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ARTICLE

Effect of Processing Parameters on Gelcasting Process for Mo/Cu Powders

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Abstract: A non-aqueous gelcasting system of 2-hydroxyethyl methacrylate (HEMA)-1 ,6-hexanediol diacrylate (HDDA) was adopted to prepare concentrated slurry of Mo/Cu powders. The effects of dispersant dosage, monomer content and solid loading on rheological behavior of slurry were studied. The effects of processing parameters such as monomer content, monomer/cross-linker ratio, initiator dosage, and temperature on the gelation behavior and green bodies' flexural strength were studied. The results show that solid loading influences the viscosity of slurry the most, followed by dispersant dosage and monomer content. The flexural strength of green bodies is increased with the increasing of monomer content and the decreasing of monomer/cross-linker ratio, while the initiator dosage has a slightly effect. On the basis of them, the optimum processing parameters for Mo/Cu non-aqueous gelcasting are as follows: HEMA content is 25 vol%~30 vol%, monomer/cross-linker ratio is 10:1~15:1, initiator dosage is 1.5 vol%~2.5 vol%, and gelation temperature is 60~80 $^{\circ}C$.

Key words: gelcasting; Mo/Cu alloy; rheological behavior; flexural strength

By virtue of the excellent combination of high thermal and electrical conductivities, low thermal expansion coefficient and special high temperature performance etc, Mo/Cu alloy has been widely used in electrical and aerospace fields[1-3]. For those applications, more and more Mo/Cu alloy and its parts are required to be equipped with high performance and complex shape, but traditional manufacture methods such as infiltration sintering and powder pressing sintering are no longer suitable. Powder injection molding (PIM) has been regarded as an effective method to fabricate Mo/Cu parts with complex shape, but it can not obtain big-size parts and need special mould and debinding process with long time[4-6]. These shortcomings restrict its application and development. Therefore, a new method needs to be exploited to fabricate Mo/Cu parts with complex shape and big size. The gelcasting technology, invented by Janney and Omatete, is thought to be candidate for preparation of big-size parts with complex shape in low cost as a new near net shape technique, which can overcome the shortcoming of PIM[7-9]. It has been developed rapidly in recent years and widely applied in ceramic industry, such as alumina, silicon carbide, silicon nitride, zirconia and ceramic matrix composites[10-14]. At the same time, the application of gelcasting in PM field has already drawn many researchers' attention. Hernandez studied the gelcasting of Ni, and a relative density above 97% could be attained[15,16]. Other researchers like Jia and Guo et al. have also carried out a lot of work involving gelcasting of Ti alloys, Ni, TiAl, stainless steel, copper and so on[17-19]. Besides, some researchers have used gelcasting to fabricate porous metal materials successfully [20-22].

But until now, few papers have reported the gelcasting of Mo/Cu alloy. Previously, we fabricated porous Mo-skeleton through aqueous gelcasting and then it was processed by Cu-infiltrating for getting Mo/Cu alloy[23], but the disadvantages of infiltration sintering were still hard to be

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avoided. Now, we are trying to prepare Mo/Cu alloy and products directly by gelcasting of Mo/Cu mixed powder. In the gelcasting technology, preparation of the slurry with high solid loading and low viscosity and its casting process are the key to the success of gelcasting. In this paper, effects of some processing parameters on the rheological behavior of slurry, the gelation behavior and flexural strength of green bodies were investigated.

1 Experiment

Gas atomized copper powder with particle size of 38 μm and plasma spheroidized molybdenum powder with particle size of 38~43 μm were used. The SEM images of powders are shown in Fig.1, and reagents involved are listed in Table 1.

Firstly, premix solution was prepared by dissolving HEMA and HDDA in CA at room temperature, and then silok-7050 was dissolved in premix solution with the help of ultrasonic cleaner. Mo and Cu powders with the mass ratio of 70/30 were added into the solution, and mixed on a stirrer around 30 min to obtain the gelcasting slurry with different solid loading. After that, appropriate amount of TBPB and DMA were dropped into the slurry. Subsequently, the slurry was poured into a mould to form the green body and held at a certain temperature for about 2 h to guarantee that the gelation process was completed. Finally, the green bodies were put into acetone to remove the remained solvent after demoulding, and then dried in a drying oven at 70 °C for 6 h for further test.

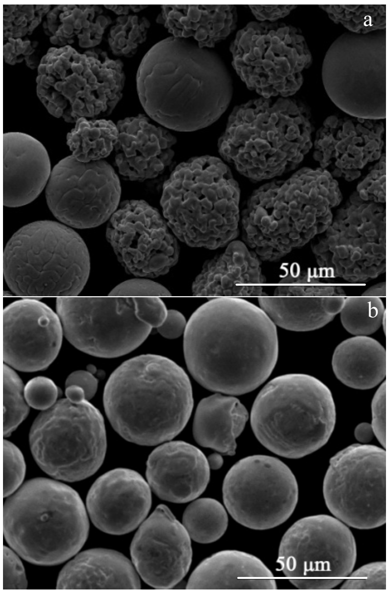

Fig.1 SEM images of Mo powders (a) and Cu powders (b)

Table 1 Reagents used in experiment

Name	Abbreviation	Function
1-octanol	CA	Solvent
2-hydroxyethyl methacrylate	HEMA	Monomer
1,6-hexanediol diacrylate	HDDA	Cross-linker
t-butyl peroxybezoate	TBPB	Initiator
N,N-Dimethylaniline	DMA	Catalyst
Silok-7050		Dispersant

The particle size distribution of Mo and Cu powders was measured by laser particle size analyzer (MICR-PLUS). The microscopic morphology of powders and fracture morphology of dried green bodies were characterized by SEM (Quanta FEG 200). The apparent viscosity of gelcasting slurries was measured by NDJ-79 rotational viscometer at a shear rate of 176 s^{-1}. By a three-point flexural method, the flexural strength of samples of 30 mm×12 mm×6 mm was obtained with an universal testing machine (CMT-5305) at the span length of 25 mm and the crosshead speed of 1 mm/min.

2 Results and Discussion

2.1 Effect of processing parameters on rheological behavior of slurry

Generally speaking, metal powders have bigger particle size and density compared to ceramic powders, and the sedimentation of powder in slurry is more serious. Therefore, it is critical to employ an appropriate gelcasting system, and find the right dispersant that can disperse metal powder effectively.

For gelcasting slurry, the fluidity has a great influence on the properties of green body, so it is quite essential to prepare slurry with high solid loading and good fluidity. Slurry with good fluidity maintains that it is easy to fill the mould, which is especially important for products with complex shape. Therefore, it is necessary to study the additives and solid loading's influence on the rheological behavior of slurry.

Fig.2 reveals the influence of silok-7050 content (based on the mass of metal powders) on the viscosity of Mo/Cu slurry with 40 vol% solid loading. It can be seen from Fig.2 that with the increasing of silok-7050 content, the apparent viscosity of Mo/Cu slurry firstly decreases rapidly and then increases sharply. Silok-7050 is a kind of polycarboxylic acid polymer, it can offer the same kind of charge for metal powders. When the powders of slurry are close to each other, electrical repulsion impedes the agglomeration of particles. Furthermore, the mean molecular weight of silok-7050 is about 2000, and steric hindrance can prevent particles from flocculation. When the dispersant content is low, potential resistance and steric hindrance dominate the mechanism of dispersion; thus the viscosity of slurry decreases and reaches to its minimum value of 230 mPa·s at the dispersant content of 1.5 wt%. Once the silok-7050 content exceeds its critical dosage of 1.5 wt%, it may form micelle, which will

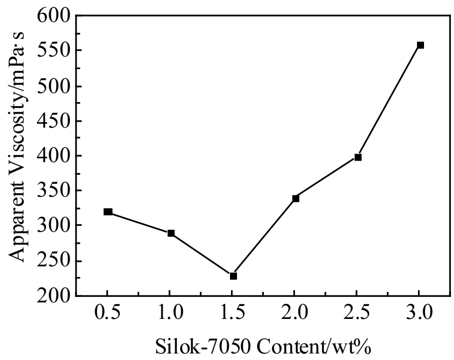

Fig.2 Influence of Silok-7050 content on the viscosity of Mo/Cu slurry

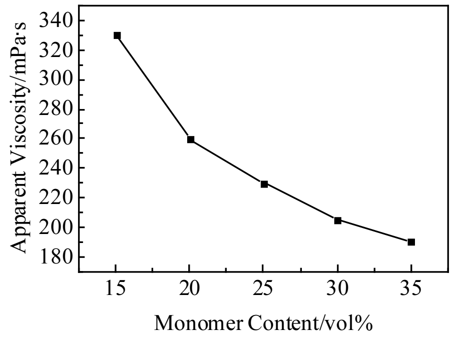

Fig.3 Influence of monomer content on the viscosity of Mo/Cu slurry

absorb a lot of solvent, and result in the sharp increasing of viscosity.

Fig.3 reveals the influence of monomer content (based on the total volume of reagents) on the viscosity of slurry. We can see that with the increasing of monomer content, the viscosity of slurry decreases from 330 to 190 mPa·s. According to Goodwin's law of non-Newtonian fluid, the viscosity of slurry can been estimated by formula (1)[24].

$$\eta = \eta_0 \left(1 + 2.5\phi + K\phi^2\right) \quad (1)$$

where η is the viscosity of slurry, η_0 is the viscosity of premix solution, ϕ is the solid loading, K is a constant (related to agglomeration of powders and electrochemical changes between powders). Since the value of ϕ is determined, η is proportional to the value of η_0. At 20 ºC, the viscosity of 1-octanol and HEMA are about 8.93 and 8.40 mPa·s, respectively. With the increasing of monomer content, the value of η_0 decreases, and it will decrease correspondingly according to the formula (1).

As it is demonstrated in Fig.4, with the increasing of solid loading, the increasing rate of viscosity becomes larger. Formula (1) also reveals that the viscosity of slurry has a great relationship with the solid loading. As we know, the slurry is composed of solvent, metal powders and other reagents, the fluidity of slurry depends on the unrestricted solvent's volume badly. When the powders' volume increases, the volume of solvent decreases correspondingly. Furthermore, metal powders absorb more solvent. With the effect of these aspects, the volume of unrestricted solvent becomes lower, resulting in increasing of viscosity of slurry. Besides, the relative distance of powders gets narrower and the interaction of particles will exacerbate at the same time, which will result in agglomeration of metal powders, and thus the viscosity of slurry increases sharply with the increasing of solid loading. When the solid loading is 43 vol%, the slurry's viscosity is about 740 mPa·s, which can still fill the mould easily. But when the solid loading is beyond 44 vol%, the viscosity is more than 1Pa·s, making the mould filling difficult.

Based on the results above, solid loading influences the viscosity of slurry the most, followed by dispersant dosage and monomer content.

2.2 Effect of processing parameters on gelation behavior

The key point for gelcasting of Mo/Cu powders is to finish casting process and in situ form gelation rapidly before the appearance of delamination in the slurry. It is necessary to research the gelation behavior for the selected HEMA gel system. Polymerization of HEMA monomer may occur as follows[10]. Firstly, the initiator decomposes into primary free radical. Then the primary free radical can be combined with monomer molecule, which produces monomer free radical. These free radicals can combine with monomers to form chain free radicals. With the proceeding of the above reactions, monomer and cross-linker polymerize into polymer chain. Processing parameters such as monomer content, monomer/cross-linker ratio, initiator dosage and temperature can all influence the polymerization process.

Unlike the AM/MBAM system, the polymerization of HEMA does not show obvious exothermic effect[25]. Thus, it is not suitable to record idle time by measuring the temperature rise during polymerization to solve this problem, the slurry was held at the given temperature by water bath and put on a stirrer to observe the viscosity change. When the polymerization starts, the viscosity of slurry changes suddenly. Time from the adding of initiator to the sudden change of slurry's viscosity is recorded as idle time.

The effect of monomer content on idle time is plotted in Fig.5. It is clear that the higher the monomer content, the shorter the idle time. In the polymerization process, the generation rate of monomer radical is much larger than the decomposition rate of initiator. Generally speaking, the polymerization rate is proportional to the monomer content. When the quantity of free radical is determined within a certain time, higher monomer content makes it easier to generate monomer radical; as a consequence, the polymerization is accelerated and the idle time decreases.

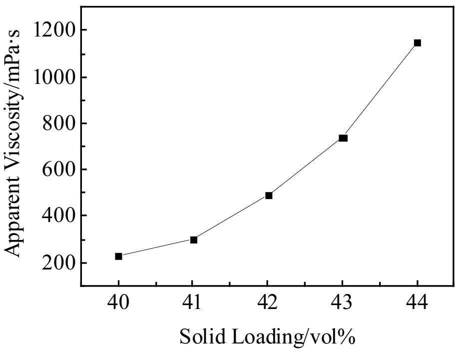

Fig.4 Influence of solid loading on the viscosity of Mo/Cu slurry

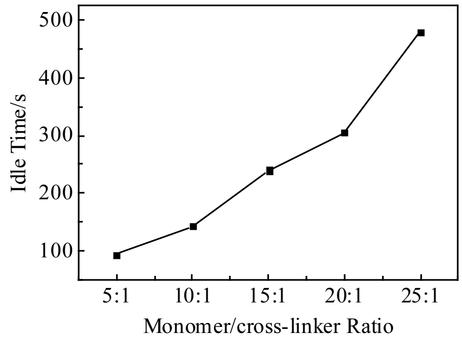

Fig.6 Effect of monomer/cross-linker ratio on idle time

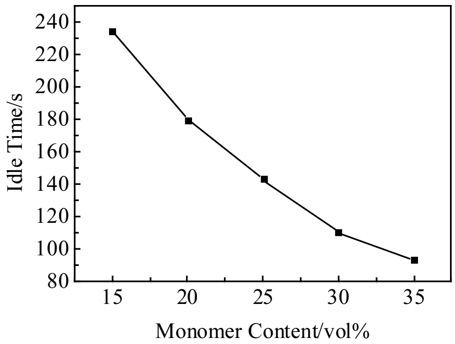

Fig.5 Effect of Monomer content on idle time

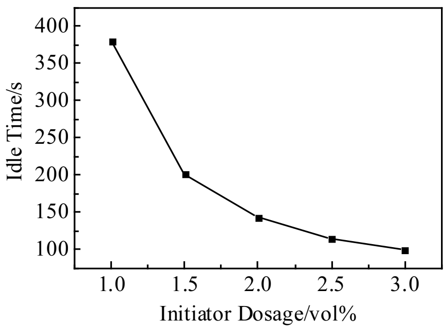

Fig.7 Effect of initiator dosage on idle time

Fig.6 reveals the effect of Monomer/cross-linker ratio (volume ratio) on idle time. The function of cross-liner is to form "bridges" with linear molecule and form polymer network. Generally, during the polymerization of monomer, chain scission is along with chain growth. In HEMA/HDDA system, HDDA can combine with chain free radicals quickly, and this kind of reaction is faster than polymer chain scission reaction. Therefore, with the increasing of HEMA/HDDA ratio, the relative HDDA content decreases, and the idle time is also prolonged.

Fig.7 reveals the effect of initiator dosage (based on the total volume of monomer and cross-linker) on idle time at the condition of monomer content 25vol% and the monomer/cross-linker ratio 10:1. As is shown in Fig.7, the higher the initiator, the shorter the idle time. The main reason is that the polymerization process strongly depends on the quantity of primary free radical. When the initiator dosage is too low, "cage effect" will impede the combination of primary free radical and monomer. Consequently, the idle time drops sharply when the initiator dosage is increased from 1.0vol% to 1.5vol%. Continuing to increase the initiator dosage will decrease the idle time, but the decreasing rate slows down.

Fig.8 reveals the effect of temperate on idle time. In the experiment process, we found that when the temperature is lower than 50 °C, the polymerization proceeds very slowly, and the sedimentation of powders is quite serious. It can be seen from Fig.8 that when the temperature rises from 50 to 60 °C, the idle time is reduced dramatically, and when the temperature continues to increase, the idle time decreases slowly. The main reason is that, TBPB starts thermal decomposition around 60 °C, but the decomposition rate is low, while DMA can accelerate the decomposition of TBPB. Thus when temperature is higher than 60 °C, the effect of temperature is not as significant as at low temperature.

Based on the results above, by controlling correlated parameters, the idle time can be controlled under a certain scope to maintain enough time for the mould filling of slurry, and then solidify fast. When the monomer content is in the range of 20vol%~30vol%, monomer/cross-linker ratio is 10:1~15:1, initiator dosage is 1.5vol%~2.5vol%, and temperature is 60~80 °C, idle time lies in the range of 100~200 s.

2.3 Effect of processing parameters on flexural strength of green bodies

For gelcasting, the polymerization of monomers in the

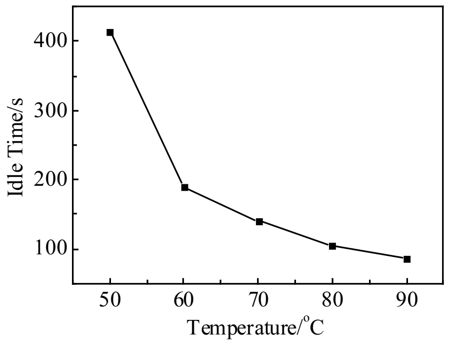

Fig.8 Effect of temperature on idle time

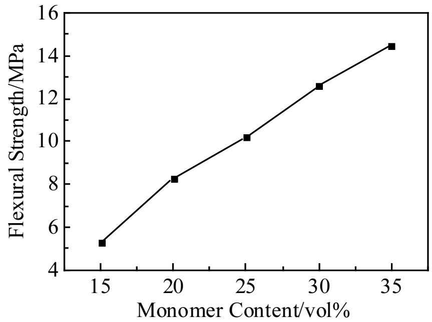

Fig.9 Effect of Monomer content on green bodies' flexural strength

slurry can form a strong macromolecule to hold the powder and make the green bodies have a certain strength. The effect of monomer content on the flexural strength of green bodies is shown in Fig.9.

The flexural strength increases with the increasing of monomer content from 15 vol% to 35 vol%. When the monomer content is 15 vol%, the flexural strength is only 5.26 MPa, and when the monomer content increases to 35 vol%, the flexural strength can reach 14.5 MPa. Fig.10 are SEM images of green bodies with different monomer contents, it can be seen that the metal powders are enclosed by polymer network, and with the increasing of monomer content, more polymer network are formed. The SEM images also prove that the increasing of monomer content increases the quantity of polymer network, thereby increasing the flexural strength. But excessive monomer content will complicate the debinding process of green bodies. Considering the idle time at the same time, the monomer content should be kept from 25% to 30%.

As shown in Fig.11, there is an optimum monomer/cross-linker ratio. When the ratio is held at 10:1, green strength reaches the maximum. When the monomer/cross-linker ratio is larger than 10:1, with the increasing of HEMA/HDDA ratio, the flexural strength of green bodes decreases. This is because the "bridges" decreases with the decreasing of cross-linker, which will reduce the strength of polymer network. But excessive amount of HDDA accelerates the polymerization process, and tends to form short chain polymer, which will also deteriorate green strength.

Fig.12 reveals the effect of the initiator dosage on green bodies' flexural strength. It can be seen that with the increasing of initiator dosage, the flexural strength firstly increases and

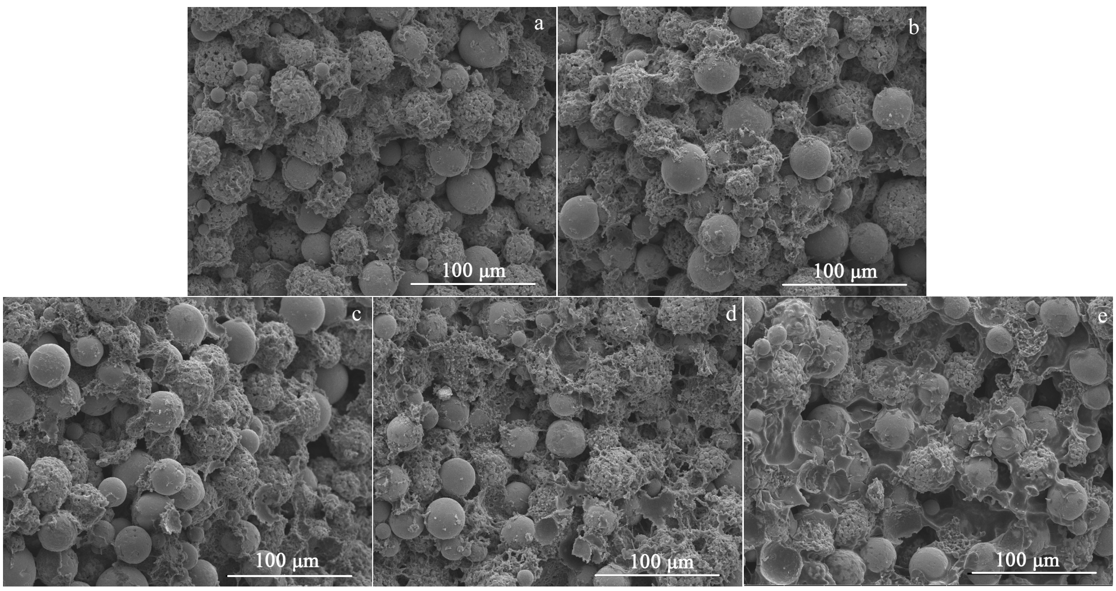

Fig.10 SEM images of green bodies with different monomer contents: (a) 15 vol%, (b) 20 vol%, (c) 25 vol%, (b) 30 vol%, and (e) 35 vol%

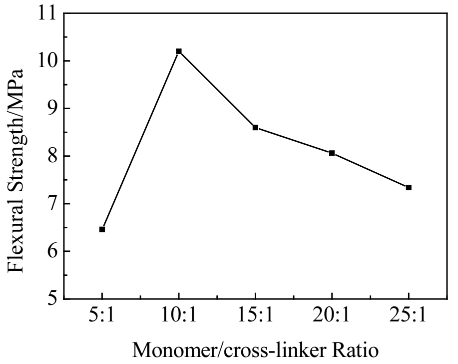

Fig.11 Effect of Monomer/cross-linker ratio on green bodies' flexural strength

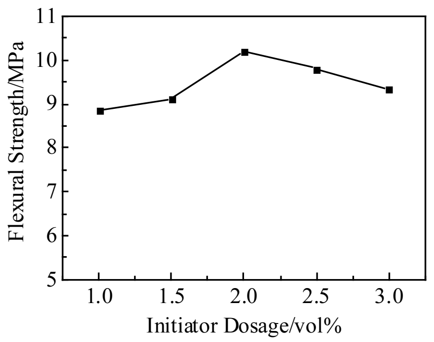

Fig.12 Effect of initiator dosage on green bodies' flexural strength

then decreases. The main reason causing the differences of green strength is that, the effect inflicted by temperature on idle time has caused chain effects on uniformity of composition and green strength consequently.

Based on the results above, we can see that the main factors affecting green strength are monomer content and monomer/cross-linker ratio. While initiator dosage has a slight influence on green strength.

3 Conclusions

1) The dispersant dosage, monomer content and solid loading have considerable effect of the rheological behavior of slurry. With the decreasing of monomer content and the increasing of solid loading, the viscosity of slurry increases. When silok-7050 content is 1.5 wt%, the viscosity of slurry reaches to its minimum value of 230 mPa·s.

2) The idle time decreases with the increasing of monomer content, initiator dosage and temperature, but increases with the increasing of monomer/cross-linker ratio. By controlling processing parameters like monomer content, monomer/cross-linker ratio, initiator dosage and temperature, the gelation time can be adjusted according to the need of production process.

3) The flexural strength of green bodies increases with the increasing of monomer content and the decreasing of monomer/cross-linker ratio, but excessive amount of cross-linker decreases green strength. Initiator dosage has a slight influence on green strength.

4) For Mo/Cu powders, when the solid loading is 40 vol%, the optimum processing parameters for Mo/Cu non-aqueous gelcasting are as follows: HEMA content is 25 vol% ~ 30 vol%, monomer/cross-linker ratio is 10:1 ~ 15:1, initiator dosage is 1.5vol%~2.5vol%, and gelation temperature is 60~80 ^{o}C. The flexural strength of green bodies can reach higher than 10 MPa, guaranteeing the feasibility of subsequent transport and machining.

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工艺参数对Mo/Cu粉末凝胶注模成形的影响

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摘　要：采用甲基丙烯酸羟乙酯(HEMA)-1，6-己二醇二丙烯酸酯非水基凝胶注模体系制备了浓Mo/Cu粉末浆料。研究了分散剂用量、单体含量和固相体积分数对浆料流变行为的影响，并讨论了单体含量、单体/交联剂比例、引发剂用量、温度等工艺参数对固化行为和坯体抗弯强度的影响。结果表明，固相体积分数对浆料流变行为的影响最大，其次是引发剂用量和单体含量。随着单体含量的增加和单体/交联剂比例的减小，坯体抗弯强度增加；引发剂用量对坯体抗弯强度的影响较小。根据上述结果，Mo/Cu粉末非水基凝胶注模的合理工艺参数如下：HEMA含量为25% ~ 30% (体积分数)，单体/交联剂比例为10:1～15:1，引发剂用量为1.5% ~ 2.5% (体积分数)，固化温度在60~80 ℃之间。

关键词：凝胶注模；Mo/Cu合金；流变行为；抗弯强度

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