt% silicon and the balance is aluminium. When Arc Spark machine was used, the composition of the Al ingot gave; Al=90.44%, Si=8.29%, Mg=0.36%, Fe=0.37%. Ti=0.12, Cu=0.12% and the balance is insignificant amounts of other elements put together. After the treatments on the Al coupons at temperatures between 550^0C to 630^0C for time ranging from 1 through 4hours, XRD results did not show peaks of AlN when N_2 was flown alone. Also, when Mg powder was placed side by side inside the furnace to reduce oxygen pressure, no AlN peaks were visible as almost all the Mg placed inside the furnace oxidized to MgO (see Figure.4B&C).

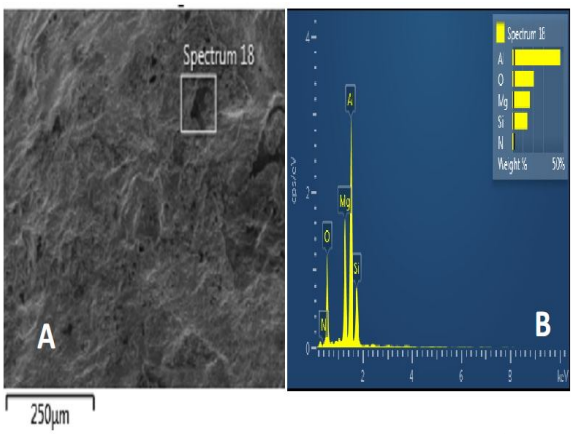


Figure 3(a) SEM image view of Al ingot heated at 575^0C for 4hrs (b) EDS analysis.

3.2 Effect of Oxygen Pressure

Theoretically, the thermodynamics and kinetics of nitridation of Al has been found to be favourable within the temperature range considered in these investigations [9, 26]. However, oxidation of Al, Mg and Si by oxygen in the furnace is more favourable even at lower temperatures than the ones used in this research; for this reason Al_2O_3, MgO and SiO_2 were preferentially formed rather than AlN as shown by XRD results [9, 27, 28]. This means that despite the initial flushing of the furnace with nitrogen gas prior to the nitridation process, oxygen was still present in the furnace, hence the increase in oxygen content in the treated sample as revealed by EDS. Though there were small amounts of nitrogen in the treated Al coupons as revealed by EDS; some of the nitrogen was in a combined form either as Si_3N_4 or Mg_3N_2.

After 4hours of holding time at 575^0C, EDS result showed that 0.56wt%N_2, and 10.35wt%O_2 were present, according to Figure 3(A & B). As the holding temperatures were increased up to 630^0C, it was observed that the amount of oxygen in the heated Al coupons increased though the increase was not consistent. The weights gained were observed to be very small. This could be as a result of the small weights of the coupons used. The increase in oxygen content with temperature could be as a result of increase in diffusion of gases and reaction rates.

When the Al coupons were heated in the furnace under the flow of N_2 and in the presence of Mg powder placed side by side in the furnace to scavenge for oxygen, almost all the Mg were oxidized to MgO as shown in Figure 4 (C). XRD analysis of the heated Mg powder after 4 hours revealed that the white powder formed was MgO, while the yellow powder was Mg_3N_2 [9, 26]. This implies that the masst of Mg

powder placed in the furnace was not capable of reducing the oxygen pressure of the furnace below the minimum required level to allow nitridation of Al [9, 29, 30].

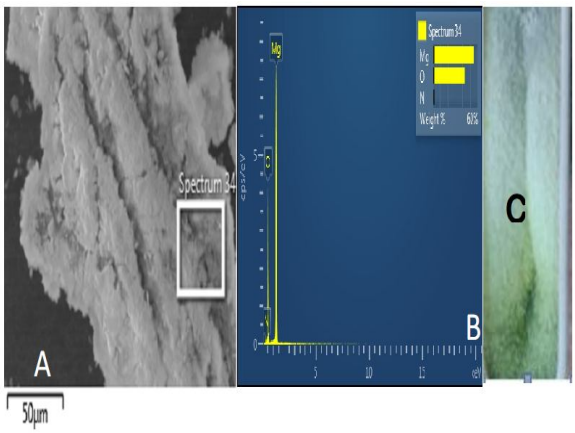


Figure 4 (A) SEM image view (B) EDS analysis (C) Mg powder placed inside furnace after 4hrs of nitridation.

When Mg powder was charged into the furnace through a separate crucible in order to remove any available oxygen in the furnace, EDS results revealed a significant increase in the Mg content on the surface of the Al coupons after the nitridation process. The reason for this anomaly could be attributed to the effect of flowing nitrogen into the furnace, which might have blown the Mg powder onto the surfaces of the Al coupons during the process. This means that the use of Mg powder contaminates the surface of the treated samples rather than reducing oxygen pressure and therefore, should not be employed.

The graph below (Fig. 5) shows the plots of weight gains by the Al coupons against holding times at various temperatures when the furnace was heated under nitrogen flow alone.

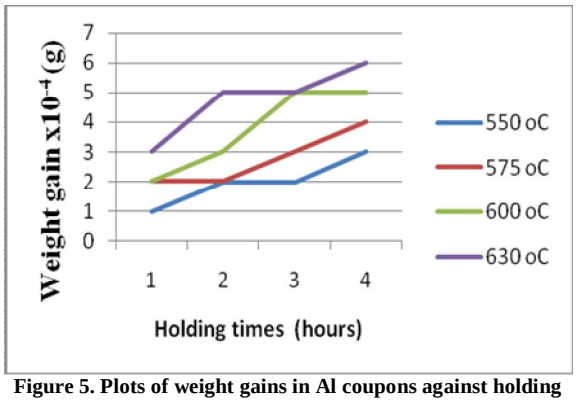


Figure 5. Plots of weight gains in Al coupons against holding times at different temperatures.

The graph above shows that the weight gains in Al coupons increase with temperature and holding time. The result shows that the weight gain was minimum at temperature of 575^0C after 1hour of nitridation, while the maximum weight gain was observed at the temperature of 630^0C after 4 hours of nitridation. It is important, therefore, to emphasize that in the absence of suitable reducing agent to reduce oxygen pressure below the tolerable value, no AlN can be formed on the Al coupons [31].

3.3. Nitridation of Al powder.

Considering the nitridation of Al powder in the absence of hydrogen in the furnace; XRD analysis of the powder shows small AlN peaks whose intensities were more significant at 630^0C than at 600^0C. When hydrogen gas was introduced into the furnace, the intensities of AlN peaks observed were higher than those in the Al powder heated in the absence H_2. The results, therefore, show that continuous flow of H_2 into the furnace can successfully reduce oxygen pressure below the minimum required to facilitate nitridation process [27]. The peaks observed in the treated Al powders had higher intensities than those obtained in the Al coupons. This could be due to ease of diffusion of N_2 into the loose Al powder than in the dense Al coupons.

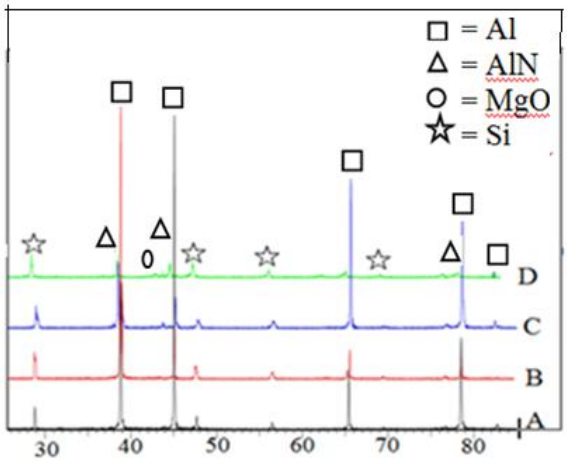


Figure 6. XRD patterns for Al coupons: (A)As-received, (B) @ 575^0C, (C) @ 600^0C, (D)@ 630^0C

The XRD patterns shown in figure 6 (C) and (D) are those of Al coupons heated under hydrogen atmosphere and both gave peaks of Al, AlN and Si. In Fig 6 (B), however, there were no AlN peaks, but there were SiO_2 peaks instead of Si probably due to oxidizing atmosphere of the furnace. Fig. 6(A) represents as-received Al ingot which is naturally not expected to show any AlN peaks. It was also observed that heating Al coupons closer to their melting points brought about softening and change of shape of the coupons.

However, XRD results of treated Al coupons showed slight overlapping of Si peaks and those of SiO_2 peaks. In the absence of H_2 gas (see Fig 7B), the atmosphere was oxidizing which resulted in SiO_2 peaks as observed. When hydrogen gas was introduced into the furnace, there was no oxygen to react with silicon hence Si peaks were observed at the same position with those of SiO_2. Reason for such overlapping could be due to prefer orientation or similarities in crystal structures [32].

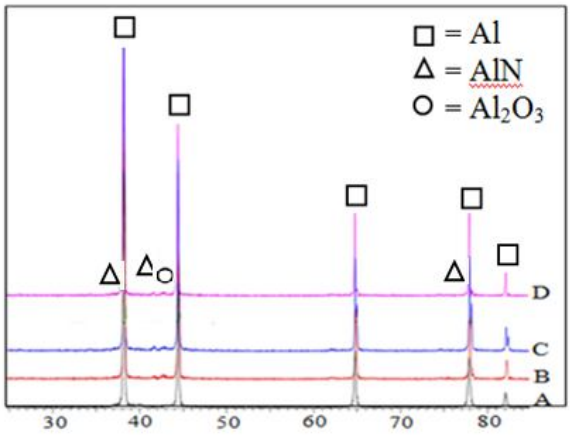


Figure 7. XRD peaks for Al powder for: (A)As-received Al powder (B) heated at 600^{0}C without H_2 (C) heated at 600^{0}C + H_2 (D) heated at 630^{0}C +H_2

Figure 7 above presents the XRD analyses for the Al powder after 4hours of nitridation at different temperatures. The results revealed small AlN peaks as shown in Fig 7(B), but the intensities of the peaks were seen to be more in Fig 7(C) and (D) when H_2 was used. From the results obtained, it could be inferred that increasing the holding temperature, prolong holding time and use of H_2 in the furnace promote formation and growth AlN [8, 25, 26, 29].

CONCLUSION

The results obtained have shown that it is possible to nitride Al in the form of ingot or powder below the melting point of Al (660^{0}C). The AlN peaks observed were found to have the higher intensities at temperature of 630^{0}C when hydrogen gas was used than at lower temperatures. The use of hydrogen gas, therefore, successfully lowers the oxygen pressure and promoted nitridation process. For the purpose of surface treatment of aluminium components, nitridation of aluminium below 600^{0}C is recommended if softening and change of shape of the components is to be avoided though this will require prolonged holding time to form a reasonable AlN film on the components.

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