Mechanical and Corrosion Properties of AlCu Matrix Hybrid Composite Materials

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Abstract:
In this study, AlCu matrix hybrid composites with various ratios of boron carbide (B4C), hexagonal boron nitride (hBN), and graphite (Gr) were produced by using hot-pressing method. The microstructure, density, mechanical and corrosion properties of these composites were investigated. Optical microscopy, scanning electron microscopy, and X-ray diffraction were used to characterize the microstructures, and the experimental densities of the composites were measured using a helium pycnometer. The mechanical properties including the hardness and transverse rupture strength were investigated using hardness and three-point bending tests, respectively. In addition, the hybrid composites were immersed in an aqueous solution of 3.5 wt.-percent NaCl at pH 3 for potentiodynamic and corrosion rate measurements. These tests revealed that a microstructure in which reinforcing particles are almost homogeneously dispersed in the matrix was obtained. Density measurements have shown that very dense and compact hybrid AMCs are produced. The hardness and transverse rupture strength of the composites were significantly increased by particulate addition to the matrix. Depending on the type and amount of reinforcement material, differences in the corrosion resistance of the hybrid composites have been determined. The results show that AlCu-8B4C-2Gr hybrid composite material has the highest corrosion resistance among the composite materials.

Keywords: Hybrid composite; Mechanical properties; Corrosion; Hot-press sintering.

1. Introduction

It is known that the specific strength of materials is an important factor in the aviation and automotive industries [1, 2]. Materials for such applications should also exhibit good conformity in their mechanical, physical, and tribological properties [2]. However, a single type of metal or alloy is insufficient to meet these requirements. Metal matrix composites (MMCs) are particularly useful due to their unique properties, which are suitable for a wide variety of engineering applications. Some of these properties are high specific strength, low thermal expansion coefficient, high thermal resistance, good damping capacity, superior wear resistance, high specific flexural strength, and satisfactory levels of corrosion resistance [3-10]. Although the requirements for materials used in the aviation and automotive industries can be met by conventional MMCs, deficiencies cannot be completely eliminated. Aluminum metal continues to be the most used as the matrix material in the development of MMCs [11, 12], and aluminum matrix composites (AMCs) are considered to be next-generation MMCs that have the potential to meet the latest demands of materials for advanced engineering
applications. This is due to their improved mechanical properties, compliance with conventional processing techniques, and the possibility of reducing the production costs. Since some process parameters are associated with reinforcing particles, the performance of materials often depends on the selected combination of reinforcing materials. Several combinations of reinforcing particles have been conceptualized in the design of AMCs [13]. Hybrid AMCs with different synthetic ceramic particles, such as silicon carbide (SiC), aluminum oxide (Al₂O₃), boron carbide (B₄C), tungsten carbide (WC), graphite (Gr), carbon nanotubes (CNT), and silica (SiO₂) [14,15], have been developed primarily for performance optimization with less consideration of production costs. Monikandan et al. [16] investigated the mechanical and tribological properties of AA6061-B₄C-MoS₂ hybrid composites. These hybrid composites are self-lubricating so they can be made into efficient materials at the source. As the added amount of MoS₂ particles increased, the fracture toughness and friction coefficient of the composite decreased. Alanemi et al. [17] investigated the production process and mechanical properties of Al-Mg-Si alloy matrix composites reinforced by alumina (Al₂O₃) and rice husk ash (RHA), with the aim of evaluating the feasibility of developing low-cost, high-performance hybrid AMCs. The specific strength, elongation, and fracture toughness of a hybrid composite containing 2 wt.% RHA were higher than those of one reinforced by Al₂O₃ alone. For this reason, RHA has been reported to serve as a complementary supplement for the development of low-cost, high-performance hybrid AMCs.

In this study, AlCu matrix hybrid composites were prepared by adding B₄C, Gr, and hexagonal boron nitride (hBN) into an AlCu matrix in different ratios using a hot-pressing method. The microstructure, corrosion and mechanical properties of these composites were investigated.

2. Materials and Experimental Procedures

In this study, Al, Cu, Gr, B₄C, and hBN powders were used for preparing hybrid AMCs. Tab. I shows the purity and grain size of the powders. Tab. II shows the addition ratios and production parameters for preparing the hybrid composites.

<table>
<thead>
<tr>
<th>Tab. I</th>
<th>Properties of powders used in hybrid composite production.</th>
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<tbody>
<tr>
<td><strong>Powders</strong></td>
<td>Al</td>
</tr>
<tr>
<td>Grain size (µm)</td>
<td>17–30</td>
</tr>
<tr>
<td>Purity (%)</td>
<td>99</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Tab. II</th>
<th>Compositions and hot-pressing parameters used in hybrid composite production.</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>No</strong></td>
<td><strong>Composition (wt.%)</strong></td>
</tr>
<tr>
<td>AICu</td>
<td>hBN</td>
</tr>
<tr>
<td>-------</td>
<td>-------</td>
</tr>
<tr>
<td>1</td>
<td>100</td>
</tr>
<tr>
<td>2</td>
<td>90</td>
</tr>
<tr>
<td>3</td>
<td>90</td>
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<tr>
<td>4</td>
<td>90</td>
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<tr>
<td>5</td>
<td>90</td>
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<tr>
<td>6</td>
<td>90</td>
</tr>
<tr>
<td>7</td>
<td>90</td>
</tr>
</tbody>
</table>
In order for the selected powders to give the desired performance in the matrix for hybrid composite production, they should be mixed well and their homogeneous distribution in the matrix should be ensured. Therefore, a powder mixer with three-axis rotation was used. The powders were weighed on precision scale according to the compositions given in Tab. II. Then the powders were put in a plastic jar and mixed at 20 rpm for 30 min. The powder mixtures were placed in graphite molds and were then converted into bulk form with dimensions of 10 mm (×) 10 mm (×) 40 mm using an SMVB (C)/3 model vacuum hot press machine (Zhengzhou Golden Highway Co. Ltd., Zhengzhou, China) working on the principle of resistance heating to a 550 °C sintering temperature with a 5 minute wait time and under 35 MPa pressure.

Three-point bending tests to determine the fracture toughness were performed in accordance with the ASTM B 528-83a standard using a Shimadzu AG-X Tensile Testing Machine with 50 kN load capacity (Shimadzu, Kyoto, Japan), and samples with dimensions of 10 mm × 10 mm × 40 mm were used. The hardness of the samples was measured in Brinell units using a Brinell hardness testing device (Digirock-RB-M model, BMS Bulut Makina Co., Turkey) with a load of 62.5 kg and a ball of 2.5 mm diameter. The densities of the hybrid composites were measured using a helium pycnometer (Ultrapyc 1200e Helium Pycnometer, Quantachrome Instruments, USA).

Hybrid composite samples containing an aluminum matrix were sanded by coarse followed by fine sanding steps. The sanded samples were sequentially polished using 3 and 1 micron diamond suspensions, and etched for 10-30 seconds using Keller solution (190 ml distilled water + 5 ml nitric acid + 3 ml hydrochloric acid + 2 ml hydrofluoric acid). For optical examinations, an Olympus GX41 inverted metallurgical microscope (Olympus Co., Ltd., Japan) was used. An FEI QUANTA 250 FEG scanning electron microscope (FEI Inc., OR, USA) was used for the fracture surface analysis of the samples after three-point bending tests. X-ray diffraction (XRD) analysis was performed to determine the phases formed in the microstructure using a Bruker D8 Advance XRD system (Bruker Optik GmbH, Ettlingen, Germany). Corrosion measurements were obtained by using a system consisting of a Reference 3000 Potentiostat/Galvanostat/ZRA corrosion system. Corrosion experiments were carried out after the samples were left waiting for 1 h at room temperature in a 3.5 wt.% NaCl solution (pH 3). A conventional three-electrode cell was used for all the electrochemical measurements. A saturated calomel electrode (SCE) was used as a reference electrode, platinum foil as a counter electrode and samples as the working electrode. Potentiodynamic sweeping was performed in range of ± 0.25 V and 1 mV/s sweeping rate. The polarization resistance values were calculated by using Stern and Geary equation.

3. Results and Discussion

Fig. 1 shows the SEM images of the powders used in the production of AlCu matrix hybrid composite materials. Aluminum powders exhibit a spherical and worm-like morphology, and copper powders have a dendritic and leaf-like form. Both boron carbide and hexagonal boron nitride powders exhibit a sharp angular morphology, but boron carbide has sharper edges than hexagonal boron nitride. In addition, graphite powders exhibit a flake-like morphology. Fig. 2 shows the XRD patterns of the powders, where no obvious oxidation of the powders can be observed.
The optical images of the AlCu matrix are shown in Fig. 3. 5 wt% Cu was added and homogeneously distributed in Al. As in samples produced by powder metallurgy, pore formation occurred in these samples. Since copper and aluminum are ductile materials, copper grains were not embedded in the aluminum but were located at the contact points between aluminum grains. An interface layer was formed between Al/Cu. Here Al–Cu forms a solid solution. Cu atoms move into the Al by solid-state diffusion and replace some Al atoms at their sites. However, this type of phase is not always possible. Instead, intermediate compounds symbolized by chemical formulas can form. Here, the possibility of the formation of a Al₃Cu phase as an intermediate compound is high. It is likely that the interface layer has an α+Al₃Cu eutectic structure.
Fig. 3. Optical images of AlCu matrix: (a) 100× and (b) 500×.

The optical images of Al matrix hybrid composite materials are present in Fig. 4. It can be seen from the photos that Cu, B₄C, hBN, and Gr were distributed almost homogeneously in the Al matrix. The heterogeneous distribution of the reinforcing particles in the matrix adversely affected the mechanical properties of the composite materials. The reinforcing particles were located on the surface of the matrix and/or embedded in the matrix. Pore formation occurred even if just a small amount for all the samples. There was no agglomeration of large-sized hBN grains, but agglomerations of small-sized Gr and B₄C grains were formed. All reinforcing particles were tightly held by the matrix.

Fig. 4. Optical images of composites: (a) AlCu-10hBN, (b) AlCu-8hBN-2Gr, (c) AlCu-5hBN-5B₄C, (d) AlCu-10B₄C, (e) AlCu-8B₄C-2Gr, and (f) AlCu-4hBN-4B₄C-2Gr.

Fig. 5 shows the XRD patterns of the composites. Two crystal phases were formed in the AlCu matrix of the unreinforced sample, and the peaks of Al were higher than the peaks of Cu. Four components were found in the XRD pattern of the AlCu-10hBN composite, which were Al, Cu and hBN phases. Al, Cu, hBN, and Gr phases were observed in the AlCu-8hBN-2Gr composite. Al, Cu, B₄C, and hBN phases were formed in the AlCu-5hBN-5B₄C composite.
composite. Al, Cu, and $B_4C$ phases were observed in the AlCu-10B$_4$C composite. In the XRD pattern of AlCu-8B$_4$C-2Gr, four crystal phases, Al, Cu, $B_4C$, and Gr, can be seen. Five crystal phases, Al, Cu, C, hBN, and $B_4C$, can be seen in the XRD pattern of AlCu-4hBN-4B$_4$C-2Gr.

![XRD patterns of composites](image)

**Fig. 5.** XRD patterns of composites: (a) AlCu, (b) AlCu-10hBN, (c) AlCu-8hBN-2Gr, (d) AlCu-5hBN-5B$_4$C, (e) AlCu-10B$_4$C, (f) AlCu-8B$_4$C-2Gr, and (g) AlCu-4hBN-4B$_4$C-2Gr.

Tab. III shows the experimental and relative densities of Al matrix hybrid composites.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Experimental density (gr/cm$^3$)</th>
<th>Relative density (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AlCu</td>
<td>2.8060</td>
<td>93.13</td>
</tr>
<tr>
<td>AlCu-10hBN</td>
<td>2.7189</td>
<td>92.52</td>
</tr>
<tr>
<td>AlCu-8hBN-2Gr</td>
<td>2.7294</td>
<td>93.05</td>
</tr>
<tr>
<td>AlCu-5hBN-5B$_4$C</td>
<td>2.8033</td>
<td>94.98</td>
</tr>
<tr>
<td>AlCu-10B$_4$C</td>
<td>2.7662</td>
<td>93.33</td>
</tr>
<tr>
<td>AlCu-8B$_4$C-2Gr</td>
<td>2.7585</td>
<td>93.40</td>
</tr>
<tr>
<td>AlCu-4hBN-4B$_4$C-2Gr</td>
<td>2.7990</td>
<td>95.09</td>
</tr>
</tbody>
</table>
The experimental densities ranged from 2.7189 to 2.8060 gr/cm\(^3\), and the relative densities ranged from 92.52 to 95.09%. The experimental density of each composite depended on the densities of the composite components. It is desirable that the strength/density ratio is high in engineering applications, which was achieved in this study as indicated by the mechanical properties that will be presented in the following sections. The relative densities of the composites were found to be close to each other under hot-pressing conditions. This showed us that the sintering parameters were suitable for the production of the hybrid composites.

Hardness tests were carried out to observe the effect of a 10 wt% reinforcement (hBN–B\(_4\)C–Gr) on the AlCu matrix. Fig. 6 shows the hardness variation of Al matrix hybrid composites. The unreinforced AlCu alloy showed the lowest hardness of about 38.30 HBN. The hardness of the composites increased upon adding 10 wt% reinforcement (hBN–B\(_4\)C–Gr). AlCu-10B\(_4\)C showed the highest hardness of about 84.15 HBN due to the presence of B\(_4\)C hard particles, which were obstacles to dislocation motion. Even though hBN and Gr addition increased the hardness, it was significantly lower compared with B\(_4\)C addition. This is due to the difference in the natural hardness of the particles. In other words, the increase in hardness can be explained by the mixture rule. The mixture rule for materials with high relative densities is described by:

\[ H_c = H_m f_m + H_r f_r \]

where \(H_c\) is the hardness of the composite, \(H_m\) is the hardness of the matrix, \(H_r\) is the hardness of the reinforcing element, and \(f_m\) and \(f_r\) are the volumetric ratios of the matrix and the reinforcing element, respectively. Hard particles prevent the dislocation movement and increase the strength of the composite [18].

To determine the transverse rupture strength of Al matrix hybrid composites, three-point bending tests were conducted using a 50 kN capacity universal-type tensile device in accordance with the ASTM B 528-83a standard at a test speed of 0.1 mm/min. Samples with dimensions of 40 mm × 10 mm × 10 mm were used for the three-point bending test, and the test for each sample was repeated five times. The effect of the reinforcing particles was determined by taking the average of the values. Fig. 7 shows the effects of boron carbide, hexagonal boron nitride, and graphite addition on the transverse rupture strength of the
composites. The transverse rupture strengths (TRS) of AlCu, AlCu-10hBN, AlCu-8hBN-2Gr, AlCu-5hBN-5B₄C, AlCu-10B₄C, AlCu-8B₄C-2Gr, and AlCu-4hBN-4B₄C-2Gr composites were 105, 112, 115, 121, 171, 155, and 133 MPa, respectively. The TRS of reinforced composites were much higher than that of the unreinforced one. This is because the reinforcing particles blocked the dislocation movement, as was explained for the case of increased hardness. The TRS of boron carbide-containing samples were higher compared with the other samples. This is because the hardness of boron carbide is high and the boron carbide used in this study had a very small grain size compared with the matrix grain size [19].

Fig. 7. Transverse rupture strength of composites: (1) AlCu, (2) AlCu-10hBN, (3) AlCu-8hBN-2Gr, (4) AlCu-5hBN-5B₄C, (5) AlCu-10B₄C, (6) AlCu-8B₄C-2Gr, and (7) AlCu-4hBN-4B₄C-2Gr.

Fig. 8 shows SEM images of the fracture surfaces of the samples after three-point bending tests. It can be seen in Fig. 8a it is understood that some particles have not been subjected to necking after the sintering process. This may be due to insufficient pressing pressure, sintering temperature, or sintering time. In addition, the presence of foreign impurities may also adversely affect the sinterability. Pore formation in the structure occurred even if just a small amount. It can be seen clearly from the fracture surface that the fracture shape is intergranular fracture. When hBN was used as reinforcing materials in the AlCu matrix, hBN grains having coarse grain size were tightly held by the matrix (Fig. 8b). hBN exhibited a spongiform structure, which is due to the lubrication properties of hBN. There was a cone-bowl-shaped fracture in the matrix and this represents ductile fracture. It can be seen from the fracture surface of the AlCu-8hBN-2Gr sample (Fig. 8c) that the Gr particles filled the interstitial voids due to the flake shape and thus caused an increase in TRS and hardness at this point. In the sample prepared by adding equal amounts of B₄C and hBN (5% and 5%) into the Al matrix, both particles were quite homogeneously distributed (Fig. 8d). This also positively affected the mechanical properties of the composite. The small size of B₄C caused it to be positioned in small voids, and the presence of impurities on the fracture surface was also seen in this composite. B₄C particles showed a homogeneous distribution in the AlCu-10B₄C sample (Fig. 8e). This homogeneous distribution was associated with the similarity in the grain size between the matrix and the reinforcing particles. The structure of the fracture surface of the AlCu-8B₄C-2Gr composite, with 2% Gr added, was similar to that of the AlCu-10B₄C composite (Fig. 8f). However, the lower hardness of Gr compared with B₄C resulted in lower hardness and TRS of AlCu-8B₄C-2Gr compared with AlCu-10B₄C. In
this way, a material with relatively high TRS and low friction was produced, because graphite and hexagonal boron nitride are solid lubricants. In addition, partial pore formation occurred in the AlCu-8B₄C-2Gr composite. In the AlCu-4hBN-4B₄C-2Gr hybrid composite where all the components are present, B₄C grains were somewhat clustered (Fig. 8g).

Fig. 8. SEM images of the fracture surfaces of composites: (a) AlCu, (b) AlCu-10hBN, (c) AlCu-8hBN-2Gr, (d) AlCu-5hBN-5B₄C, (e) AlCu-10B₄C, (f) AlCu-8B₄C-2Gr, and (g) AlCu-4hBN-4B₄C-2Gr.

The potentiodynamic polarization curves of the composites are illustrated in Fig. 9. Corrosion potential ($E_{corr}$), anodic and cathodic Tafel slopes ($\beta_a$ and $\beta_c$), corrosion resistance ($R_p$), corrosion rate and corrosion current ($I_{corr}$) were found from Tafel curves. $R_p$ was calculated by the Stern and Geary equation 1 [20]:

$$I_{corr} = \frac{\beta_a \times \beta_c}{2.303 \times R_p (\beta_a + \beta_c)}$$

where $I_{corr}$ is the corrosion current density in $\mu$A cm$^{-2}$, $R_p$ is the corrosion resistance in kΩ cm$^2$, and $\beta_a$ and $\beta_c$ are the anodic and cathodic Tafel slopes in V or mV, respectively. The corrosion potential ($E_{corr}$) values of the substrate and coating layer are slightly different. The $R_p$ values of the AlCu, AlCu-10hBN, AlCu-8hBN-2Gr, AlCu-5hBN-5B₄C, AlCu-10B₄C, AlCu-8B₄C-2Gr, and AlCu-4hBN-4B₄C-2Gr are 1.526 kΩ cm$^2$, 0.650 kΩ cm$^2$, 0.006 kΩ cm$^2$, 0.053 kΩ cm$^2$, 0.199 kΩ cm$^2$ and 0.182 kΩ cm$^2$, respectively. As the particles were added to the AlCu matrix, the corrosion resistance of the composites was
reduced. AlCu-8B₄C-2Gr hybrid composite material has the highest corrosion resistance among the composite materials.

![Fig. 9. The potentiodynamic polarization curves of hybrid composites: (1) AlCu, (2) AlCu-10hBN, (3) AlCu-8hBN-2Gr, (4) AlCu-5hBN-5B₄C, (5) AlCu-10B₄C, (6) AlCu-8B₄C-2Gr, and (7) AlCu-4hBN-4B₄C-2Gr.](image)

4. Conclusion

In this study, several hBN–B₄C–Gr-reinforced AlCu matrix hybrid composites were prepared by a hot-pressing method, and the microstructure, hardness, density, corrosion and transverse rupture strength of these composites were experimentally investigated in detail. The conclusions drawn from this study are given below:

1. Microscopic studies showed that the reinforcing particles in the AlCu matrix were almost homogeneously distributed. The microstructures of all composites were generally similar. The reinforcing particles were located at the contact points of the matrix grains and/or partly embedded in the matrix.
2. The experimental densities of Al matrix hybrid composites ranged from 2.7189 to 2.8060 gr/cm³, and their relative densities ranged from 92.52 to 95.09 %.
3. The hardness of the Al matrix was increased by adding reinforcing particles. The hardness of the AlCu matrix was 38.30 HBN, and the highest hardness of 84.15 HBN was achieved by the AlCu–10B₄C composite. The hardness of the other hybrid composites varied from 52.45 to 75.83 HBN.
4. The transverse rupture strength of Al matrix hybrid composites varied with the amount of added boron carbide, hexagonal boron nitride, and graphite. The highest strength of 171 MPa was achieved by the AlCu-10B₄C composite, and the strength decreased upon the addition of graphite and hexagonal boron nitride. Materials with a high strength/density ratio suitable for engineering applications were successfully prepared in this study.
5. As a result of corrosion tests, the corrosion resistance of composite materials decreased according to matrix. However, when the composite materials are evaluated, the best is the AlCu-8B₄C-2Gr hybrid composite. Considering both mechanical and corrosion properties, the AlCu-8B₄C-2Gr hybrid composition has the best results.
Acknowledgments

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5. References

разлике у корозивној отпорности. Резултати су показали да хибридни композитни материјал AlCu-8B4C-2Gr има највишу вредност отпорности на корозију од свих композита.

Кључне речи: хибридни композити; механичка својства; корозија; топло пресовање.