Microstructure and Properties of Ni/Al₂O₃ Composites Prepared by Powder Injection Molding

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Abstract. Ni/Al₂O₃ composite was prepared by powder injection molding, the effects of Ni content and different sintering process on the microstructure and mechanical properties of Ni/ Al₂O₃ composites were studied. The results show that when the Ni content is 10%, the comprehensive performance of Ni/ Al₂O₃ composite is better. The optimum vacuum sintering process of 10%Ni/ Al₂O₃ composite is as follows: sintering temperature of 1500 °C for 1 hour, with the relative density of 96.7%, bending strength of 312 MPa, Vickers hardness of 1528HV and fracture toughness of 5.3 MPa·m⁰.⁵².

1. Introduction

With characteristics of high hardness, high tensile, high temperature resistance, corrosion resistance, etc., Al₂O₃ ceramic is one of the most commonly applied ceramic materials at present. However, with the deficiencies of great fragility, mechanical processing difficulty, etc., its application is restrained [1]. Metal has good heat stability and ductility, but it may be easily oxidized at high temperatures. Therefore, the composites combined with metal and ceramic have not only the high tensile and high hardness of ceramic, but also the ductility and good toughness of metal [2].

The Al₂O₃ based ceramets are mainly manufactured by vacuum sintering, hot isostatic pressing, self-propagating high-temperature synthesis, sol-gel method, etc [3-5]. In recent years, laser near net shaping, pseudo-semi-solid thixoforming, gel casting, powder injection molding and other powder near net shaping techniques have all been applied in the manufacturing of alumina ceramic matrix composites [6-7]. Powder injection molding (PIM) is a new near net shaping technology of metal/ceramic components combining injecting molding with traditional powder metallurgy processing [8]. PIM overcomes the deficiencies of traditional powder metallurgy processing, including large density gradient [9]. With this technology, near net shape components can be manufactured with high material utilization rate and excellent mechanical property. Therefore, it is widely applied in automobile, medicine, military, aerospace, etc. due to automation and bulk manufacturing. This work
manufactured Ni/Al2O3 composites by powder injection molding and studied the effects of vacuum sintering on the microstructure and properties of Ni/Al2O3 composites with different Ni contents.

2. Experimental

Table 1 shows the basic performance parameters of Al2O3 powder and Ni powder used in the experiment and figure 1 shows the powder morphology. By mechanical alloying, powder of Ni/Al2O3 composites with Ni content of 0%, 5%, 10% and 15% (mass fraction) can be manufactured. For convenience of sintering, a trace of Y2O3 and MgO with mass fraction of 0.5% is added into powder of Ni/Al2O3 composites as sintering additive. Binding agent is wax based with components of paraffin wax (PW), low-density polyethylene (LDPE), EVA ethylene (EVA) and stearic acid (SA). The mass fractions are 65%, 20%, 10% and 5%, respectively and the powder loading is 58% (volume fraction). The injection processing parameters obtained by orthogonal optimizing experiment are: injection pressure 90MPa, injection temperature 140 °C and injection time 8s. The degreasing of injection green parts is conducted by solvent degreasing + thermal debinding where the solvent is n-heptane. Thermal debinding process: heat for 30min to 100 °C at room temperature (insulation for 30min) and then heat for 60min to 200 °C (insulation for 30min), heat for 90min to 350 °C (insulation for 40min), heat for 120min for 550min (insulation for 60min) and heat for 60min to 650 °C (insulation for 30min). Then frozen to room temperature in the furnace.

Table 1. Basic characteristics of powder

| Powder | True Density (g·cm⁻³) | Average particle size (µm) | Apparent density (g·cm⁻³) | Tap density (g·cm⁻³) |
|--------|-----------------------|---------------------------|--------------------------|---------------------|
| Al2O3  | 3.92                  | 0.52                      | 0.7                      | 2.12                |
| Ni     | 8.8                   | 4.5                       | 2.1                      | 3.13                |

Figure 1. SEM morphology of powders (a) Al2O3; (b) Ni

HAAKE PolyLab torque rheometer is used to prepare feedstock, HAAKE MiniJet trace injection molding machine used to injection molding, WZDS-20 vacuum sintering furnace used for vacuum thermal debinding and sintering, DH-300X electronic hydrometer used for measuring the density of sintering sample, HV-30 Vickers hardness tester used for measuring the hardness of sintering sample, CMT-5205 electronic universal testing machine used for measuring the three-point bending strength, Axio vert.A1 microscope used for observing the microstructure of samples, and HELIOS NanoLab 600i scanning electron microscope of U.S. FEI Company and Japan JSM-6390LV scanning electron microscope used for observing the powder morphology and fracture morphology of sintering pieces.

3. Results and discussion

3.1. Effect of vacuum sintering process on microstructure and properties
Ni/Al$_2$O$_3$ composite with Ni content of 10% is used for vacuum sintering. Table 2 shows the properties of pieces sintered at different temperatures with the insulation time of 1h. According to Table 2, the density, bending strength and hardness will reduce after increase with the increase of sintering temperature in the same insulation time. When the sintering temperature is slightly lower than Ni melting point (1453 °C), the sintering is solid phase sintering. The binding force of Ni/Al$_2$O$_3$ composite in solid phase sintering without pressure action is not as the binding force between powder in liquid phase sintering. The sintering temperature of Al$_2$O$_3$ is about 1600 °C, so the relative density is not high, the pores are many, and bending strength and hardness are low. When sintering temperature is slightly higher than Ni melting point, Ni is in liquid state which is liquid phase sintering. In sintering, Ni may evaporate, causing uneven distribution of Ni in Al$_2$O$_3$ matrix with increasing pores and reducing relative density, bending strength and hardness. Therefore, the sintering temperature should be controlled and sintering pressure be increased in vacuum sintering to improve the microstructure and properties of Ni/Al$_2$O$_3$ composites [10].

**Table 2. Properties of sintered samples with different sintering temperatures**

| Sintering temperature (°C) | Density (g·cm$^{-3}$) | Bending strength (MPa) | Hardness (HV) |
|---------------------------|-----------------------|------------------------|---------------|
| 1400                      | 4.013                 | 293                    | 1443          |
| 1500                      | 4.053                 | 312                    | 1528          |
| 1600                      | 4.028                 | 300                    | 1426          |

Figure 2 shows the microstructure at different sintering temperatures. The distribution of Ni is relatively even in Al$_2$O$_3$ matrix. When sintering at 1400 °C and 1500 °C, respectively, the combination of Ni and Al$_2$O$_3$ matrix is good with few Ni reunion. When sintering at 1600 °C, there will be hole in Ni and Al$_2$O$_3$ matrix with Ni reunion. The main reason is the thermal expansion coefficients of Ni and Al$_2$O$_3$ mismatch. The higher the sintering temperature is, the worse the binding capability will be and the easier Ni reunion may occur [11]. Figure 3 shows the fracture morphology of bending sample. When sintering at 1400 °C and 1600 °C, there are many pores between Ni and Al$_2$O$_3$ matrix, affecting the mechanical property of sintering pieces. When sintering at 1500 °C, the fracture has fewer pores and better mechanical properties.

**Figure 2. Microstructure of sintered samples at different sintering temperatures**

(a) 1400 °C; (b) 1500 °C; (c) 1600 °C

### 3.2. Effect of Ni content on microstructure and properties

Table 3 shows the mechanical properties of Ni/Al$_2$O$_3$ composites sintering sample with different Ni contents (0%, 5%, 10% and 15%) in vacuum sintering at 1500 °C with thermal insulation for 60min.
Figure 3. Fracture morphology of bending specimens at different sintering temperatures (a) 1400 °C; (b) 1500 °C; (c) 1600 °C.

With the increase of Ni content, the relative density of sintering sample gradually increases. When Ni content reaches 15%, the relative density of sintering sample will reduce. When Ni content is small, active sintering cannot be realized. When Ni content is large, Ni reunion may occur at crystal boundary with the intragranular Ni content reducing and Ni content at crystal boundary increasing due to the viscous flow and plastic flow of powder. Therefore, too large Ni content may be disadvantageous against the improvement of relative density [12]. Figure 4 shows the microstructure of Ni/Al$_2$O$_3$ composites with different Ni contents.

Table 3. Mechanical properties of sintered samples with different Ni content

| Sintering process parameters | Ni content (%) | Relative density (%) | Bending strength (MPa) | Vickers hardness (HV) | Fracture toughness (MPa·m$^{1/2}$) |
|-----------------------------|---------------|----------------------|------------------------|----------------------|----------------------------------|
| 1500 ℃ for 60 min          | 0             | 96.1                 | 291                    | 1648                 | 3.9                              |
|                             | 5             | 96.4                 | 298                    | 1573                 | 4.6                              |
|                             | 10            | 96.7                 | 312                    | 1528                 | 5.3                              |
|                             | 15            | 95.9                 | 303                    | 1427                 | 4.6                              |

Figure 4. Microstructure of sintered samples with different Ni content (a) 0%; (b) 5%; (c) 10%; (d) 15%.
Figure 4 shows that the distribution of Ni is relatively even in Al$_2$O$_3$ matrix. With the same sintering process, the evenness of microstructure in figure 5 (c) is good. When Ni content is low, the active sintering is not good enough. When Ni content is large, Ni reunion may occur with particle size increasing, causing adverse effects on sintering densification. Moreover, due to the mismatch of thermal expansion coefficients, pores may gradually increase, while the relative density decreases[13].

With the increase of Ni content, the bending strength of sintering sample will reduce after increasing. Ni can inhibit the growth of Al$_2$O$_3$ grain, so the higher the Ni content is, the better the inhibition effect and bending strength will be. When Ni content is larger than 10%, the thermal expansion coefficient of Ni ($15 \times 10^{-6}/\degree C$) will be the twice of Al$_2$O$_3$ ($8.4 \times 10^{-6}/\degree C$). When sintering cools down, the thermal expansion coefficients may mismatch to cause pores at crystal boundary. Meanwhile, with the growth of Ni, Ni may preferentially absorb the neighboring Ni to cause reunion. When the content of Ni is larger than 10%, the bending strength may reduce. Li et al.[14] used homogeneous deposition and coating technology to study the mechanical properties of Ni/Al$_2$O$_3$ composites with different Ni contents. With the increase of Ni content, the bending strength tends to reduce after increasing. This is consistent with the research results of this work. Figure 5 shows the fracture morphology of sintering sample.

According to figure 5, the fracture morphology shows the change from neat and leveling to irregular with the increase of Ni content. It is mainly because Ni is liquid phase at the sintering temperature of 1500 $\degree$C. It is easy to find pores at fracture which are mainly caused by the mismatch between the thermal expansion coefficients of Ni and Al$_2$O$_3$. Pores at the crystal boundary in fracture morphology (d) are significantly more than those in fracture (c), showing the reason of bending strength reduction.

![Figure 5. Fracture morphology of sintered samples with different Ni content](image-url)
The type and performance of added phase have great impacts on the hardness of Al$_2$O$_3$-based composites. Table 3 shows that with the same sintering process, the hardness of sintering sample may gradually decrease with the increase of Ni content. This rule meets with the rule of metal as the second phase toughening and the hardness of Ni/Al$_2$O$_3$ composite is related to that of Ni and Al$_2$O$_3$. With good ductility and toughness, Ni can toughen the matrix. Therefore, with the increase of Ni content, the overall hardness of composite will gradually decrease.

With the increase of Ni content, the fracture toughness of Ni/Al$_2$O$_3$ decreases after increasing. Ni is introduced to Al$_2$O$_3$ matrix. Compared with Al$_2$O$_3$, the composite has its fracture toughness improved. The toughness will reach the maximum when Ni content is 10%. The research proves that the introduction of hard particle into Al$_2$O$_3$ matrix as the second phase can improve the fracture toughness of composites [15].

4. Conclusions
When Ni content is 10%, Ni/Al$_2$O$_3$ composite has better comprehensive properties. The optimal vacuum sintering process for 10% Ni/Al$_2$O$_3$ composite is as follows: sintering temperature 1500 ℃, insulation for 1 hour, relative density 96.7%, bending strength 312 MPa, Vickers hardness 1528 HV and fracture toughness 5.3 MPa•m$^{1/2}$.

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