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Fabrication of Ni-P alloy closed cellular solid containing polymer by the pulse current hot pressing technique

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Phenol resin sphere particles covered with nickel-phosphorus alloy were used for fabricating a metallic cellular solid with a fine structure by using the pulse current hot pressing (PCHP), which is also called spark-plasma-sintering (SPS) technique. During the sintering process, strong electric current pulses were applied on the particles in a die. The particles in the die were sintered in a shorter time and at lower temperature than that of normal sintering methods. The polymer materials inside the cells seem to remain partly after the sintering process. The mechanical properties of the cellular materials containing phenol resins were measured. The influence of the PCHP process on the mechanical properties of the specimens was examined.

1. Introduction

Cellular metals are well-known to have many interesting combinations of mechanical, physical and chemical properties, such as high stiffness with a low weight, thermal and acoustic insulation, damping and energy absorption. Particularly, since the 1980 [1], cellular metals have received more and more attention as structural and functional materials. Subsequently, a series of reports on the fabrication of closed cellular metallic materials have been published on techniques, such as direct gas foaming from liquid metal, powder metallurgy from solid metal particles, vapor deposition, *et al*. A review of the manufacture and applications of the metallic cellular materials was recently reported [2]. The shape, porosity and the size distribution of the cellular structure are different depending on the methods. The porosity of the structure is in the range from 50% up to more than 95%. Generally, the cellular structures of the materials fabricated by the mentioned methods have a common relative macro-scale ranging from hundreds of micrometers to several centimeters. There is a lack of technique to produce a metallic closed cellular material with a finer structure. This situation localized the application of this kind of materials for producing micro-scale components.

Hollow spheres made of Ni, Cu and steel can be used to fabricate cellular structures by bonding, brazing or sintering [3, 4]. Using one of these methods, the size of the hollow spheres is quite controllable. Further more, the spheres can even be assembled in a special lattice structure. It could be used for fabricating a finer cellular structure. Kishimoto *et al*. proposed a method using fine metal-coated polymer-solid spheres (about 10 μm diameter) to fabricate a closed cellular material containing organic materials for lightweight structures by sintering [5]. In his method, the polymer spheres covered by alloy were sintered at a high temperature. After sintering, the metallic coat became joined together, and a cellular structure was formed. Therefore, the polymer materials inside the metallic cellular structure were carbonized by high temperature. However, the polymer material inside the cell benefits the mechanical properties of the cellular structure, such as damping and rigidity. Normal sintering methods always need a high temperature and a longer sintering time. It is impossible to avoid the polymer carbonizing. Thus, a new sintering technique, like SPS, was introduced to fabricate the cellular metal with the polymer still remaining. This material can also be regarded as a composite.

The SPS system for sintering powder particles was based on the idea of using an electric spark supplied by an electric discharge machine in the early 1960 [6]. This system has been developed recently for a sintering method that consists of a pulse electrical discharge step when plasma is generated between the powder particles, accompanied by resistance heating while a uniaxial pressure is applied [7, 8]. However, it has not been clear how the plasma was generated in this process. A reasonable explanation is that a weak plasma at the contact point between the metallic particles was generated in the primary stage of the process [9]. Therefore, the SPS was also called pulse current hot-pressing (PCHP) [10]. Overall, compared with normal sintering methods, such as hot-pressing and hot-isostatic-pressing, the SPS technique possesses advantages such as lower temperature and shorter holding time during the sintering

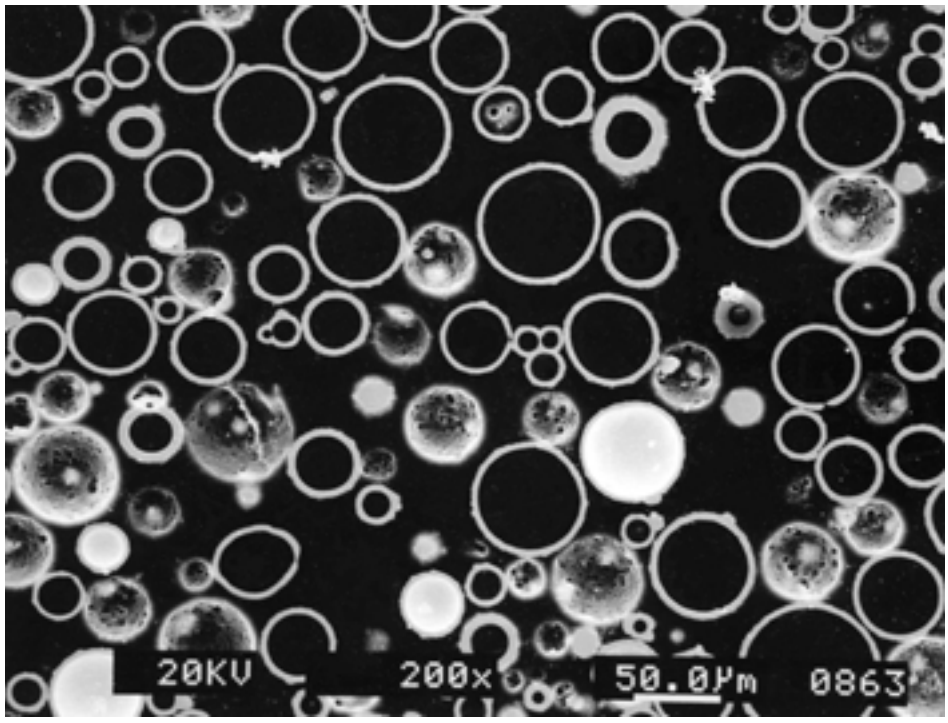

Figure 1 Cross-section of the phenol resin particles coated with Ni-P alloy.

process. It is easier to fabricate some materials or structures by this method than by normal sintering methods.

In a general way, one of the important aims of sintering methods is how to obtain a densified specimen. In this paper, we tried to fined another uttermost sintering method to fabricate the metallic closed cellular structure containing phenol resin by using the PCHP. The mechanical behavior of the material fabricated by this method was studied.

2. Experimental methods

2.1. Metal coated polymer particles

Particles of phenol resin (Kaken, Ltd.) coated with a Ni-P alloy by electroless plating were used in this study. The weight percent of the phosphorus in the alloy was 2.5%. Depending on the particles size, the thickness of the coated Ni-P alloy was distributed in a range between 1.7 and 4.2 μm. The average thickness was about 3.5 μm. A cross-section of the phenol resin particles coated with Ni-P alloy is shown in Fig. 1.

2.2. SPS system

An SPS machine (SPS-515S, Sumitomo Coal Mining Co., Ltd.) was used in the fabrication process. The particles were filled into a ceramic die of 20 mm diameter, and pressure was applied by a pair of graphite punches in a vacuum chamber (Fig. 2). The pressure for keeping the loose particles in contact can be controlled from 2.5 KN to 7.0 KN. A thermocouple was placed at the surface of the punch near the die for detecting the temperature.

During the PCHP procedure, a pulse current ($>$300 A/cm^2) flowed through the particles from the

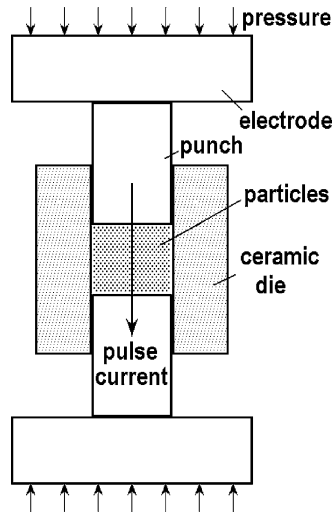

Figure 2 The schematic image of the SPS system.

graphite punches. One pulse persisted for about 2.8–3.0 ms. Pulse voltage varies during the sintering proceeding with the changing resistance due to the degree of the contact conditions between particles. Fig. 3 shows the waves of a series of the electric current pulses passing through the particles generated by the SPS machine. When the voltage becomes large enough, the current starts to flow. If a strong enough pulse current is applied to the particles, a very efficient heating and even arc discharges were generated at the contact points between the particles. Then atoms at the surface near the contact points were activated and the particles can join in a short time. As this heating effect was created at the particle surfaces, the average temperature of a particle will not become as high as the local temperature at the particle's surface. Therefore the centers of the particles can maintain a lower temperature. It was possible

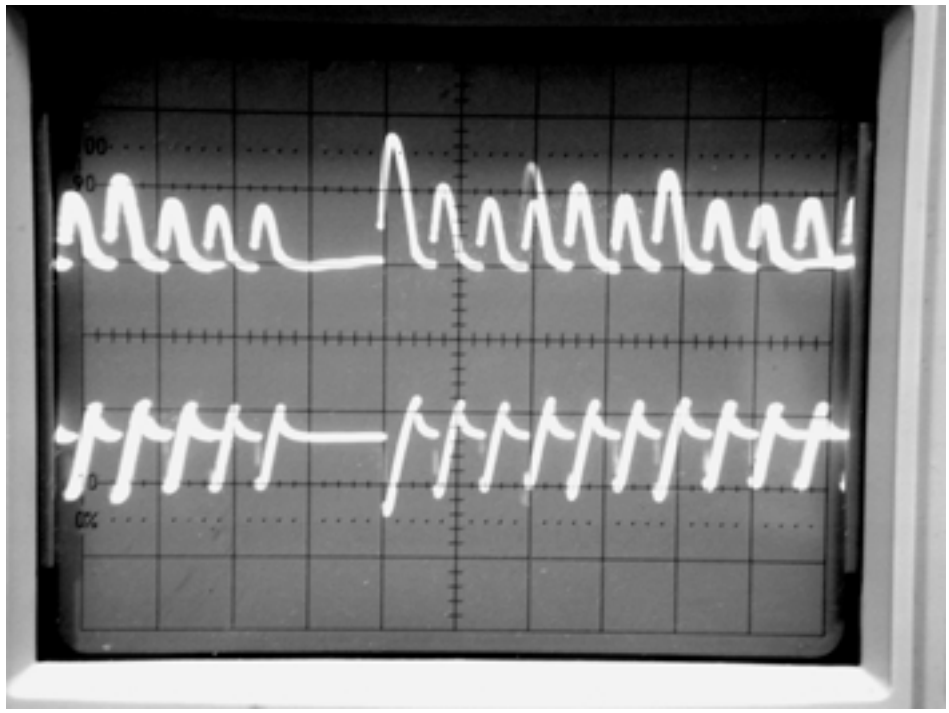

Figure 3 The waveforms of a series of the current pulses in the PCHP process. (The upper waveform is voltage, the lower waveform is current, and the unit of scanning time is 5 ms/division.)

to keep the polymer remaining after the sintering process.

2.3. Structure and mechanical properties

The microstructure of the specimens was observed by a scanning electron microscope (SEM). The compressive properties of the specimens fabricated with different process parameters were determined.

3. Experimental tesults

3.1. Size distribution of the particles

The size of the phenol resin particles coated with Ni-P alloy were distributed in a range of 8 to 100 μm. The size distribution of the particles used in this paper is shown in Fig. 4. Assuming that all particles after sintering were deformed into a polyhedral shape. The theoretical volume percent of the alloy in the sintered material is about 38.6%.

3.2. Sintering process

From the viewpoint of the particle inside the die, when a current pulse passes through the sample, the temperature at the contact point between the particles becomes very high while the temperature is rather low in the center of the particle. But it will become homogeneous soon. The average temperature of this particle is quite small depending on the particle size and contact conditions. However, a too long heating time can still elevate the temperature in the center of the particle to a very high level. In order to protect the contained materials from overheating, the actuation time of the PCHP should also be controlled. A large current, a short actuation time and a multiple-action program were used. For

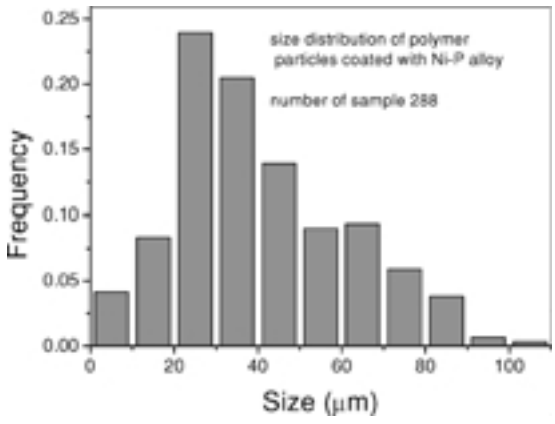

Figure 4 The size distribution of the phenol resin particles coated with Ni-Pa as measured by optical microscope.

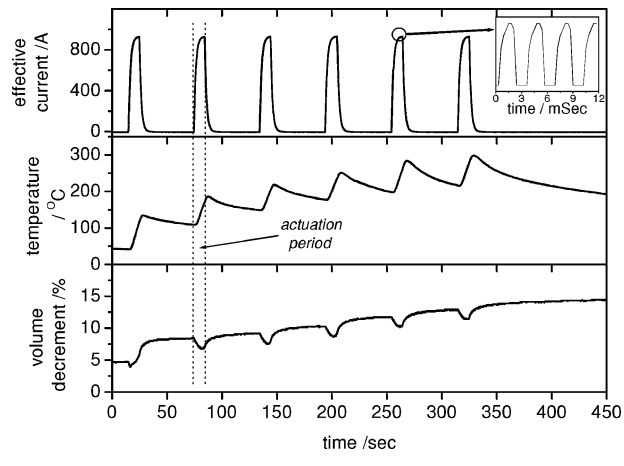

Figure 5 Typical sintering process using the SPS system.

cooling the particles, the pulse current was turned off after a few seconds of heating and then the current was applied again. The temperature of the punches detected by a thermocouple was controlled below 300°C during the sintering. The typical PCHP processing for the fabrication of the cellular material is shown in Fig. 5. This figure shows the affective current, temperature of die and volume decrement during the sintering. A uniaxial pressure applied on the particles inside the die is fixed at 2.5 KN. When the pulse current was applied, the temperature increased steeply. At the same time, the volume of the particles inside the die expanded. Once the actuation of the pulse current stopped, the temperature of the specimen soon decreased gradually and the expanded volume contracted quickly. Anyway, the temperature and the shrinkage of the specimen increased with the actuation time. Compared with the volume of the packed particles before sintering, the volume of the specimen decreased by about 15% to 20% after the process.

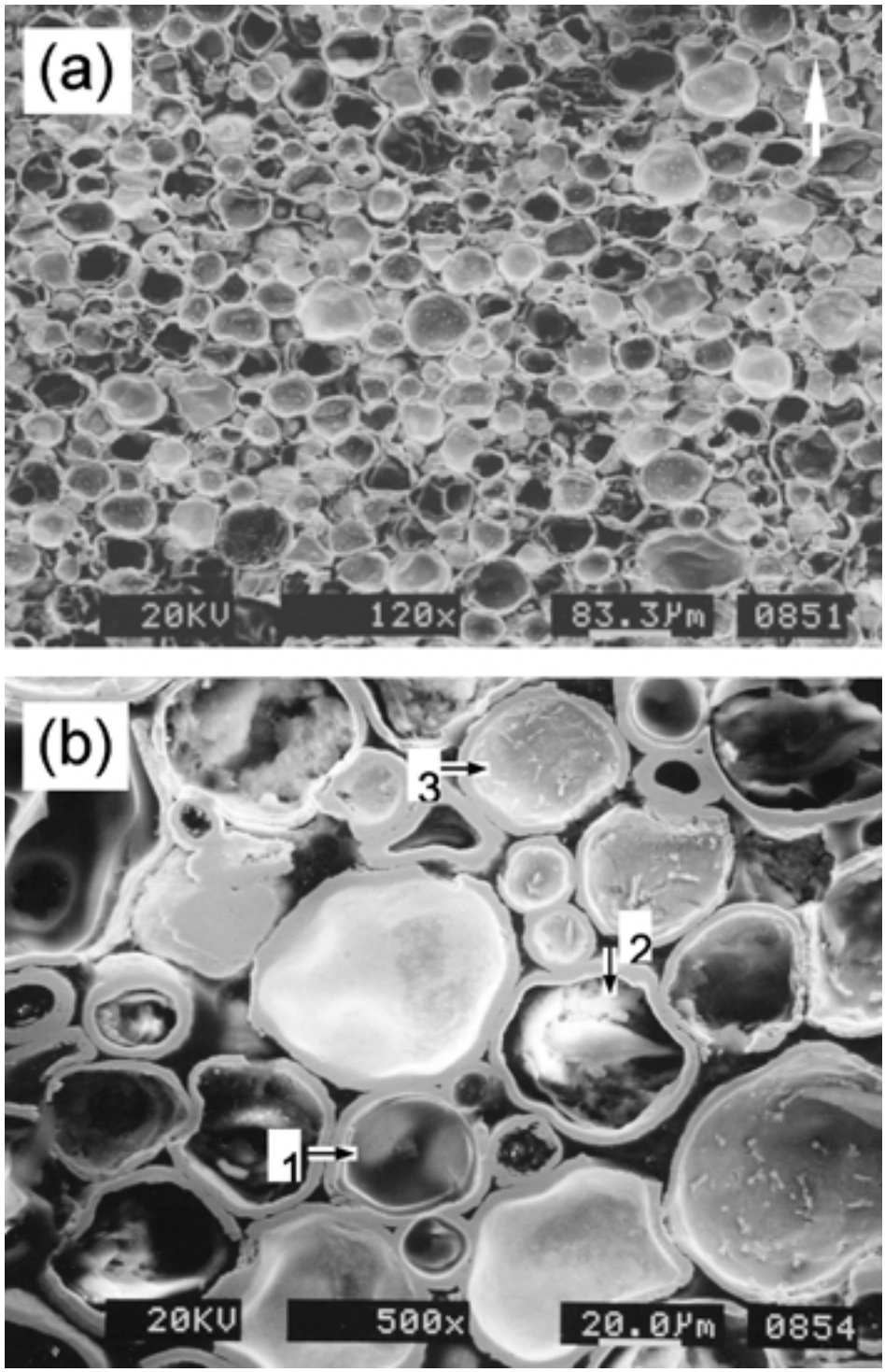

Figure 6 The structural SEM images of a specimen. (The direction of the current and the pressure are identified by the white arrow.) (a) Low magnification: This image shows that the cells were flattened by the pressure. (b) Middle magnification. In this image, 1 shows the remaining phenol resin, 2 shows the half-carbonized phenol resin, and 3 shows the complete carbonized phenol resin. (c) High magnification. This image shows that the sizes of the joints between particles are direction-dependent. The smooth inner wall of the left cell indicated that the polymer or partly carbonized polymer was removed in the process of polishing. (*Continued*)

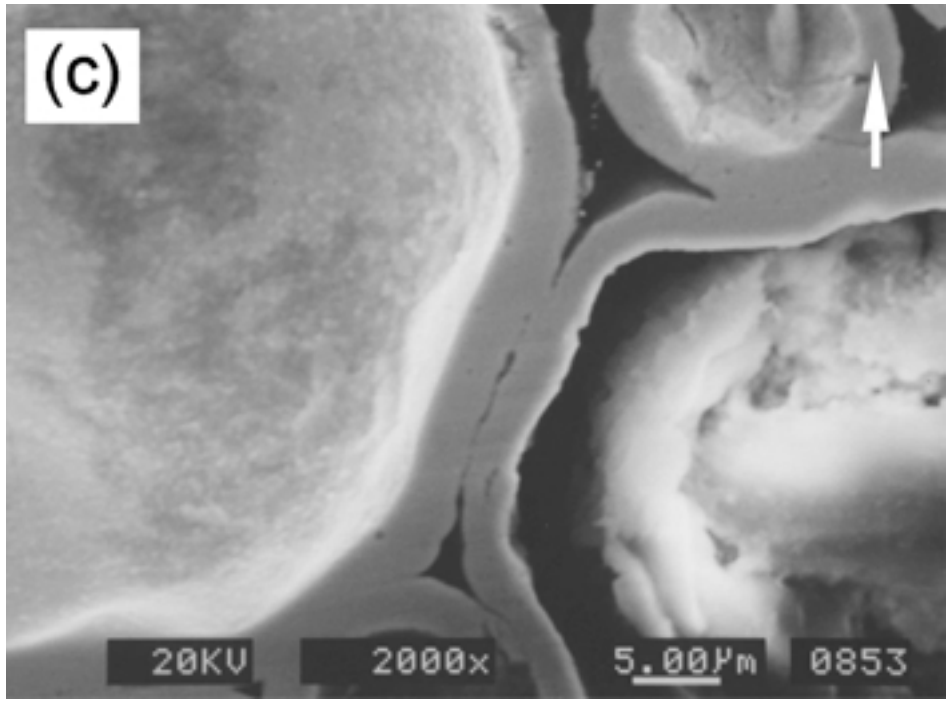

Figure 6 (*Continued*).

3.3. Cellular structure

Fig. 6a, b and c show the SEM images of a specimen. From these images, it was found that the cells in the specimen were deformed into polyhedral shapes and were flattened in a direction perpendicular to the loading axis. From the closer image (Fig. 6c), some parts of the interface between two particles can be found to be joined. Depending on the position of the interface between the particles, the condition of the each joint was different. The joints normal to the current direction were better than those parallel to the current direction. From the indicated parts shown in Fig. 6b, it can be observed that some of the phenol resin in the cells was burned, some was carbonized and quite a bit of the phenol resin remaining inside the cells.

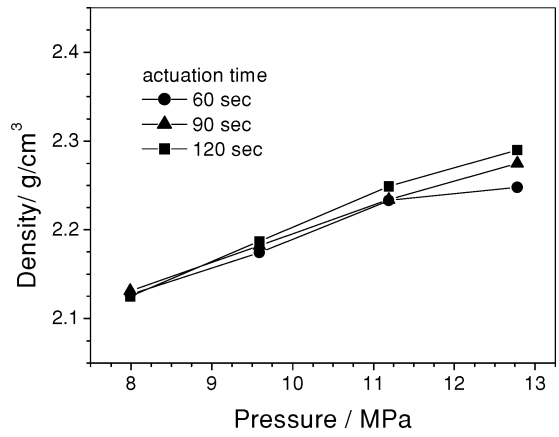

Figure 7 The relationship between the densities of the specimens and the applied pressure with different the heating time.

3.4. Density change

Normally, the densities of the specimens are about 2.10–2.30 g/cm^3. The densities of this material were thought to be varied by changing the actuation time and pressure. Fig. 7 shows the densities of the specimens as functions of the heating time and the applied pressure.

Two aspects, the deformation of the particles and the carbonization of the phenol resin, affect the density control. Fig. 7 also shows that the pressure is a dominant element in controlling the density of the specimen in this PCHP process.

3.5. Compression behavior

The compressive tests were carried out at room temperature. Fig. 8a shows stress-strain curves of the cellular specimens. For those specimens fabricated in a shorter actuation time, it was found that the stresses dropped down suddenly when the strains reached the collapse points. On the contrary, the specimens fabricated in a longer actuation time showed a plateau region in the stress-strain curve. The plateau regions of the stress-strain curves increased with the increasing of actuation time. The strength of the specimens was thought to be dependent on the pulse current actuation time. Fig. 8b shows a loading-unloading loop of during the compressive test. The first loading reached a strain of about 3.5%, near its yield strain. After unloading, the strain of the specimen returned to zero. That is to say, up to about 3.5% strain, the specimens were deformed elastically.

In general, the deformation behavior of the cellular solids under loading involve three types, elastomeric, plastic and brittle. At low strains (<4%), the cellular structure deforms in an elastic way. Comparing with the collapse behavior of the mentioned specimens shown in Fig. 8a, specimen A and B were brittle, C was better and

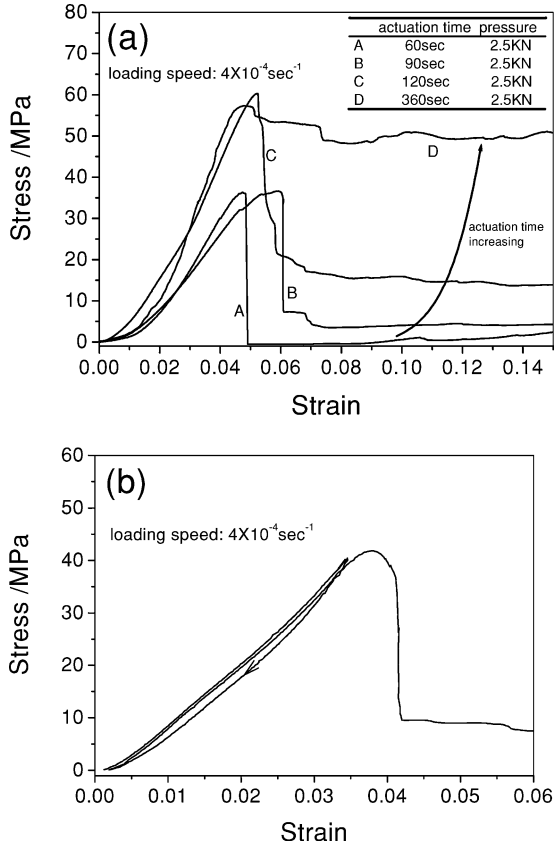

Figure 8 Mechanical response of the cellular specimens: (a) The stress-strain curves of four specimens fabricated with a different PCHP process and (b) A loading-unloading loop of a specimen.

D was the toughest. Specimens C and D possessed the possibility that the energy absorption is much greater than that of A or B. Normally, they collapsed at a strain of about 3.5–4.5% and a stress of 30–60 MPa. For the specimen fabricated by a longer actuation time, the phenomenon of collapse became unremarkable at the yield point, and the specimen deformed plastically instead. However, the amount of polymer inside the specimen fabricated with a longer time was less.

The relationship between the strength and the parameters of the PCHP process is shown in Fig. 9. The actuation time of PCHP was found to affect the strength more than the pressure. Because the strength increased with the increasing actuation time. However, too long time (for example, >300 sec) in the PCHP process cannot achieve a much better strength. The relationship between the yield points and the parameters of the PCHP process is shown in Fig. 10.

The relationship between Young's modulus and the actuation time is shown in Fig. 11a, and the relationship between the Young's modulus and the pressure during the process is shown in Fig. 11b. It was found that Young's modulus increased with the actuation time and the pressure in the PCHP process.

For a specimen fabricated with a longer actuation time (>120 sec), there is a long plastic period (strain 5–20%) accompanying the growth of the strain during the compression test. SEM photographs of the surface of a specimen (actuation time, 360 sec; pressure, 2.5 KN) and the fractures surfaces after a compression of 25% are shown in Fig. 12a, b, and c. Fig. 12a

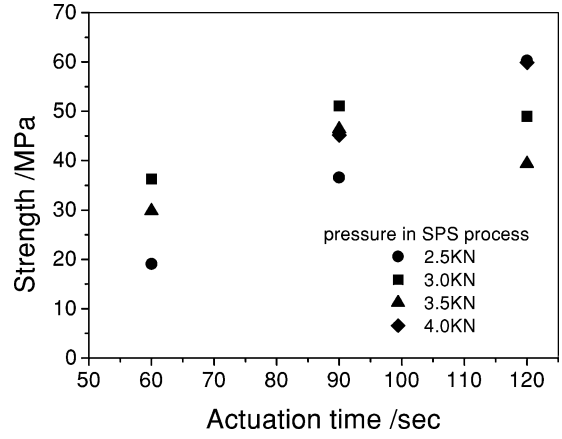

Figure 9 Relationship between strength and PCHP process.

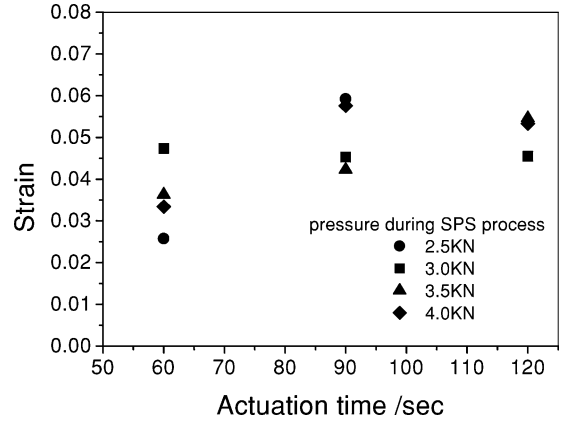

Figure 10 Relationship between yield point and PCHP process.

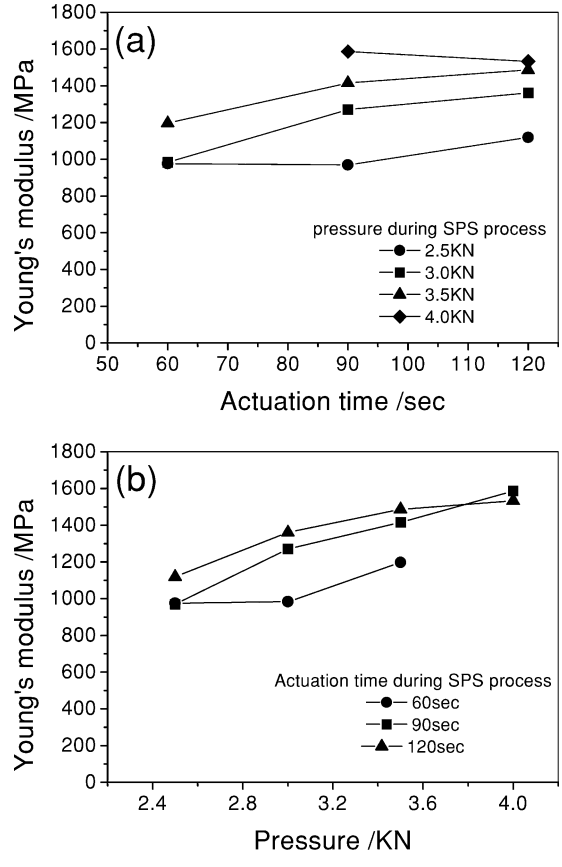

Figure 11 Relationship between PCHP process and Young's modulus.

shows that the cells at the top surface were planished. In this photo, a crack propagation in the cells in this surface from the right to the left can be found. It looks that the crack starts from several broken cells. Fig. 12b shows a fracture surface normal to the pressure direction. Half of the cells were broken and the other half retained their shape. Fig. 12c shows a fracture surface in the direction parallel to the stress axis. Some big deformed cells and some broken cells were observed.

4. Discussions

4.1. Fabrication of the cellular structure

It is not clarified how the plasma generates between metallic particles in the die and what role the plasma plays in the sintering process. Tokita gave some possible effects which could be caused by the plasma, including surface activation and diffusion speeding [12]. When a strong current pulse was applied to the particles, some phenomena will occur, including electrical discharge, resistance heating (Joule heating) and mechanical pressure. For the insulator particles, it is reasonable that plasma was generated when large current pulses pass through. For conducting particles, it is difficult to distinguish whether or not the plasma was generated. No matter whether or not discharge occurred, it should be thought that when a pulse current passes through a narrow gap or the contact point between the particles, a local high temperature is generated momentarily.

The sintering process was controlled by the thermal diffusion of the particles. In the PCHP process, both the thermal diffusion and the discharge plasma will act on the particles. They supplied both surface cleaning and high efficiency heating action. For the cleaning effect, positive ions were generated and the oxide layer of the particles was broken [11]. This cleaning effect can increase with the increasing of the energy of the atoms at the surface of the particles. Then the barrier to surface diffusion relatively decreases. For the heating effect, the diffusion process was accelerated greatly by the efficient heating created at the contact regions between the particles. This method was less influenced by the container coated by the alloy. Therefore, it is possible to realize a general method for the metallic cellular closed materials containing different materials from that of all walls.

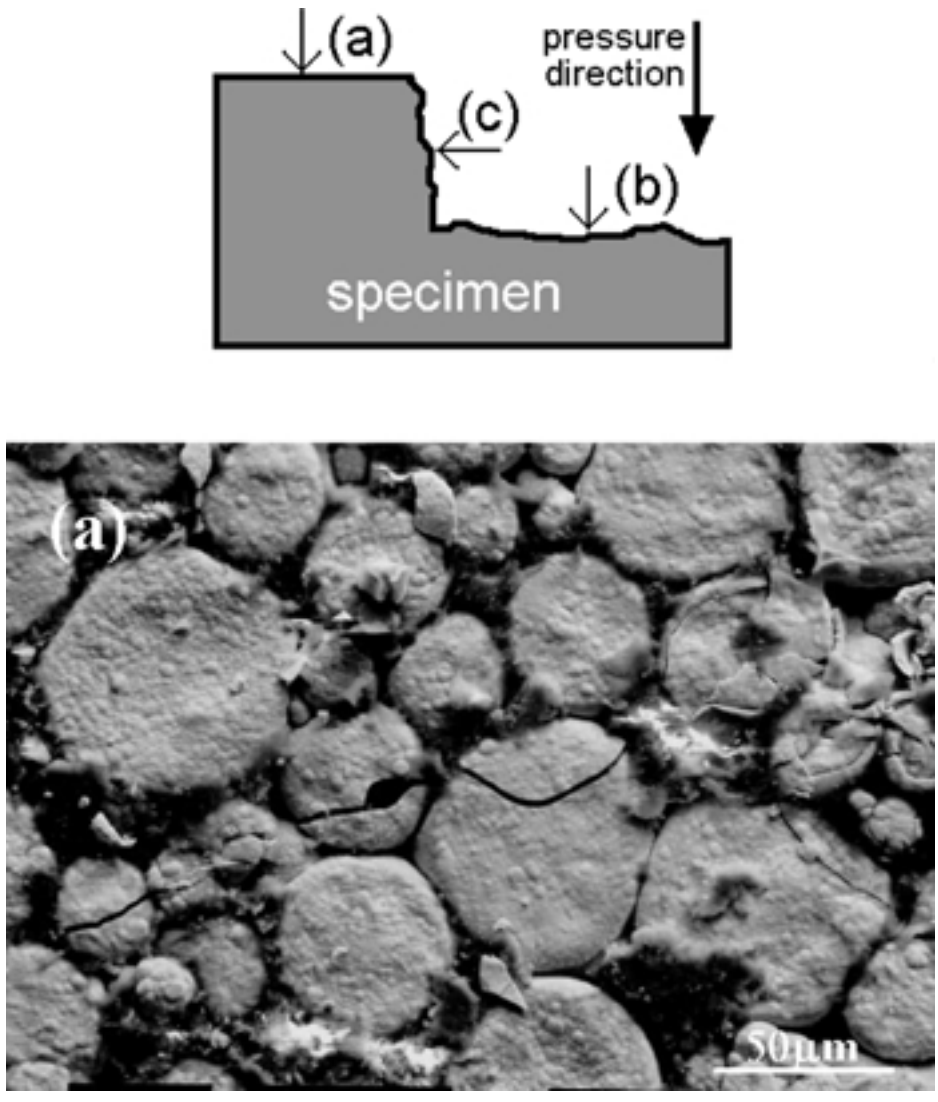

Figure 12 SEM images of the specimen after compression: (a) Top surface of the specimen, (b) fracture surface normal to the loading direction, and (c) fracture surface parallel to the loading direction. (*Continued*)

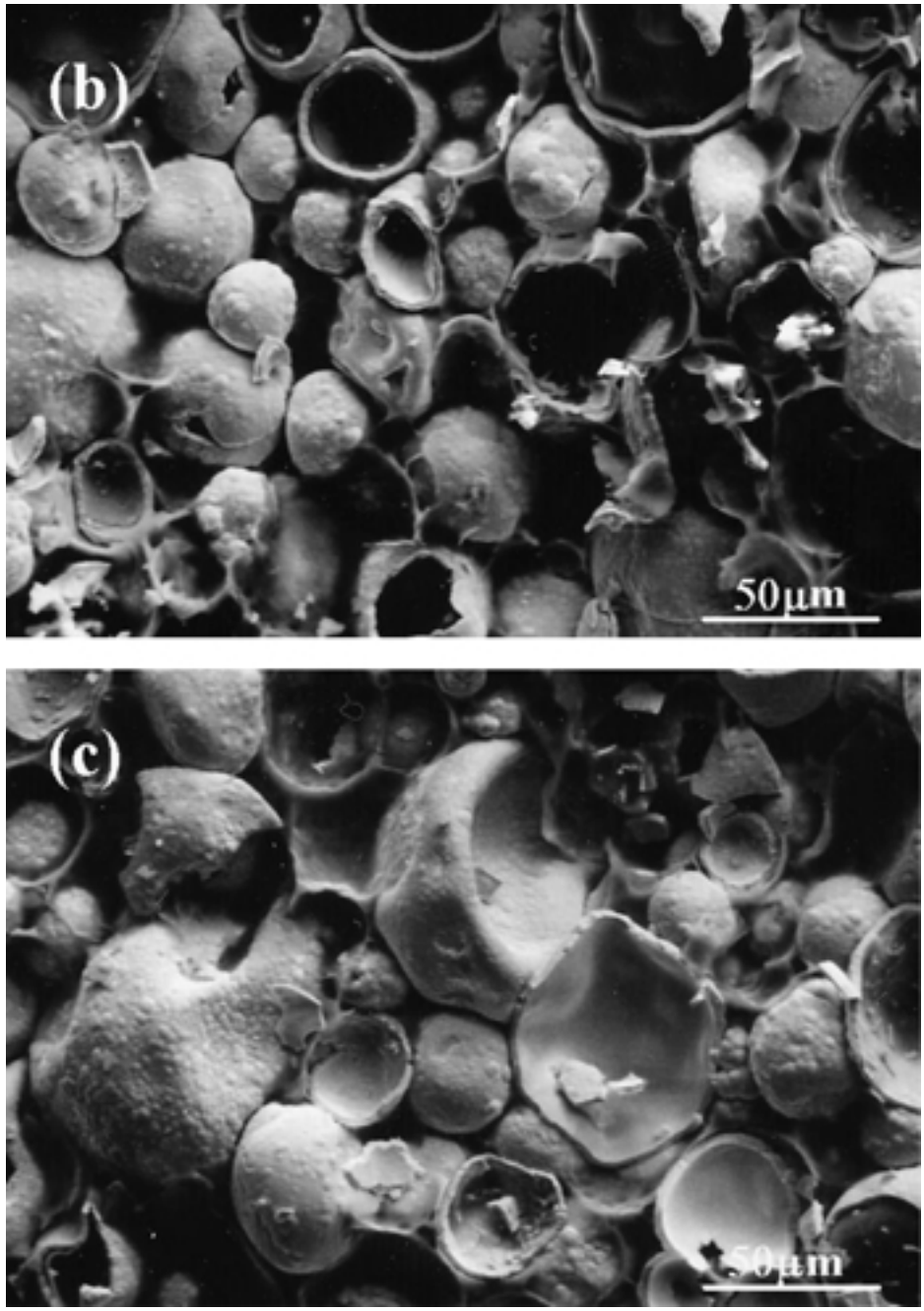

Figure 12 (*Continued*).

4.2. Strength of the joints

Depending on the position of the contact interface between the particles, the current was different. At the contact that lies in the direction of the current, the current is larger than that against the direction of the current. This will lead to a temperature distribution at the surface of a particle. Because the diffusion process is controlled by the temperature, the sizes of the joints between particles were different depending on the direction. Considering the effect of the pressure, the situation will be more complex. However, it should the strength of the joint between particles is direction-dependent. From Fig. 6a, b and c, the joints parallel to the current direction in the PCHP process is stronger than that normal to the current. Fig. 13 shows a schematic image of the joints.

For the cellular materials are always used under a pressure, it is very important to study their compression behavior. Two important aspects can be thought to influence the compression properties. One is the compression strength of the particles themselves, and the other is the strength of the contacted areas between particles.

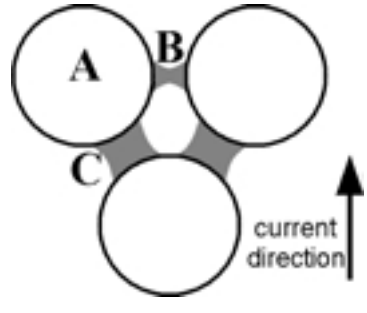

Figure 13 The joints are different with the direction of the PCHP current. (Loading direction in the PCHP process is parallel to the current direction.)

For the first aspect, the coating condition and how much polymers which remains inside the cells after sintering determines the strength of the particles. For the second aspect, there is a direct factor, the strength of the joints in different parts were different. In Fig. 13, if the particle A mainly undergoes the compression stress, a relatively lower compressive or tensile stress occurs at joint B, and a compressive stress and sometimes a small shear stress occurs at joint C.

4.3. Fracture process

To protect the phenol resin inside the alloy from high temperature, the sintering time must be shortened as much as possible. Normally, the joints between particles are vulnerable areas in this structure. During the PCHP process, the direction of the pressure in the PCHP process is normal to the joint B of Fig. 13. Therefore, joint B seems to be weaker than joint C. A cleavage fracture always extends along the joints. It is interesting that the fractures occurred more frequently through the particles rather than along the boundary. Therefore, compared with the strength of all walls, the joints were not so weak. Further work is needed to find a balance between the PCHP intensity and the mechanical strength.

Because there is a size distribution of the particles in this material, a larger particle is easier to deform under forces than a smaller one. The particles may sometimes be missed in the packing process or be broken in the PCHP process. The adjacent particles bear a larger stress concentration, and finally, cracks are generated. Small particles are hard to deform and can enter the interstices between the large particles. This may also cause deformations of the adjacent particles. These defects may become the sources of the cracks and can affect the pattern of failure under pressure.

5. Conclusions

A closed cellular Ni-P alloy was fabricated by the PCHP method by using the SPS technique. The SEM images of the structure showed that part of the phenol resin remained inside the Ni-P cells after the sintering.

The results of the compressive tests showed that the specimens fabricated in a shorter actuation time are brittle and the specimens fabricated in a longer actuation time are tough. The plateau regions of the stress-strain curves during the compressive tests increased with increasing actuation time. The yield point of this material occurs at a strain range about 4.0–6.0%. The compressive strength and the collapse strain increase with the increasing actuation time in the PCHP process. And Young's modulus increases with the increasing of pressure in the PCHP process. A cleavage fracture always occurs along the loading direction during the compressive test.

Acknowledgement

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References

1. G. J. DAVIES and Z. SHU, *J. Mater. Sci.* **18** (1983) 1899.
2. J. BANHART, *Prog. Mater. Sci.* **46** (2001) 559.
3. K. M. HURYSZ, J. L. CLARK, A. R. NAGEL, C. U. HARDWIKKE, K. J. LEE, J. K. COCHRAN and T. H. SANDERS, *Mater. Res. Soc. Symp. Proc.* **521** (1998) 191, edited by D. S. Schwartz, D. S. Shih, A. G. Evans and H. N. G. Wadley.
4. O. ANDERSEN, U. WAAG, L. SCHNEIDER, G. STEPHANI and B. KIEBACK, *Adv. Eng. Mater.* **2** (2000) 192.
5. S. KISHIMOTO and N. SHINYA, *Mater. Des.* **21** (2000) 575.
6. K. INOUE, US Patent no. 3241956 (1966), 3250892 (1966).
7. S. H. RISBUD and J. R. GROZA, *Philosophical Magazine* B **69**(3) (1994) 525.
8. Special Issue for SPS Method, *J. Jpn Soc. Powder and Powder Metall.* **47**(3) (2000).
9. M. OMORI, *Mater. Sci. & Eng.* A **287** (2000) 183.
10. M. TOKITA, *J. Soc. Powder Tech. (Jpn)* **30** (1993) 790.

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