Study on Mechanical and Thermal Expansion Properties of Oxide Coated Magnesium Borate Whiskers Reinforced Aluminum-based Composite

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Abstract. The surface of magnesium borate whiskers was coated with oxide coatings of different components by chemical precipitation method, and magnesium borate whisker-reinforced aluminum-based composites were prepared by squeeze casting method. The compressive deformation resistance of the prefabricated whisker and the tensile and thermal expansion properties of the composite were tested. The experimental results show that the oxide coating can effectively improve the anti-deformation ability of the whisker preform, and the whisker preform prepared by MgO and Al₂O₃ coating has better strength, and the compressive strength at room temperature reaches 0.98 MPa and 0.96 MPa. The composite material prepared by Al₂O₃ coated whiskers has the highest room temperature tensile strength of 263 MPa, and the composite material prepared by ZnO coated whiskers has the lowest room temperature tensile strength of 224 MPa. The thermal expansion curve of the composite material shows that as the temperature increases, the thermal expansion coefficient of the composite material gradually increases, and the thermal expansion coefficient of the composite material decreases slightly after a temperature cycle.

1. Introduction
Whisker-reinforced aluminum-based composites have the characteristics of light weight, high strength, and low thermal expansion, and have wide application prospects in aviation, aerospace, and new energy vehicles. With the development of composite material preparation technology, they have received widespread attention from scientific researchers [1, 2]. Magnesium borate (Mg₂B₂O₅, MBO for short) whiskers have high strength and high elastic modulus, especially the density is only 2.9 g/cm³ [3], as a reinforcement of aluminum-based composites, it can maintain the low density of aluminum-based composites Features. However, the research on magnesium borate whisker reinforced aluminum-based composites (MBOw/Al) is not in-depth.

In the whisker-reinforced aluminum-based composite material prepared by the squeeze casting method, better microstructure and performance can be obtained because of the uniform dispersion of the whisker-reinforced phase. However, due to the preparation process of the preform, the composite material prepared when the strength of the preform is low has obvious defects, and the whisker volume fraction in the composite material is not easy to control. Therefore, it is often necessary to add adhesive binder during the preparation of the preform to improve the strength of the preform and adjust the volume fraction of the enhanced phase [4]. In this paper, magnesium borate whisker
preforms were prepared with oxide adhesives of different components, and the effects of different coating layers on the structure and properties of the preforms and composite materials were studied, and the purpose of using oxide coating whiskers to improve the properties of the preforms was realized. The influence mechanism of whiskers on the properties of composite materials is also discussed.

2. Experimental method
The matrix of the MBOw/Al composite material adopts industrial pure aluminum, the reinforcement magnesium borate whiskers are produced by Shenyang Meixi Fine Chemicals, and the raw materials for preparing the oxide coating are metal salts and ammonia produced by Tianjin Continental Chemical Reagent Factory.

The modifier was mixed with magnesium borate whiskers and distilled water in a certain proportion. After the ultrasonic stirring treatment, dilute ammonia water was slowly added to the mixed solution until the PH value was set, so that all the metal cations were converted to hydroxide and coated on the whisker surface. Then, we poured it into a mold and press it into a preform with a whisker volume fraction of about 25%. After unmolding, it is dried at room temperature and then sintered at a high temperature of 900°C for 2 hours to obtain an oxide coating whisker preform for preparing MBOw/Al composites, in which the mass ratio of the coated oxide coating to the whiskers is about 1:20, as shown in Table 1. The MBOw/Al composite was prepared by the squeeze casting method, the casting temperature was 800°C, the mold preheating temperature was 560°C, and the pressure was 100 MPa.

| Serial number | Material system | Coating ratio | Modifier | Basic titrant | PH value | whisker volume fraction |
|---------------|----------------|---------------|----------|---------------|----------|------------------------|
| 1             | MgO/MBOw       | 1:20          | MgCl2    | Hartshorn     | 10.5     | 25%                    |
| 2             | Al2O3/MBOw     | 1:20          | Al(NO3)3 |              | 8        |                        |
| 3             | ZnO/MBOw       | 1:20          | Zn(NO3)2 |              | 7.5      |                        |
| 4             | NiO/MBOw       | 1:20          | Ni(NO3)2 |              | 4.5      |                        |

The Instron-1186 mechanical testing machine was used to perform room temperature compression experiments on the preforms with a size of Φ20×30mm and perform room temperature tensile experiments on the composite materials. The compression and extension rates were both 0.5mm/min. The H-3000 scanning electron microscope (SEM) produced by Hitachi was used to observe the whisker coating morphology and tensile fracture morphology.

The thermal expansion test of the composite material was carried out on the DIL402C thermal dilatometer produced by Netzch, Germany. The sample size was Φ6×20mm, the heating rate was 5°C/min, the experiment temperature was from room temperature to 450°C, and the cooling method was furnace cooling. To avoid the influence of the instability in the initial stage of temperature change on the experiment, the data selection range is 50~400°C. We used the software package provided by the company to calculate the thermal expansion coefficient.

3. Experimental results and analysis
3.1. Micro-morphology and strength of oxide-coated magnesium borate whiskers preforms
Figure 1 is a scanning electron micrograph of magnesium borate whiskers coated with different metal oxides obtained after high temperature sintering (the coating mass ratio is all 1:20). It can be seen from Figure 1 that under the coating process conditions of the chemical precipitation method adopted in this paper, no obvious agglomeration of magnesium borate whiskers was found. The metal oxide coating with a mass coating ratio of 1:20 will not affect the degree of whiskers dispersion. The surface roughness of magnesium borate whiskers increases after coating, which is beneficial to improve the molding ability of magnesium borate whisker preforms.
Figure 1 shows the room temperature compressive strength of the whisker preforms prepared after coating with different oxides. It can be seen from Figure 2 that the strengths of MgO/MBOw and Al₂O₃/MBOw whisker preforms are 0.98 MPa and 0.91 MPa, respectively, which are significantly higher than the strengths of ZnO/MBOw and NiO/MBOw whisker preforms (0.42 MPa and 0.45 MPa, respectively). Combined with Figure 1, it shows that the micro-morphology of the coating material coated on the whisker surface is an important factor influencing the strength of the whisker preform. Regardless of the reaction between the coating material and the substrate and the whisker, the micro-morphology effect of the coating with fine particles is obviously better than that with the microscopic appearance of the coating with large particles, because the coating with large particles has a bonding effect on the overlap of the whiskers, and at the same time, it may become the stress concentration area in the stress process due to the size relationship. The stress concentration area in the process reduces the overall strength of the preform.

3.2. The tensile strength and fracture structure of composite materials

Figure 3 shows the room temperature tensile curves of different oxide coated magnesium borate whisker reinforced aluminum-based composites. It can be found from Figure 3 that the room temperature tensile strengths of MgO/MBOw/Al, Al₂O₃/MBOw/Al, ZnO/MBOw/Al and NiO/MBOw/Al composites are 257 MPa, 263 MPa, 224 MPa and 252 MPa, respectively. Similar to the change trend of the deformation resistance of the whisker preform, the tensile strengths of MgO/MBOw/Al and Al₂O₃/MBOw/Al composites are higher than that of ZnO/MBOw/Al and NiO/MBOw/Al composites. In Figure 3, we can also observe that the NiO/MBOw/Al composite material with a slightly lower tensile strength has better elongation after fracture, but the ZnO/MBOw/Al composite material does not comply with this rule, combined with Figure 2(c), we can find that ZnO coating forms coarse particles on the surface of the whiskers. This microscopic morphology is prone to complex stress concentration due to the difference in properties between the whiskers, aluminum substrate and coating material when the material is deformed under force, thereby reducing the plasticity index of the composite material.
Figure 2. Room temperature compressive strength of magnesium borate whisker preforms coated with different coatings

Figure 3. Tensile curves of magnesium borate whisker reinforced aluminum-based composites with different types of whisker coatings

Figure 4 is the SEM photograph of the tensile fracture of the MBOw/Al composite. It is found from the photos that there are many whiskers pulled out or broken from the whisker and traces of whisker debonding on the tensile fracture. During the stretching process, the whiskers arranged approximately parallel to the stretching direction can bear the load well. The whiskers are pulled out or broken apart from the matrix to form the fiber pullout holes in the photo (as shown in point A of the figure); while the whiskers arranged approximately perpendicular to the stretching direction cannot bear the load well during stretching. Due to the low interface bonding strength, the interface between the whiskers and the substrate is torn apart, causing the debonding of the crystal whiskers (point B in the figure), which has little effect on improving the mechanical properties of the composite material.

Figure 4. SEM photo of tensile fracture of MBOw/Al composite

3.3. Thermal expansion behavior

Figure 5 shows the thermal expansion coefficient test results of MBOw/Al composites prepared by coating magnesium borate whiskers with different oxides. We define the first test of the same sample as the initial state and the second test as the cyclic state. It can be seen from Figure 5 that the thermal expansion coefficient of the composite material shows an upward trend with the increase in temperature. Among them, the thermal expansion coefficient increases rapidly at the initial stage of heating, and tends to be flat at about 100°C, but still slowly increases. The thermal expansion coefficients of NiO/MBOw/Al, ZnO/MBOw/Al and Al2O3/MBOw/Al composites are basically the same. The engineering thermal expansion coefficient at 100°C is about $14 \times 10^{-6}/^\circ C$, and the engineering thermal expansion coefficient at 350°C is about $18 \times 10^{-6}/^\circ C$, which is lower than the thermal expansion coefficient of MgO/MBOw/Al composite. The reason is that the different properties...
of the different coating materials, the thermal expansion curve is different. However, after NiO and ZnO are coated on the surface of the whiskers, they have thermite reaction with the liquid aluminum during the squeeze casting process, as Equations (1) and (2) show:

\[
\begin{align*}
3\text{NiO} + 2\text{Al} & \rightarrow \text{Al}_2\text{O}_3 + 3\text{Ni} \\
3\text{ZnO} + 2\text{Al} & \rightarrow \text{Al}_2\text{O}_3 + 3\text{Zn}
\end{align*}
\] (1) (2)

The solid solution of Ni and Zn into the Al crystal lattice did not change the thermal expansion coefficient of the base aluminum, and the product between the magnesium borate whisker and the base aluminum interface was transformed into Al$_2$O$_3$, resulting in three different coating materials NiO. The thermal expansion curves of ZnO and Al$_2$O$_3$ coated magnesium borate whisker reinforced aluminum-based composites tend to be consistent.

In addition, by comparing Figure 5(a) and Figure 5(b), it can be found that the initial thermal expansion coefficient of the composite material is slightly higher than the cyclic thermal expansion coefficient. The reason is that, for whisker-reinforced aluminum-based composites, the thermal expansion coefficient of the matrix is much greater than that of whiskers, there is residual tensile stress in the as-cast composite material without temperature cycle [5], and the residual tensile stress of the matrix will inevitably lead to an increase in the thermal expansion coefficient of the composite material; after a temperature cycle, part of the residual tensile stress in the matrix is relaxed, resulting in a decrease in the cyclic thermal expansion coefficient of the composite material.

![Figure 5. Thermal expansion curves of different oxide coated magnesium borate whisker reinforced aluminum-based composites](image)

3.4. Discussion

This article uses room temperature compression experiment to investigate the relative strength of the preform, but the stress state on the mechanical testing machine is very different from the stress state in the actual squeeze casting process. At the same time, the preheating and pouring temperature in the preparation process of composite materials will also have an impact, so the room temperature compressive strength can only be used to evaluate the deformation resistance of the whisker preform qualitatively or semi-quantitatively.

It can be seen from the experimental results that different coating materials have little effect on the tensile strength of aluminum-based composites. The tensile strength of MBOw/Al composites is about 240 MPa, which indicates that the surface modification treatment of magnesium borate whiskers only improves the performance of the whisker preform, which has little effect on the mechanical properties of aluminum-based composites. The low sensitivity of whisker reinforced aluminum-based composites to the surface modification process of magnesium borate whisker gives a greater degree of freedom to the material design. The suitable whisker surface modification process can be selected according to the other requirements of the material application without changing the mechanical properties of the
material.

4. Conclusion
(1) Oxide coating by chemical precipitation method can effectively improve the deformation resistance of magnesium borate whisker preform. Among the four systems studied in this paper, the room temperature compressive strengths of Al₂O₃/MBOw and MgO/MBOw preforms are higher, which are 0.98 MPa and 0.91 MPa, respectively, while the room temperature compressive strengths of ZnO/MBOw and NiO/MBOw preforms are lower, which are 0.42 MPa and 0.45 MPa respectively.

(2) The room temperature tensile properties of the aluminum-based composites prepared after coating whiskers with different oxides are in the range of 224~263 MPa, and the room temperature tensile strength of Al₂O₃/MBOw/Al composites is the highest with 263 MPa, the room temperature tensile strength of the ZnO/MBOw/Al composite is the lowest with 224 MPa.

(3) The thermal expansion coefficient of whisker-reinforced aluminum-based composites increases with the increase of temperature, and the thermal expansion coefficients of Al₂O₃/MBOw/Al, ZnO/MBOw/Al, NiO/MBOw/Al composites are lower than that of MgO/MBOw/Al composite material, and at the same time, due to the influence of the internal tensile stress of the composite material, the cyclic thermal expansion coefficient is slightly lower than the initial thermal expansion coefficient.

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