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Binder composition and debinding process in PIM of AlN①

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[Abstract] The thermal degradation behaviors of AlN green specimens were studied by thermogravimetry analysis during the ceramic powder injection molding debinding process. The optimum binder composition and the debinding cycle were demonstrated by observing the TGA and DTA plots of AlN green specimens and analyzing the microstructure at different temperatures. By adding HDPE into the PW-EVA binder used in powder injection molding AlN can effectively reduce the mass lose rate in debinding process and improve the shape retention ability. At last, aluminum nitride ceramic with high room-temperature thermal conductivity of 162.5 W•m^{-1}•K^{-1} was produced.

[Key words] aluminum nitride (AlN); ceramic powder injection molding (CIM); binder; debinding
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1 INTRODUCTION

Aluminum nitride (AlN), which has excellent multiple properties received worldwide concern in recent years. The theoretical thermal conductivity of AlN is 320 W•m^{-1}•K^{-1}, which is 10~ 15 times as that of alumina, and close to that of BeO. Such high thermal conductivity, along with good electrical insulation characteristics and thermal expansion coefficient which is closely matched to that of silicon, makes aluminum nitride a very promising electronic packaging materials and heat-conducting substrates for high-density circuits, semiconductors and power applications[1, 2]. Unfortunately, because of the hardness and the brittleness of ceramic materials, it is difficult to make complex shape ceramic part with traditional PM forming technology. In recent years, a new ceramic complex part forming technique —ceramic powder injection molding (IM), which developed from powder injection molding[3~ 5], gives a reasonable solution to the problem.

In CIM, the binder composition is the key factor in injection process for the need to add 40% ~ 50% (volume fraction) organic substance[6]. The binder not only attributes to the feedstock's rheological behavior and injection characteristic, but also determines the debinding cycle. Unsuitable binder composition may lead to the defects which originate from the injection molding and debinding processes. The binder system are usually composed of low molecular mass binder, high molecular mass polymeric components and some kinds of dispersants. The low molecular mass binder, such as wax, has low viscosity, good flow ability and is easy to remove. The high molecular mass polymeric has low ductility and gives the greenbody great strength. The high solid content in the feedstock can be reached when the above components are properly cooperated, and near net shape products can be produced.

2 EXPERIMENTAL

2.1 Raw materials

The AlN powder was produced by SHS (self-propagation high-temperature synthesis) method. 5% Y_2O_3 was selected as sintering additives. The compositions and particle size of AlN powder is summarized in Table 1.

Table 1 Properties of AlN powder

Particle size / μm	Specific area / (m^2•g^{-1})	Tape density / (g•cm^{-3})
0.59	1.77	2.52

Mass fraction/ %

Fe	Mn	Mg	Ca	Pb	Ti	C	O
0.05	0.001	0.001	0.001	0.001	0.01	0.07	0.7

Three different binders were designed and shown in Table 2. The binders used are mainly composed of paraffin wax (PW), Ethylene-Vinylacetate Copolymer (EVA), High Polyethylene (HDPE), stearic acid (SA) and other organic acid. Among them, EVA and HDPE are used as "backbone" material to give the greenbody enough strength; the PW is used to reduce viscosity and increase flow ability because of its small molecule size, thermoplastic character, and low melting temperature; SA can improve adhesive strength of the polymer-ceramic interface, which may

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Table 2 Different binder compositions

Sample	Mass fraction/ %				
	PW	EVA	HDPE	SA	Other organic substance
A	64	10	20	5	1
B	64	20	10	5	1
C	64	30	0	5	1

enhance the toughness of the molded material and reduce the tendency to crack during shrinkage in the mould.

2.2 Experimental procedure

The mixture of the compound AlN-Y_2O_3 powder and designed binder were prepared using XSS-300 type mixer with a constant solid loading of 61% (volume fraction). In this procedure, the binder was added to the container prior to the powder. When the binder was melted, the powder was added gradually into the container until the torque was stabilized. After 2 h mixing, a homogeneous feedstock was acquired. Granulation of the mixture was performed during cooling.

Cylinder-shaped AlN ceramic products were molded using ST28 type injection molder, and several AlN disks with dimensions of d12 mm × 5 mm were prepared to measure thermal diffusivity. The specimens were thermally debound using a coarse alumina powder as wicking powder. The debound specimens were thereafter sintered in a graphite furnace at 1 850 ℃ under a flowing N_2 atmosphere.

2.3 Property measurement

The feedstock's TGA and DTA graphs can be characterized by using DT-40 thermal analysis. The decomposed temperature of the binder's components can be drawn from the graphs, which are the basics to determine the debindering cycle. SEM (JSM-5600LU) was used to characterize the microstructure changes during debinding on the fracture surface of the AlN ceramics. Thermal diffusivity of the specimens was measured by a laser flash method on JR-2 type laser thermal conductive instrument.

3 RESULTS AND DISCUSSION

3.1 Thermal decomposition behavior of binder components

The binder is the core of CIM. Unsuitable binder may lead to defects, which are generated from injection and debinding process. Generally speaking, the requirement of the binder is more important in CIM than in PIM. It is because that the particle size of ceramic powder is smaller than metal powder. So the powder has lower flow ability, greater surface area, and is easy to form agglomerates which will reduce the uniformity of feedstock when the powder and the binder mixes, and reduce the flow ability of feedstock in injection machine[7]. On the other hand, the AlN powder used in this research has spherical shape, which can give high packing densities and thereby minimizes the quantity of binder needed in molding and reduces the shrinkage in sintering, but in debinding process, this kind of powder has weak "backbone" ability and may cause deforming defects. Generally, several macromolecule polymers were added as backbone to improve component shape retention. Based on the above reasons, we choose wax binder system, that is, use PW as filling substance which has low softening temperature and good flow ability, macromolecule polymers such as EVA and HDPE as backbone material which have high melting point and strength, and a little SA agent as flow modifier for suspensions, not only reducing the viscosity of feedstock, improving the lubricative ability of powder particles, but also improving the adhesive strength of binder-powder interface, enhancing the binder-particle junctions and the toughness of the moulded material.

The thermal degradation behavior determines debinding cycle. The TGA and DTA plots of the feedstocks with different binder compositions are shown in Figs. 1(a~ f), respectively. The plots show different thermal behaviors of three feedstocks with different binder compositions. The TGA graph of sample A that contains only PW and EVA is a continuous and smooth slur. There is no obvious boundary between two mass loss region, the main mass loss occurs in the first stage, in which the body lose mass fraction of 10.56% means most binder is burn out at the same time (Fig. 1(a)); the two heat release peaks in sample A's DTA plot (Fig. 1(b)) have narrow temperature range and wide temperature interval, which means the decomposition speed of the binder is very quick[8]. For sample B formed by adding 10% HDPE into the binder based on sample A, the mass fractions of two mass loss region have been obviously changed, the mass fraction in the second mass loss region increased (Fig. 1(c)). It is clearly shown that the mass loss speed of the binder was slowed down by adding the third composition HDPE. From DTA graph in Fig. 1(d), it can also be seen that the high temperature heat release peak in sample B was widened. It is because HDPE has higher decomposition temperature (430 ℃) than that of EVA, thus can prolong the decomposition temperature range of macromolecule polymers, and decrease the decomposition speed of the binder. Figs. 1 (e) and (f) show the TGA and DTA plot of sample C which contains 20% HDPE. Compared with above TGA plots, Fig. 1(e) has three mass loss stages in which the decomposition temperature range becomes more obvious. Binder C has the slowest decomposition speed and the widest heat release peak.

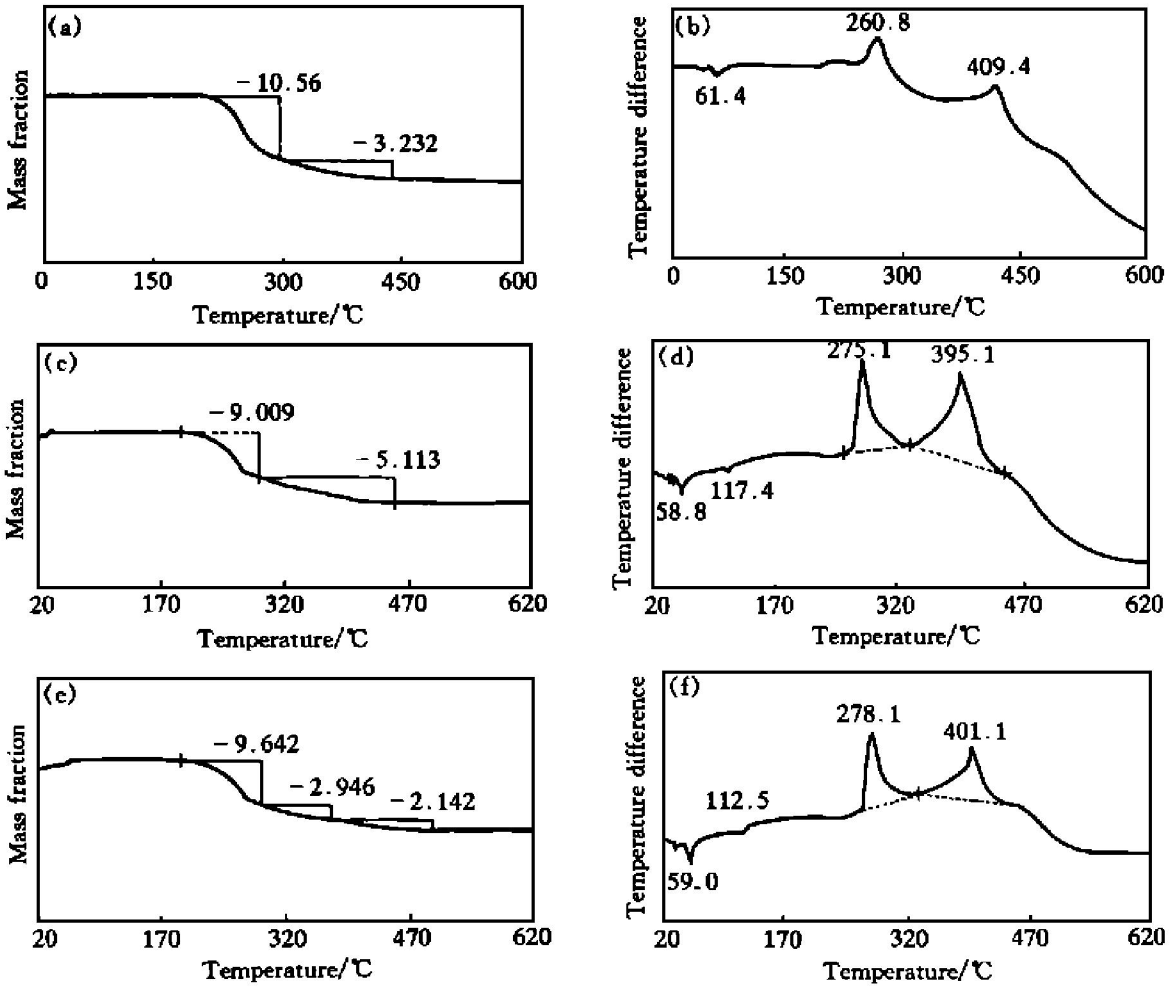

Fig. 1 TGA and DTA plots of feedstock with different binder compositions
(a) —TGA plot of Sample A; (b) —DTA plot of Sample A; (c) —TGA plot of Sample B;
(d) —DTA plot of Sample B; (e) —TGA plot of Sample C; (f) —DTA plot of Sample C

3.2 Debinding process of AlN ceramic

Thermal debinding is the longest step in CIM process, and also is a very critical point[9]. In this stage, burnout defects in injection-molding ceramic, such as cracking, deformation, and voids which may lead to poor yield of good parts and influence the successful sintering, may occur. So the shape retention ability of moldings in thermal debinding is the foundation of sintering, and the important factor controlling the products' dimension precision[10].

3.2.1 Comparison of shape retention ability of different binders

The three binders in this research have different shape retention ability under the same debinding cycle. Samples B and C have better shape retention ability than Sample A, and sample C has the best ability and the highest eligible finished product rate. Function mechanism of this phenomenon is described below. Ref. [11] says the beginning thermal decomposition temperatures of PW, EVA and HDPE, are 180 ℃, 320 ℃ and 430 ℃, respectively. In the above description the TGA graph of sample A is a continuous and smooth slur. The decomposition stages of PW and EVA have no distinguishable difference. The EVA begins to soften when the PW reaches its highest decomposition rate in sample A, which lacks the effective shape retention composition and generates deforming defects (Fig. 2(b)). Comparatively, sample C has the slowest decomposition rate. The feedstock has three main mass loss stages: the first stage loses 9.64% mass from 190.4 to 291.4 ℃ corresponding to the PW decomposition; the second stage loses 2.946% from 291.4 to 377 ℃ corresponding to the EVA decomposition; the final stage loses 2.14% mass from 377.5 to 500 ℃ corresponding to HDPE and remained EVA decomposition. Thus it can be seen that the debinding process is divided into three stages according to the mass loss rate. The thermal decomposition stage of PW, EVA and HDPE link up. When all PW burns out, EVA which has poor shape retention ability melts prior to HDPE, and at the same time, HDPE can still keep the molding part shape as the backbone. Thus in every binder burnout stage, there is binder composition which has no burnout to keep the original form until most binder burns out and the interaction effect of powder particles come into powder bone to avoid the deforming danger. The figure of sample C after debinding is shown in Fig. 2(a). This picture shows the excellent molding after debinding without any form defects. In

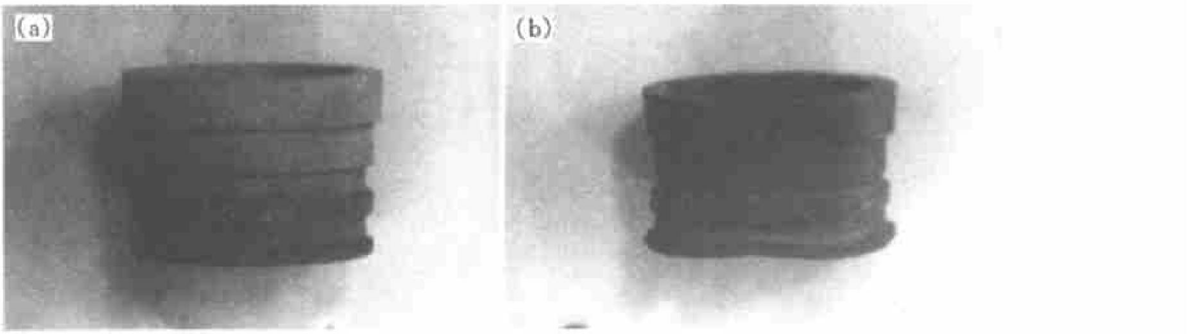

Fig. 2 Appearance of moldings containing different binders after debinding
(a) —Sample A; (b) —Sample C

the same way, the TGA plot of sample B only has two stages, which means when PW all burns out, HDPE and EVA have no obvious change in detractive temperature point because there is more EVA than HDPE in sample B. When EVA burns out, some HDPE also begin to decompose, and there is no much HDPE in the body to maintain the powder interaction. The function of HDPE, which is used to reduce the dedinding defect, is lessened. Synthetically, as to the shape retention ability, sample C is the best.

3.2.2 Determination of debinding cycle and microstructure changes

To investigate the rationality of debinding cycle, we chose sample C as example. From DTA graph of sample C, two heat release peaks reach tops at 278 ℃ and 404 ℃ respectively. They are corresponding to the highest decomposition speeds of different binder composition. Combined with its TGA plot we can draw the conclusion that the first peak is related to the PW decomposition, and the second peak to macromolecule EVA and HDPE decompositions. The endothermic peak at 59 ℃ is related to the endothermic reaction of ethanol which is remained after wet-milling of AlN-Y_2O_3 compound powder. By summarizing and analyzing the all above results and after experiment optimizing, the optional debinding cycle is acquired (Fig. 3). The top temperature is 600 ℃, and the total debinding time is 60 h.

In the first two stages of debinding, from room temperature to 140 ℃, fast temperature rising speed is chosen because the binder doesn't melt yet. At this moment, the remained ethanol is cleaned out for later process. From stage 2 to 4 (140~ 338 ℃), the temperature rising speed must slow down, because the fusible PW melts and enwraps the powder, the interspaces among powder particles don't form (Fig. 4(a)). If the temperature rises too fast, the organic substance decomposes so quickly that generates great organic gas to cause the sample to crack and deform. From stage 4 to 5(338~ 420 ℃), a little faster temperature rising speed can be used, because the PW which has 65% binder has been burn out, the interspaces among powder emerge (Fig. 4(b)). In this temperature range, EVA will burn out before HDPE because of its lower melting point. From 420 to 600 ℃, the stages can be more rapidly finished because in 440 ℃ most EVA have been burn out, enough interspaces has been formed in the body, just only a little HDPE stick among the particle to give the powder final backbone support (Fig. 4(c)). The debinding will be over after preserving at 600 ℃ for 1 h then furnace cooling. The finished sample has uniform interspaces and totally depends on the interaction of particles to maintain strength (Fig. 4(d)), so it must be carefully handled.

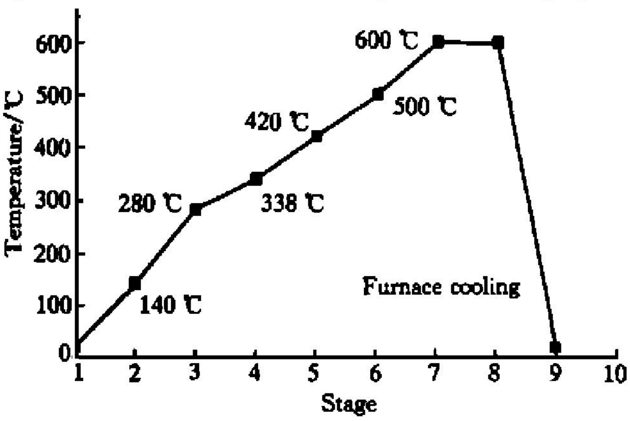

Fig. 3 Debinding cycle of AlN injection moldings

The debinded compacts were heated in flowing nitrogen to 1 850 ℃ in a carbon furnace for 2 h. The thermal conductivity was measured to be 162.5 W/(m·K).

4 CONCLUSIONS

1) By adding HDPE into the PW-EVA binder which used in powder injection molding AlN can effectively reduce the mass loss rate in debinding process. The thermogravimetry analysis shows that when HDPE amount reaches 20%, the TGA plot of feedstock has three mass loss stages and the heat release peak in DTA plot becomes wide. In this paper, sample C has the best shape retention ability, while sample A without HDPE can't maintain compact form after debinding. It can be said that using multi-compositions to let them decompose step by step is good for debinding in CIM.

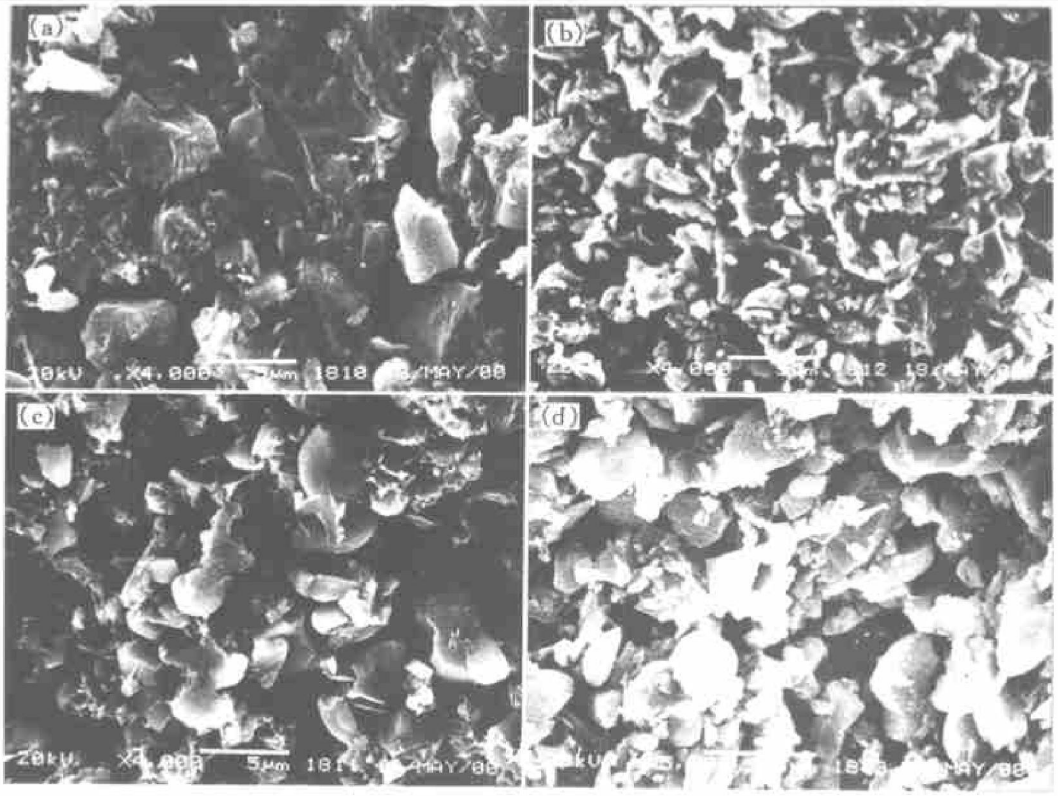

Fig. 4 Microstructures of sample C at different temperatures during debinding process
(a) —220 ℃; (b) —340 ℃; (c) —440 ℃; (d) —600 ℃

2) During CIM process, optional debinding cycle should be carried out according to the binder's composition. For the PW-EVA-HDPE system, very slow temperature rising speed must be kept between 140 ℃ and 338 ℃ in order to prevent the debinding defects such as cracking, slump, deforming, caused by great organic gas produced in short time. After 338 ℃, the speed should properly be quick to reduce the total debinding time and improve the working efficiency.

3) Powder injection molding is used to produce AlN ceramic with complex shape. The thermal conductivity of sintered sample is 162.5W/(m•K). It is necessary to improve the debinding cycle, and the combination of thermal diffusion and solvent extraction will be a good choice.

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