Wear characteristics of Al-AlN composites produced in-situ by nitrogenation

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Abstract: In the present scenario most of the parts used in automobile and aerospace industries are made of composites. Aluminium metal has a very high strength to weight ratio. Al-AlN metal matrix composites have excellent mechanical properties like good wear resistance, high hardness and high strength to weight ratio which are obtained from low density of aluminium and high hardness and wear resistance of AlN. Therefore, use of Al-AlN MMC leads to advantages in automobile industries as it reduces fuel consumption and gives better structural strength. The composites can be produced ex-situ by introducing AlN as reinforcement into the metal matrix and in-situ by nitrogenation process. In the present process Al-AlN composites were fabricated by treating molten aluminium with a mixture of CaO and NH₄Cl and held at temperature range at 750-930 C and then cast into a metal mould. Addition of CaO to NH₄Cl is found to have a more pronounced effect as a nitrogenation agent in comparison with NH₄Cl in the molten aluminium in the temperature range of 700-1000°C. Castings of aluminium and Al-AlN composites were prepared by mixing different ratios of aluminium and NH₄Cl, at different casting temperatures and holding time. Wear resistance and hardness of the samples were determined, and microstructure studies were carried out. The composite formed using higher amount of NH₄Cl had higher hardness and wear resistance.

1. Introduction

Aluminium and aluminium alloy based composites are gaining importance due to their specific properties like excellent strength, high ductility, low density and better wear resistance and find applications in automotive and aerospace industries. The in-situ process is a simple, economical method of synthesizing MMCs and is a one-step process of establishing ceramic particles into the metal matrix. AlN due to its non-reacting behaviour with aluminium makes it a suitable reinforcement for forming aluminium matrix composites. CaCO₃ is used as a catalyst for efficient nitridation. In the present investigation NH₄Cl+CaO are taken as nitriding agents for the formation of AlN in aluminium. And a comparative study between aluminium and Al-AlN composite is done for wear resistance and hardness characteristics [1, 3].

1.1. Aluminium Nitride

Aluminium nitride has high thermal conductivity. It is stable at high temperatures in inert atmospheres and melts at 2800°C. In a vacuum, AlN decomposes at ~1800°C. In the air, surface oxidation occurs above 700°C, and even at room temperature, surface oxide layers of 5-10 nm have been detected. This oxide layer protects the material up to 1370°C. Above this temperature bulk oxidation occurs. Aluminium nitride is stable in hydrogen and carbon dioxide atmospheres up to 980°C. The material dissolves slowly in mineral acids through grain boundary attack, and in strong alkalis through attack.
on the aluminium nitride grains. The material hydrolyzes slowly in water. Aluminium nitride is resistant to attack from most molten salts, including chlorides and cryolite.

1.2. Al-AlN Composites

Al-AlN composites are fabricated by milling and hot pressing of composite powders [1]. The physical properties such as thermal expansion, thermal conductivity, electrical conductivity, hardness, Young’s modulus, and fracture strength of these composites change with the AlN content [2]. It has been observed that Al-AlN MMCs exhibit better properties than those of Al-SiC and Al-Al₂O₃ composites.

Al-AlN composites have been made by forming aluminium nitride by in situ reactive nitrogen gas injection into molten aluminium alloys experimentally over the temperature range from 700 to 1500°C [4,5]. It has been seen that aluminium nitride can be melt formed in the presence of Mg and Si, with nitrogen and/or ammonia as the reactive gases at temperature above 1100°C. In this, magnesium serves as a catalyst [6]. Magnesium nitride is first formed in the vapour phase by the reaction of vaporized magnesium and nitrogen gas, followed by incorporation of magnesium nitride particles into the molten aluminium. Then by in-situ substitution reaction, aluminium nitride forms between magnesium nitride and aluminium [7,8]. Up to 17 wt. % aluminium nitride in an aluminium alloy has been formed with an average reinforcement size of 3 μm [9]. The potential for this process permits economical liquid phase processing of aluminium nitride-aluminium metal matrix composite with nitrogen gas injection for structural, thermal and wear applications [12,13].

Al-AlN composites have been synthesized using NH₄Cl and NH₄Cl+CaO powders as sources of nitrogen in molten aluminium in the temperature range of 700-1000°C [14]. Active nitrogen dissociated from ammonia at high temperature is used to form AlN. The addition of CaO to NH₄Cl is found to have a more pronounced effect as a nitrogenation agent in comparison with NH₄Cl [10,11].

2. Chemical Reactions

At high temperatures, ammonium chloride dissociates into ammonia and hydrogen chloride as per the following equation [1]:

\[
\text{NH}_4\text{Cl} \rightarrow \text{NH}_3 + \text{HCl} \quad \Delta G = +91.2 \text{ KJ/mol} \quad (1)
\]

Powders of CaO and NH₄Cl when mixed in the ratio of 1:1 by weight and added to aluminium melt at temperatures of 700-900°C, the following reactions occur:

\[
2\text{NH}_4\text{Cl} + 2\text{CaO} \rightarrow 2\text{NH}_3 + \text{CaCl}_2 + \text{Ca(OH)}_2 \quad \Delta G = -33.3 \text{ KJ/mol} \quad (2)
\]

\[
2\text{Al} + 2\text{NH}_3 \rightarrow 2\text{AlN} + 3\text{H}_2 \quad \Delta G = -270.6 \text{ KJ/mol} \quad (3)
\]

3. Experimental Procedure

Commercially pure aluminium is used for the experiment. The aluminium was melted in a graphite crucible in a pit type resistance furnace. After attaining a steady temperature, ammonium chloride powder and calcium oxide powder, of 1:1 ratio, wrapped in thin aluminium foil was added into the molten aluminium. The melt was manually stirred by a steel rod until the gas evolution stopped. After removing the dross the melt was poured into a metal mold. The MMC thus prepared was then cut into specific size for further testing.

3.1. Sample -1, Al-AlN Composite

For preparing sample-1, 400 g of aluminium was melted in a graphite crucible and held at 750°C [15]. Then 96g of ammonium chloride powder and 96g of calcium oxide powder wrapped in thin aluminium foil was added into the molten aluminium. The mixture of the powders was in 1:1 ratio. The melt was held for 30 minutes in furnace and manually stirred by a steel rod. Then the melt was poured into a cylindrical metal mold of 20mm diameter.
3.2. Sample -2, Al-AlN Composite
For preparing sample-2, 400 g of aluminium was taken for melting and held at 900 °C. For higher amount of nitrogenation in sample-2, 120g of ammonium chloride powder and 120g of calcium oxide powder wrapped in thin aluminium foil was dipped into 400 g of molten aluminium held at 900 °C [15]. Then the temperature was maintained at 930 °C and held for 2 hours 30 minutes. During this period the melt was manually stirred periodically to prevent porosity and then it was cast in a horizontal metal mould.

3.3. Hardness Test
Hardness of the samples were determined by using the Brinell hardness tester with the application of 750 kgf load for 15 seconds. A 5 mm diameter steel ball was used as an indentor. Hardness of each sample was measured at least five times.

3.4. Wear Resistance
Wear resistance by weight loss method.
In this test the wear rate is calculated by measuring initial and final weight of specimen before and after the test respectively and their difference gives the amount of material loss due to wear. It is also known as gravimetric analysis.

\[
\text{Let Initial weight of specimen } = W_1 \text{ gm} \\
\text{Final weight of specimen } = W_2 \text{ gm} \\
\text{Weight loss due to wear } = W_1 - W_2 \text{ gm} \\
\text{Wear rate of specimen } = \frac{(W_1 - W_2)}{t} \\
\text{Where } t = \text{ time of sliding}
\]

The metal matrix composite (Al-AlN) specimens were polished and prepared as a pin by machining. The specimen was weighed and the initial weight was noted. Then the sample pin was mounted on the wear testing machine. The machine used to measure the abrasive wear is a DUCOM pin on disk tribometer, which consists of a pin on disc, loading panel and controller. The sample machined as a pin is attached to the pin holder mechanism of the machine. The wear disk is a EN31 Steel disk, hardened to 60HRC. The machine is connected to controller to control and measure rotational speed, applied load, sliding time. The pin was weighed before and after each test and the weight loss was used as the measure of wear. The wear test was conducted by varying the load and keeping the speed and time constant. Then graphs between weight loss vs load were plotted [6, 7].

4. Results & Discussion
4.1. Hardness
Brinell Hardness
(Load= 750 kg, D= 5 mm, Time= 15 secs.)

| Table 1. Hardness of aluminium and Al-AlN composites. |
|-----------------|-----------------|-----------------|
| Brinell Hardness | Al (kgf/mm²) | Al-AlN (24-24) (Sample-1) | Al-AlN (30-30) (Sample-2) |
| Test 1 (kgf/mm²) | 54.56 | 56.55 | 57.64 |
| Test 2 (kgf/mm²) | 54.60 | 56.33 | 58.98 |
| Test 3 (kgf/mm²) | 54.51 | 56.50 | 58.60 |
| Test 4 (kgf/mm²) | 54.55 | 56.49 | 58.12 |
| Test 5 (kgf/mm²) | 54.54 | 56.19 | 58.35 |
| Mean Hardness (kgf/mm²) | 54.55 | 56.41 | 58.34 |
Figure 1 shows that Al-AlN composite, sample 1, has higher hardness than aluminium and the hardness of sample-2 which has higher amount of AlN is higher than that of sample 1 indicating that increase in the amount of AlN in the composite increases the hardness of the composite.

4.2. Wear Resistance
4.2.1. Wear of Al and Al-AlN composites at different loads and at 500 rpm speed and 10 minutes.

Figure 2. Wear of Al and Al-AlN composites at different loads and at 500 rpm speed and 10 minutes.
Figure 2 shows that wear increases with increasing load in aluminium as well as Al-AlN composites. But Al-AlN (24-24), sample-1, and Al-AlN (30-30), sample-2, composites have greater wear resistance as compared to pure aluminium. Among the composites Al-AlN (30-30), sample-2, composite has superior wear resistance.

4.2.2. Wear of Al and Al-AlN composites at 500 rpm speed and 20 minutes.

![Figure 3](image-url)

**Figure 3.** Wear of Al and Al-AlN composites at different loads at 500 rpm speed and 20 minutes.

Figure 3 shows that at 500 rpm speed (Sliding velocity of 2.1 m/s) and 20 minutes the weight loss of all samples have further increased compared to that at 10 minutes. In all samples the weight loss increases with increasing load. The wear resistance of Al-AlN (24-24) composite, sample-1, is slightly better than that of pure aluminium but the Al-AlN (30 -30) composite, sample-2, shows much higher wear resistance compared to both aluminium and Al-AlN (24-24) composite, sample-1.

4.2.3. Wear of Al and Al-AlN composites at different loads at 1600 rpm speed and 10 minutes.

![Figure 4](image-url)

**Figure 4.** Wear of Al and Al-AlN composites at different loads at 1600 rpm speed and 10 minutes.
Figure 4 shows that at 1600 rpm speed (Sliding velocity of 6.7 m/s) and 10 minutes the weight loss in all samples increases with increasing load and at all loads both Al-AlN (24-24), sample-1, and Al-AlN (30-30), sample-2, composites have higher wear resistance than pure aluminium. At lower loads the difference in weight loss between aluminium and the composites is not much but at higher loads the difference increases indicating that the composites are more effective in improving the wear resistance at higher loads. Al-AlN (30-30) composite, sample-2, shows higher wear resistance compared to both aluminium and Al-AlN (24-24) composite, sample-1.

4.2.4. Wear of Al and Al-AlN composites at different loads at 1600 rpm speed and 20 minutes.

Figure 5 shows that at 1600 rpm speed (Sliding velocity of 6.7 m/s) and 20 minutes the weight loss in all samples is much higher than that seen at lesser rpm and at lower times. The weight loss in all samples increases with increasing load. The wear in all samples drastically increases when the load is increased to 10kg as compared to the wear at 5 kg load. The Al-AlN (24-24) composite, sample-1, breaks when loaded to 10kg. Al-AlN (30-30) composite, sample-2, shows higher wear resistance compared to both aluminium and Al-AlN (24-24) composite, sample-1, at all loads.

5. Conclusions

Al-AlN Metal Matrix Composites could be fabricated in-situ by treating molten aluminium with a mixture of CaO and NH₄Cl and then cast. The composites produced had better mechanical properties like higher hardness and higher wear resistance than aluminium metal. Hardness of the Al-AlN composites increases with addition of more NH₄Cl + CaO, which indicates hardness increases with the increase in the amount of AlN present in the composite. A maximum hardness of 58.34 kgf/mm² was achieved in Al-AlN (30-30) composite, sample-2, which was produced by treatment of NH₄Cl + CaO with Al at temp 930°C and 2 hours 30 minutes holding period. Increasing the melt temperature, holding period after treatment and periodically stirring lead to better mechanical properties of the composites. Wear resistance was found to increase with higher amount of NH₄Cl + CaO added as compared to Al.

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