The High-temperature Oxidation Resistance and Thermal Shock Resistance of Al$_2$O$_3$-Ti(C,N)-(Ni,Mo) Cermet Die Material

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ABSTRACT

The experiment prepared Al$_2$O$_3$-Ti(C,N)-(Ni,Mo) cermet die material by vacuum hot-pressing sintering method, and researched the high-temperature oxidation resistance and thermal shock resistance by the method of SEM, XRD and metallographic microscope to analyze the material’s surface feature and phase ingredient. The results show that the Al$_2$O$_3$-Ti(C,N)-(Ni,Mo) cermet die material has better high-temperature oxidation resistance and thermal shock resistance. The material have slight oxidation reaction in 800℃ and the reaction become sharply in 1000℃. After oxidation reaction, the staple resultant is TiO$_2$. After 20h oxidation reaction in 1000℃, the material surface form platelike successive pyknotic oxidation film. The material’s critical temperature difference is 290℃~320℃, improving 26.1% and 45% respectively compared with Al$_2$O$_3$-Ti(C,N) and Al$_2$O$_3$ ceramics. Thermal shock damage mainly for criss-crossed and throughout the matrix crack.

INTRODUCTION

In the process of thermoplastic processing today, die material working environment is extremely bad, that its long-term under high temperature environment and get the thermal shock and mechanical extrusion of uninterrupted, makes the wastage of the mould is accelerated, shorten service life. Therefore, the research and development new die material instead of the traditional die steel, hard alloy, such as die material, requires that its good thermal fatigue resistance, high temperature oxidation resistance and thermal shock performance, etc[1]. Ceramic materials because of its good oxidation resistance, high wear resistance, hardness and as mold material is attained more and more extensive attention. Jiao Chen et al[2], developed the Al$_2$O$_3$(W, Cr) metal ceramic die material, have good...
mechanical properties and thermal shock resistance, can be well applied in the field of mould. Yufen Xu etc.[3] developed ceramic wire drawing die instead of the traditional drawing die, its service life is longer, and help to improve the quality of the wire. In recent years, the development of new Al$_2$O$_3$-Ti (C, N)-based composite ceramic with its excellent mechanical strength, fracture toughness and high temperature oxidation resistance and so on[4,5] used in cutting tool materials at the earliest[6,7]. Al$_2$O$_3$-Ti(C,N)-based ceramic materials by Chonghai Xu et al.[8] show that the Al$_2$O$_3$-Ti (C, N)-based composite ceramic material has the advantages of being used as a mold material, which has a good development prospect[9].

This experiment prepared Al$_2$O$_3$-Ti (C, N)-(Ni,Mo)(hereinafter referred to as ATNM) cermet die material by vacuum hot-pressing sintering, analyzes its oxidation resistance and thermal shock resistance in high temperature environment. Ceramic material itself has excellent antioxidant capacity, but in actual use, especially under high temperature oxygen atmosphere, the matrix material non-oxide may be oxidized to affect the performance of the material, thus to study the antioxidant capacity is one of the important areas[10]. Thermal shock resistance is an important index to evaluate the ability of the material to resist damage when temperature changes. Die material in high temperature working environment, good thermal shock resistance effectively extend the service life of materials, so as to achieve the purpose of reduce the production cost.

EXPERIMENTAL

This experiment prepared ATNM cermet die material by vacuum hot-pressing sintering. Al$_2$O$_3$, Ti(C,N), Ni and Mo were mixed according to certain proportion, loaded into graphite mold after ball milling and dried, and sintering in vacuum hot-pressing furnace to get ATNM sample. The sintering temperature is 1650℃ and insulation time is 25min. The prepared sample was cut into strips on a cutting machine, and then grinding and polishing to mirror surface. The oxidation resistance experiment: Putting the polished ATNM sample into the Muffle furnace warm up to 800℃ and 1000℃, and maintain a constant temperature for 5h, 10h, 15h and 20h respectively under each temperature. Oxidized sample with an accuracy of 0.1mg analytical balance scales weighing, take 3 times average of the results. The surface morphology of before and after oxidized sample was observed by SEM, its phase composition by XRD analysis. The thermal shock experiment: Putting the polished ATNM sample into the chamber electric furnace warm up to 250℃, 280℃, 310℃, 340℃ and 370℃ respectively, the heating rate is 4℃/min. After maintaining the temperature constant for 10min, take out the sample immediately cooling in 20℃ water. Using metallographic microscope observe the surface morphology of crack of the sample, measuring the flexure strength of the sample by three point bending method.

RESULTS AND DISCUSSION

The Oxidation Resistance

The oxidation increases the weight calculated by the equations 1:
\[ w = \frac{m_1 - m_0}{m_0} \times 100\% \]  

(1)

Among them: \( m_1 \) is the quality of the samples after the oxidation; \( m_2 \) is the quality of the sample before the oxidation. After oxidation weight gain by shown in Fig. 1:

![Figure 1. The increased weight of the sample after oxidation.](image1)

As can be seen from Figure 1, the quality of the sample after oxidation with the growth of oxidation time increases in air. When the oxidation temperature is 800°C, the sample occurs slightly oxidized and sample quality change is very small, after 5h oxidation, the quality weight gain of 0.13%, with the oxidation time reaching 20h, quality weight gain of 0.41%. When the oxidation temperature increase to 1000°C, the oxidation rate of the sample accelerated, the sample weight gain of 0.76% after 5h oxidation. With increasing oxidation time, the quality of the sample continue to increase, the sample quality weight gain of 2.53% after 20h oxidation.

![Figure 2. The XRD pattern of the sample before and after oxidation.](image2)

Fig. 2 shows the XRD pattern of the sample before and after oxidation in 1000°C and 20h. From the Fig. 2 we can see that the main oxidation products of the ATNM cermet material is \( \text{TiO}_2 \). After oxidation, the change of XRD diffraction peak of
Al₂O₃ is little and the diffraction peak intensity of Ti(C,N) is smaller than before. This can be inferred that in high temperature environment the Ti(C,N) in ATNM cetmet material was oxidized to TiO₂. Chemical reactions occur as follows:

\[
\begin{align*}
2\text{TiC} + 3\text{O}_2 & \rightarrow 2\text{TiO}_2 + 2\text{CO} \quad (2) \\
2\text{TiN} + 2\text{O}_2 & \rightarrow 2\text{TiO}_2 + \text{N}_2 \quad (3)
\end{align*}
\]

Fig. 3 (a), (b) and (c) show the sample before oxidation, after oxidation in 800°C with 20h and after oxidation in 1000°C with 20h respectively. From the diagram, it can be seen that at the beginning of oxidation, the surface of the sample appeared needlelike TiO₂. At this time, the degree of oxidation is lower and TiO₂ loose distribution. As the oxidation temperature was increased to 1000°C, relatively full oxidation reaction is carried out, the surface of the specimen to form a continuous sheet-like dense TiO₂ oxide film which hinders oxygen into the internal matrix, and the oxidation rate of material is relatively slow.

Will to carry on the bending strength of the samples after oxidation experiments, oxidized by 900°C after 20h sample of bending strength from 862MPa to 687MPa, reduced by 20.3%; Oxidized by 1000°C after 20h the sample of bending strength from 849MPa to 450MPa, reduced by 46.3%. It can be concluded from this, after oxidation, the TiO₂ damaged the stagger skeleton structure created by Al₂O₃ and Ti(C,N), so that affect the mechanics performance of the ATNM cermet material.

**The Thermal Shock Resistance**

The sample after thermal shock experiments under different temperature, the results are shown in Fig. 4.
The Fig. 4 shows that as the thermal shock temperature increase, the residual flexural strength is reduced. When the thermal shock temperature is 200°C~290°C, the flexural strength changed little, from 862MPa to 784MPa, was reduced by 9.0%. Between 290°C~320°C, the flexural strength fell sharply, down from 784MPa of 290°C to 275MPa, was reduced by 64.9%, compared with the bending strength before thermal shock, was reduced by 68.1%. Then in improving thermal shock temperature difference, the flexural strength continued to gentle decline. Thus it can be seen that ATNM cermet material thermal shock temperature difference is bigger, therefore thermal shock performance is better. Compared with Al₂O₃-Ti(C,N) ceramic material[11] and Al₂O₃ ceramic material[12], the thermal shock temperature increased by 26.1% and 45%, respectively.

The Fig. 5 (a), (b), (c) and (d), respectively, are the sample surface crack morphology when the thermal shock temperature is 260°C, 260°C, 320°C and
350°C. By the figure can be seen when thermal shock temperature is low, the surface of the material have a small amount of tiny cracks. With the increase of thermal shock temperature, crack propagation on the surface of the material, the number and width of crack are also corresponding increase. When the thermal shock temperature is higher than 230°C, material of surface crack in criss-cross, the maximum crack width is 12.53um, and appear more crack throughout the surface of the material. According to Kingery's critical stress fracture theory[13], that is

$$ R = \frac{\sigma_t(1-\nu)}{E\alpha} $$

(4)

The $R$ is the thermal shock evaluation parameters and the $\sigma_t, \nu, E$ and $\alpha$, respectively, is the material’s strength of extension, Poisson’s ratio, elasticity modulus and coefficient of thermal expansion. When material thermal stress caused by temperature difference is greater than the intrinsic material strength, the material fracture occurs. Therefore, to improve thermal shock resistance of materials will increase the inherent strength of the material. In the $\text{Al}_2\text{O}_3$-Ti (C, N) substrate to add a certain amount of metals (Ni, Mo), metal Ni and Mo disperse in the matrix, “pinning” on the grain boundary of $\text{Al}_2\text{O}_3$, strengthening the $\text{Al}_2\text{O}_3$ grain boundary, blocking effect on the propagation of the crack, consuming energy of the crack tip, so as to improve the inherent strength of the material, also improve the thermal shock resistance of the material.

CONCLUSIONS

Experimental results show that ATNM cermet material has good oxidation resistance and thermal shock resistance. The material has slight oxidation reaction in 800°C and the reaction become sharply in 1000°C. The material oxidation product is TiO$_2$ and in the material surface to generate a continuous dense oxide film, it having large effect on the mechanical properties of the material. The ATNM cermet thermal shock critical temperature is 290°C~320°C, improving 26.1% and 45% respectively compared with $\text{Al}_2\text{O}_3$-Ti(C,N) and $\text{Al}_2\text{O}_3$ ceramics. Thermal shock damage mainly for crack, the existence of metal Ni and Mo can effectively improve the thermal shock resistance of materials.

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REFERENCES