

RAPID PATTERN BASED POWDER SINTERING WITH ROOM TEMPERATURE POLYMER INFILTRATION

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ABSTRACT

In this paper a new rapid tooling technique, named Rapid Pattern Based Powder Sintering (RPBPS), is introduced. Due to limitations of common infiltration methods used in rapid tooling such as high temperature caused cracks, distortion, shrinkage and poor surface quality, a low temperature polymer infiltration method is proposed. Based on the curing principles of polymer materials, several kinds of infiltration materials were selected, and their main mechanical and thermal properties and chemical resistances were discussed. With various infiltration methods and materials, a series of testing samples were made, and their microstructures and thermal resistances were observed and tested. In order to calculate the needed amount of the polymer materials and their infiltration height in the sintered molds or parts, an infiltration model was also proposed and compared with experiments.

INTRODUCTION

Rapid prototyping/tooling and manufacturing have experienced tremendous growing and drawn great attention in national and international manufacturing industry (Jocobs, 1996). Although rapid prototyping has brought in a new revolution in manufacturing processes of materials by using additive and layer by layer material processing technique, its crown has gradually shifted to rapid tooling/manufacturing, i.e. not only prototype but also functional products. The development list of Rapid Tooling (RT) technology based on rapid prototyping and manufacturing has been growing during recent years (Vanputte, 1994). Over ten RT methods have been proposed, and examples are 3D Systems's Keltool, DTM's RapidSteel, CEMCOM's NCC Tooling, Dynamic Tooling's PolySteel, ExpressTool's Electroforming, and Extrudehone's PROMETAL (Ashley, 1998). Rapid Pattern Based Powder Sintering (RPBPS) technique (Zhou and He, 1998, 1999) developed by the authors is a new rapid tooling technique. This technique is suitable for a variety of materials and any complex geometry, and also has the advantages of rapid process and low cost. Like many other RT techniques, such as Keltool, RapidSteel and NCC Tooling, RPBPS technique involves two main processing steps: sintering and infiltration. After a green mold or part, having desired cavity/geometry, is made through laser scanning (such as in RapidSteel) or casting the mixture of metal powder and polymer binder (such as in Keltool, NCC Tooling and RPBPS), it will be sintered in protective atmosphere. During this process the binder material will vaporize and/or carbonize and then escape from the green products, and the remains, i.e. the metal particles will be sintered to form a solid body. To increase the strength and hardness, the sintered mold/part will be infiltrated with some alloys, such as brass and bronze. In general, the infiltration alloy should have a lower melting temperature than that of the powder material, so that the melted alloy can soak into the sintered product and fill into all porous. During the infiltration process the product will have a linear shrinkage of 2%-5%. The shrinkage depends mainly on two factors. First is the temperature for melting the infiltration alloy. For brass, zinc amount is over 30% by weight and

copper around 70%. For bronze, the tin amount is over 35% by weight and copper around 65%. Their melting temperature are both over 1830 F. The second factor is the time for maintaining the high temperature which depends on the size and geometry of the product to be infiltrated. In general, the time will be controlled as short as possible. Based on our experiments when infiltrating a sintered one-inch-cube part of low carbon steel powder with brass, the furnace should maintain a temperature of 1830 F for at least 25 minutes. Under these conditions the linear shrinkage of the infiltrated product will reach 2.5%-3%. Another problem in the infiltration process is the distortion of the product caused by the non-uniform temperature distribution in the furnace and the complex geometry of the product. In some special cases the product may crack on the positions with sharp angle change or discontinuous change of wall thickness. The research presented in this paper is an effort toward a new infiltration method. Based on RPBPS technique some special polymer materials to infiltrate the sintered mold/part in room temperature have been used. First, a brief introduction on RPBPS technique and main processing steps is given. According to the desired characteristics the infiltration materials are chosen, and their properties are listed and compared. Then some details on the infiltration process are discussed. Furthermore, the microstructures and thermal properties of the infiltrated samples is illustrated and tested. Finally, a model on the infiltration process was deduced and compared with experiments.

TECHNICAL PROCESSES

Rapid Pattern Based Powder Sintering (RPBPS) technique is to seek out more efficient way to make rapid tooling and manufacturing. This new technique includes the following main steps (see Figure 1). First, a master pattern made of polymer material is fabricated by using a rapid prototyping machine based on a 3-D solid model designed in a CAD system. Then the pattern is positioned on a substrate in a metal box or frame, and then a mixture of metal or ceramic powder and binder is cast around the pattern under certain pressure. After removing the pattern and separating the substrate, a green compact having desired cavity/geometry can be obtained. Then the green compact will be sintered and infiltrated in a protective gas, such as nitrogen or hydrogen, to finally form a tool, mold or part. The reason that the RPBPS is better than other rapid tooling methods can be concluded as that it overcomes the defects of other RT methods and adopts the merit from various tooling techniques. RPBPS technique is suitable for a variety of materials and any complex geometry, and also has the advantages of rapid process and low cost. In order to save time and energy and reduce the shrinkage, the sintering and infiltration processes can be carried out in one step (see Zhou and He, 1998). Figure 2 shows a typical program on the sintering/infiltration process, in which the powder material is carbon steel, the infiltration alloy is brass, and the protective gas is nitrogen. There are still some problems when using this program. One is the reaction between the escaping carbon smoke and the infiltration alloy. Based on our experiments, from about 600–650 F the binder material will carbonize to form a large amount of carbon smoke. a temperature-keeping stage (see Figure 2) for the escape of smoke from the furnace is designed. However, some carbon particles will still remain on the surface of infiltration alloy, with the increase of temperature the alloy will react with carbon to form carbide.

On the other hand, for improving the temperature distribution to reduce the distortion of the green compact we can use ceramic powder, such as alumina, to fill all concave angles, hollows or holes of the compact to reduce uneven temperature distribution. But the powder may

hinder the carbon smoke's escape so that some carbon particles will remain in the compact. The remainder will cause two problems: the metal particles can not be sintered well and the melted alloy can not soak into the compact well due to the poor wettability of the metal particles. Using some special polymer materials to infiltrate the sintered compact in room temperature have been developed. We hope by using this technique not only the products will have very small shrinkage and distortion, but also the time and energy can be saved. We also hope the infiltrated parts have better mechanical and thermal properties to be applied in practical production.

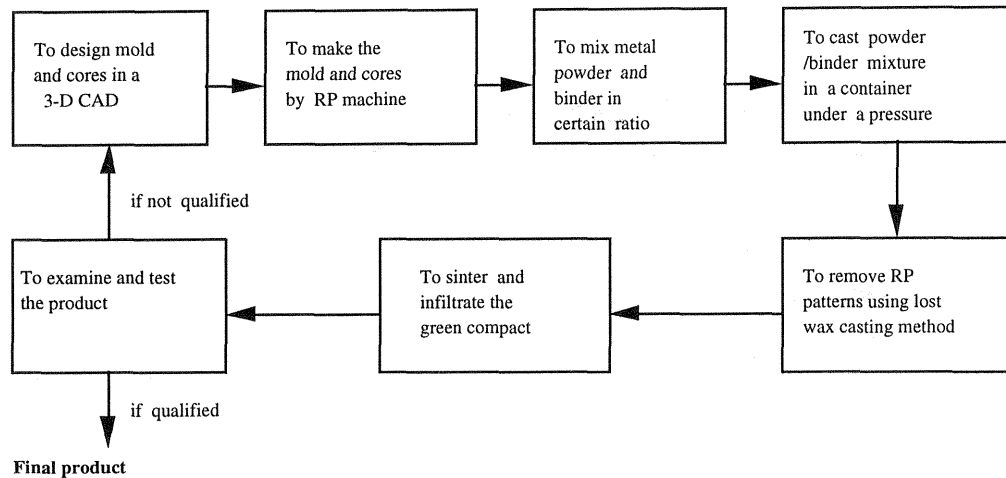


Figure 1. The main steps of RPBPS process

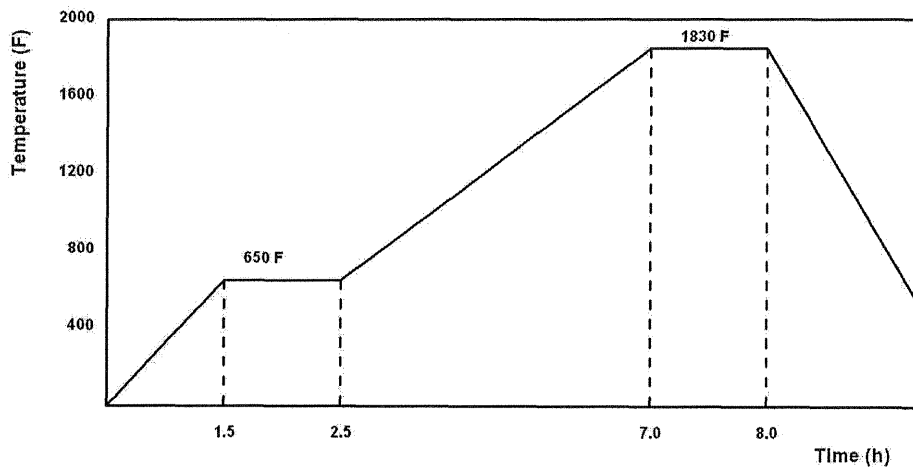


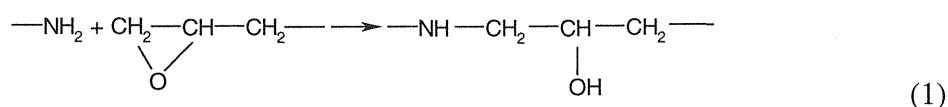
Figure 2. The program of sintering/infiltration process

SELECTION OF INFILTRATION MATERIALS

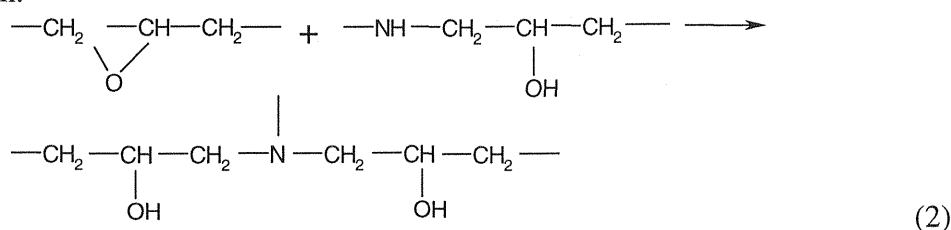
It is expected that a suitable infiltration material should have the following characteristics. (1) It should have a liquid state in room temperature, but in certain conditions it can transform into solid. (2) The transformation from liquid to solid should be irreversible, and the volume change caused by the transformation should be as small as possible. (3) In liquid state the material should have a lower viscosity and higher wettability to the metal powder in order to soak into the sintered compact easily and quickly. (4) When solidified the material

should have a certain strength, hardness and chemical resistance. (5) For making mold or tool the solid material should bear a higher temperature and a hot-cold temperature cycle for a longer time, and it has a higher thermal conductivity.

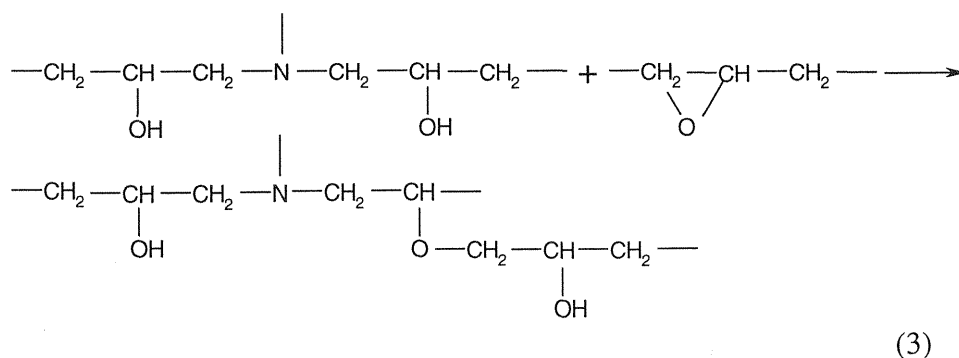
Metallic materials have high strength, hardness, heat-resistance and thermal conductivity, but they can not satisfy the above condition (1). It is also difficult for ceramic or inorganic materials to meet the above conditions (1) to (3). Most organic materials have lower strength and hardness. Especially they can not withstand higher temperature. However some polymer materials can meet above mentioned five requirements. Because of the advantages of its very applicable structure, behavior, and fundamental properties, polymers are used in many manufacture areas (Flory, 1953, Gedde, 1996). Our focus is on special resins and their thermal properties. For example, before cured an epoxy resin may have a lower viscosity like a liquid, but after cured it may have a higher strength and rigidity like a solid. A resin's cure can be carried through cross-linking of linear molecules. The degree of cross-linking depends mainly on the hardener and/or surrounding temperature. If using polyamine or other kinds of amine as hardener, the cross-linking process can be described as follows. First a cyclic chain in epoxy resin radical will be opened:



Then another cyclic chain can be opened under the action of the resultant of the first step reaction.



The next etherification reaction is



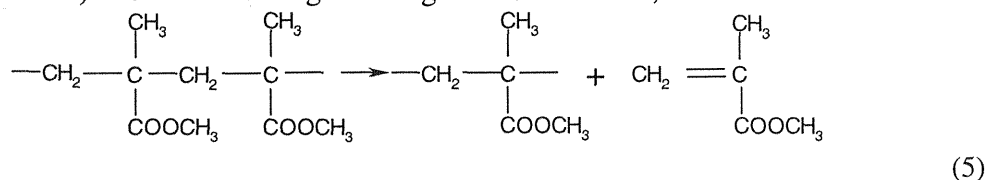
The produced hydroxyl can continuously react with epoxy resin radical to form net structure. Some resins can be cured through heating not using any hardener, and the curing temperature is only little higher than room temperature. In general the cure of resin is an irreversible process, and its volume change during the process is very small (for most epoxy resins it is less than 0.15%). So the second condition can be satisfied. Because some resins or their solutions have very low viscosity, and most metal materials can be wetted by them. So the third condition is also not a problem. But the strength and hardness of most resins are not so high. Especially,

their heat deformation resistance and heat stabilization are all much lower than that of metallic materials. The last two conditions limit our choice space greatly.

For polymer materials, a high heat deformation resistance means the high glass transition temperature T_g . The glass transition is analogous to a melt. As the temperature is raised, crystalline solid like metal or polyethylene melt and become liquids. Amorphous solids like glass and resin pass through a temperature range where the molecules rapidly gain in mobility. This molecular mobility results in flow or creep, and in rapid dimensional change. We are able to use several methods to increase T_g : (1) To change the structures of main chain of the existing polymer binders. If the main chain is composed with saturated single bond, such as - C - C -, - O - C - or - Si - O -, its T_g will be very low; (2) To increase the polarity of lateral group. Due to stronger forces between bonds, the polymers with strong polar lateral group will have a higher T_g ; (3) To increase the molecular weight M . In general, T_g will increase with the increase of M . There is a relationship between them,

$$T_g = T_g(\infty) - K / Mn \quad (4)$$

where $T_g(\infty)$ denotes the glass transition temperature when molecular weight is infinite, K is a constant and Mn denotes the number mean molecular weight. (From this equation one can see when Mn is big enough the effect of increasing T_g will decrease greatly.) (4) To use cross linking method. Cross-linking among molecules can hinder the movement of molecular chain segments, thus T_g will be raised; (5) To use copolymerization method. In fact, if the monomers have similar properties, the T_g of the copolymer has a linear relationship with the weight ratios of monomers. The heat stabilization means the thermal decomposition resistance. In general, degradation and cross-linking of polymers can occur simultaneously under high temperature. The two reactions are both related to the break of chemical bonds. The heat degradation has two modes: depolymerization and random break of bonds. For example, polymethyl methacrylate (PMMA) has the following heat degradation reaction,



Degradation will result in tacky and soft of polymers. We can use several methods to increase the heat stabilization of the existing polymer binder. (1) To increase the strength of bond in the molecular chains and avoid weak bonds, such as (C - CL), (C - S) and (O - O). (2) To add in aryl heterocycle structure and decrease (- CH₂ -) structure in main chain. (3) To add in some heat stabilization agents, such as stearates. The above analyses provide us a choice direction among hundreds of resins.

PROPERTIES OF SELECTED INFILTRATION MATERIALS

We have found several kinds of resins as the candidates. (1) Phenolic resin. Phenolic resin is classified as a condensation reaction polymer. In this type of reaction, the polymer grows by combining two large molecules and releasing a third small molecule, usually water. A wide range of characteristics can be designed into a phenolic resin. Reactivity, moisture content, molecular weight, pH value, monomer level, viscosity, flow and lubricity all may determine the suitability of the resin for our needs. A key property of phenolic resin is the ability to withstand higher temperature. Unlike most polymers, the T_g of phenolic resin can be further elevated to

levels in excess of 260°C by a correct design. Considering that an injection mold needs to bear only 100°C-150°C for the manufacture of common plastic parts (for ABS parts, the mold needs to withstand 215°C), we select phenolic resin for the infiltration of injection molds. The solution can penetrate and soak very easily into the sintered compacts no matter what kind of powder materials. Its curing temperature is around 150°C, the shrinkage during the cure process depends on the density of the solution. The lower the viscosity, the lower the density, but the larger the shrinkage will be. Main specifications of Plenco 06582 are in Table 1.

Table 1 Typical Properties of Infiltration Materials

Resin	AboCast50-3	AboCast50-6	AboCast50-24	Plenco 06582
Hardener	Cure50-17	Cure50-17	Cure50-17	
Ratio (resin/hardener) by wt.	100/26	100/28	100/115	100/0
Bl. Viscosity (cps/°C)	110/70	70/70	80/25	50/25(50%alcohol)
Specific Gravity (H ₂ O=1)	1.87	1.75	1.89	1.59
Flexural Strength (Mpa)	94.9	107.3	90.5	93.8
Flexural Modulus (Mpa)	3,900	3,520	3,450	7,952
Tensile Strength (Mpa)	67.1	70.3	57.8	59.0
Tensile Modulus (Mpa)	3,750	2,170	4,250	8,982.0
Compressive Strength (Mpa)	118.1	124.0	110.6	115.0
Tensile Elongation (%)	4.4	3.0	4.7	0.7
Hardness, Rockwell	106(M scale)	109(M scale)	104(M scale)	42(E scale)
Mold Shrinkage (m/m)	0.001	0.0012	0.002	0.0023
Water Absorption (%)				0.17
Deflection Temperature (°C)	160	157	170	221
Heat Resistance (°C)	230	257	298	238
Thermal Expansion (°C)				5.3E-5
Thermal Conduction(W/m°C)				0.44
Thermal Degradation (wt. loss) After 100 hrs, 160°C	0.55%	0.44%	0.65%	
Chemical Resistance (wt. loss) Aft 120days, 30% Sulfuric Acid	2.60%	1.96%	1.96%	
Chemical Resistance (wt. loss) After 120 days, 50% Sodium Hydroxide	0.05%	-0.12%		
Chemical Resistance (wt. loss) After 120 days, JP 4 Fuel	0.27%	0.11%		
Cure temp.& time (°C/hour)	80/1.5	80/2.5	25/14	80/(12-20)

(2) Epoxy resin. The principle of the cure of epoxy resin has been shown in Equations (1)-(3). Most epoxy resins have higher viscosity and lower heat-resistance. But some modified epoxy resins can be as ideal candidates. For example, the viscosity of Resin AboCast 50-3 (see Table 1) is 110 cps (at 70°C), it is just like that of light motor oil. The viscosity of Resin AboCast 50-16 is even less than 110 cps. However, as above mentioned in phenolic resin, the resin with lower viscosity must have a lower strength and heat-resistance and a larger shrinkage. We should compare all properties of various resins to make the decision, see Table 1.

METHODS OF INFILTRATION PROCESS

Before infiltration, the green compact will be sintered. For steel powders the sintering temperature and keeping time are controlled not over 1400 F (760°C) and 30 minutes. In this case the linear shrinkage of the sintered compact can be controlled less than 1%. After sintered the surface of the compact needs to clean carefully to remove oxidized layers, then the compact will be put into the prepared infiltration material. Figure 3 shows three methods for infiltrating a sintered mold. If the infiltration material has a higher viscosity and the viscosity increases continuously even in room temperature, the process may be carried so slowly that the sintered

mold can not be infiltrated completely. In other word, before the center parts of the mold are infiltrated the materials close to the surface have been cured to form a solid “outside shell”. Thereby, when using some epoxy resins, such as AboCast 50-3 or AboCast 50-6, we must consider the thickness of the mold and the surrounding temperature. If the thickness is bigger and the temperature is higher we will use the Method (a) shown in Figure 3. In this method the inside surface of the mold (called working surface) is kept to not contact with the resin, which will soak into the mold from its bottom and outside wall. The whole container is kept in a refrigerator with a lower temperature for a longer time until the top surface of the mold is infiltrated. Because the above two kinds of epoxy resins have dark colors, the color of the infiltrated surface is different from that not treated, from which we can guess if the process has been finished. Then the infiltrated mold will be heated for further cure of the resin.

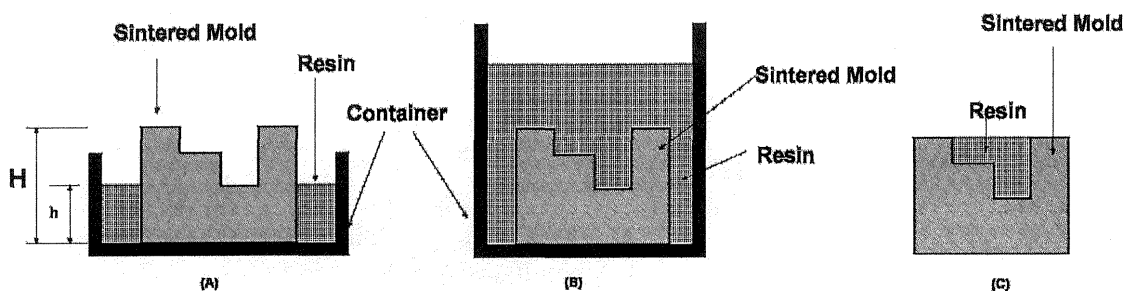


Figure 3 Three methods for infiltrating a sintered mold

If the infiltration material has a lower viscosity and it increases very slowly during the process, then we can choose Method (b). In this method the whole mold sinks into the resin for a period of time, then it is taken form the container to remove remain resins. Then the mold will be heated for the cure of the infiltration material. For those molds with a smaller thickness we can use Method (c). In this method the resin is directly poured into the concave part of the mold, more resin will be added until whole mold is infiltrated, then the mold will be heated. No matter what methods we use, we must guarantee all porous to be filled and the mold has a clear working surface. For this object we should know the accurate amount of the needed resin and the mechanism of the infiltration process.

MODELING OF INFILTRATION PROCESS

When a sintered mold or part sinks into a resin that has a lower viscosity and higher wettability to the sintered material, the resin can enter the inside of the mold automatically. This is caused by the capillarity. The capillarity effect depends on several factors: the surface tension of resin, the size of the capillary tube and the contact angle between resin and tube wall that represents the wettability of the resin. In a straight circular tube a pressure difference caused by the capillarity effect will be (Sears et al, 1984),

$$\Delta p_s = 2\sigma \cos \theta / r \quad (6)$$

here σ denotes the coefficient of surface tension, θ is the contacting angle and r is the radius of the tube. The height difference that the liquid can rise in the tube from its top surface due to the capillarity will be

$$H - h = \Delta p_s / d \quad (7)$$

here H is the height of the tube, h is the height of the liquid top surface and d is the density of the liquid. We can not directly use the above formulas to calculate the infiltration height of a sintered mold as shown in Figure 3(a), because gaps and holes contained in the sintered mold are not straight circular tubes. If we want to simplify them into straight circular tubes, we must first know their equivalent radius r' , i.e. the radius of a circular cross section that has the same area as that of the gap/hole. In fact, r' is related to the size of the powder particle and the gap ratio of the sintered mold. As shown in Figure 4, we assume that the microstructures of sintered mold can be simplified as many cylinders that are bonded together after sintered. From the cross section view there are several simplified arrangement modes (see Figure 4). Every mode has the corresponding gap ratio λ . For Mode (a), we have $\lambda_a = [S_{abc} - 3(\pi R^2) / 6] / S_{abc} \approx 0.092$, in which S_{abc} denotes the area of triangle abc and R denotes the radius of a particle. For Mode (b), we have $\lambda_b = [S_{abcd} - 4(\pi R^2 / 4)] / S_{abcd} \approx 0.215$, in which S_{abcd} denotes the area of square $abcd$. For Mode (c), we have $\lambda_c = [S_{abcdef} - 6(\pi R^2 / 3)] / S_{abcdef} \approx 0.395$, in which S_{abcdef} denotes the area of hexagon $abcdef$. Based on our experiments the gap ratio of sintered molds or parts is about 0.20-0.42, so Mode (b) and (c) are more reasonable than Mode (a). Considering that the gap ratio depends mainly on the binder ratio in the green compact and the casting pressure, when the binder ratio is smaller and the casting pressure is bigger we select Mode (b), or select Mode (c).

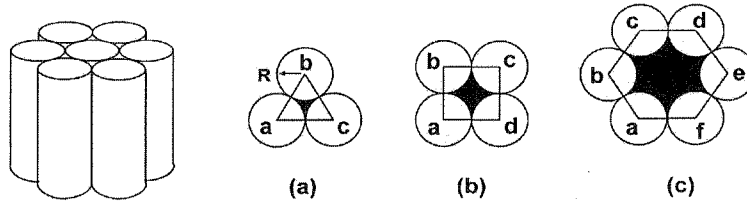


Figure 4. The simplified microstructure of sintered particles and three arrange modes

Now we calculate the equivalent radius r' . In the Mode (b), the area of the black part will be $S_b = (2R)^2 - 4(\pi R^2 / 4) = \pi r'^2$, from which we have

$$r' = \sqrt{4/\pi - 1}R \quad (8)$$

Considering that $\lambda_b = S_b / (2R)^2$, we have

$$r' = \sqrt{4\lambda_b / \pi}R \quad (9)$$

In the Mode (c), the area of the black part will be $S_c = 6\sqrt{3}R^2 - 2\pi R^2 = \pi r'^2$, which will be

$$r' = \sqrt{6\sqrt{3}/\pi - 2}R \quad (10)$$

Considering $\lambda_c = S_c / (6\sqrt{3}R^2)$, we have

$$r' = \sqrt{6\sqrt{3}\lambda_c / \pi}R \quad (11)$$

Let r in Eq. (6) be replaced by r' in Eq. (9) and (11) and considering Eq. (7), we can deduce two relationship formulas

$$H - h = \sqrt{\pi} \sigma \cos \theta / (dR\sqrt{\lambda}) \approx 1.77 \sigma \cos \theta / (dR\sqrt{\lambda}) \quad (12)$$

and
$$H - h = 2\sqrt{\pi} \sigma \cos \theta / (\sqrt{6\sqrt{3}} dR\sqrt{\lambda}) \approx 1.10 \sigma \cos \theta / (dR\sqrt{\lambda}) \quad (13)$$

As above mentioned, only when the ratio of binder is very small (less than 1% by wt.) we can use Eq. (12), in general case we use Eq. (13) to estimate the infiltration height (see Figure 3). For example, if the infiltration material is water, then $\sigma = 7.3 \times 10^{-2} N/m$, $\theta = 0^\circ$ (complete wettability), $d = 1 g/cm^3$, $R = 50 \times 10^{-6} m$, $\lambda = 0.3$. According Eq.(13), the height that water can rise automatically in the sintered sample is about 0.286m. But if using brass alloy (zinc 35% by wt) as infiltration material, we have $\sigma = 0.12 N/m$, $\theta = 0^\circ$ (complete wettability), $d = 6.4 g/cm^3$, $R = 50 \times 10^{-6} m$, $\lambda = 0.3$. Then the infiltration height is about 0.075m, so if the thickness of the sintered sample is over 8cm the top surface may not be infiltrated by the melted alloy. If using epoxy resin AboCast 50-24 for infiltration, we have $\sigma = 4.0 \times 10^{-2} N/m$, $\theta = 30^\circ$ (good wettability), $d = 1.89 g/cm^3$, $R = 50 \times 10^{-6} m$, $\lambda = 0.3$. Then the infiltration height is 0.074m, so if the thickness of the sample is not over 7cm we will use the method (a) shown in Figure 3. But for a mold with a much bigger thickness we may consider other methods or using different infiltration materials. The above calculation results are in better accord with experiments.

CONCLUSIONS

RBPBS is a rapid tooling technique and is suitable for a variety of materials and any complex geometry, and also has the advantages of rapid process and low cost. Some epoxy and phenolic resins with lower viscosity and higher thermal resistance can be used in the RBPBS technique as infiltration materials. Based on the simulation, the parts infiltrated with phenolic resins have enough thermal resistances so that we can use them in injection machining process. According to the deduced infiltration model, we can estimate the needed amount of the resin and their infiltration height in the sintered molds or parts.

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