Study on fabrication and mechanism in of porous metals by spark plasma sintering

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Abstract Porous stainless steel with regular spherical particles were fabricated by spark plasma sintering (SPS) and compared with those obtained by conventional hot pressing (HP). The effects of the parameters during sintering processes on properties, such as porosity and compressive strength, were investigated. Microstructure studies showed that the regular spherical stainless steel particle could form porous ingots with regular pores in the way of close sphere package. Results indicated that the compressive properties of the SPS samples were superior to those of the HP samples. The study on relative diffusion coefficient in SPS and HP specimens indicated that SPS enhanced neck growth and accelerated the atom diffusion. Porous metals could be superfastly prepared by SPS under the conditions of higher heating rate, shorter holding time and lower sintering temperature.

Introduction

Porous metals with both functional and structural properties have been developing rapidly in recent years. They have been widely applied in many fields of engineering (e.g. the chemical, metallurgical, and medical industries, etc.) [1]. Sintering of metal powder is the most effective route to meet the various design and performance characteristics of porous parts—high strength, heat and corrosion resistance, durability, shock resistance, good permeability and controlled porosity and pore-size. The higher porosity is favored by lager particles size, lower sintering temperature and shorter sintering times [2]. However, the influences on strength proved to be just the opposite. Spark plasma sintering (SPS) is a newly developed process, which makes possible sintering and bonding at low temperature and short time by charging the intervals between powder particles with electrical energy and effectively applying a high temperature spark plasma generated momentarily [3]. SPS has been used for the sintering of Functionally graded materials (FGM), hard alloys, transparent ceramics, functional ceramics, etc. [4, 5]. SPS is capable of sintering at lower sintering temperature and shorter time compared with hot pressing (HP) sintering. Because of these advantages, SPS is suggested to be effective on the fabrication of porous metals.

In this paper the porous metals were manufactured in short processing time by SPS process and effectiveness of SPS for the atom diffusion in the sintering neck was investigated.

Experimental procedure

Raw materials used in this study were regular spherical particles of stainless steel. There were four classes classified by diameters of those particles, 0.5, 1, 2 and 3 mm. The sized spherical particles were put into a graphite mold and sintered using a spark plasma sintering apparatus (model SPS-1050, Sumi-tomo Coal

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Mining Co. Ltd. Japan). Figure 1 showed the schematic diagram of SPS device employed in the experiments.
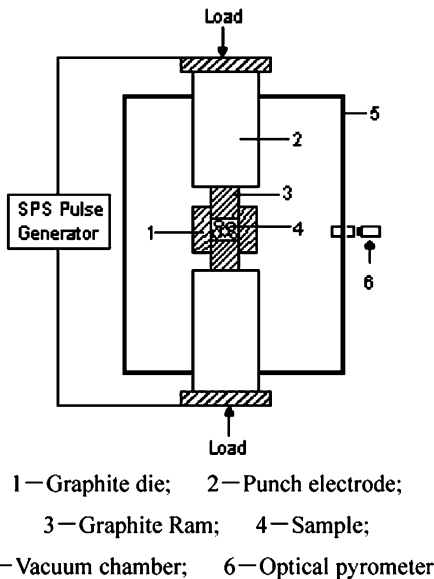
SPS processing was carried out in a vacuum (≤ 6 Pa) by heating to the required temperature (1273–1373 K) at heating rate of 100 K/min, with 5–20 min of holding time and an applied pressure of 48 kPa as shown in Fig. 2. Temperature was measured by optical pyrometer. For comparison, the same particles were compacted using a hot pressing (HP) procedure under the same condition.
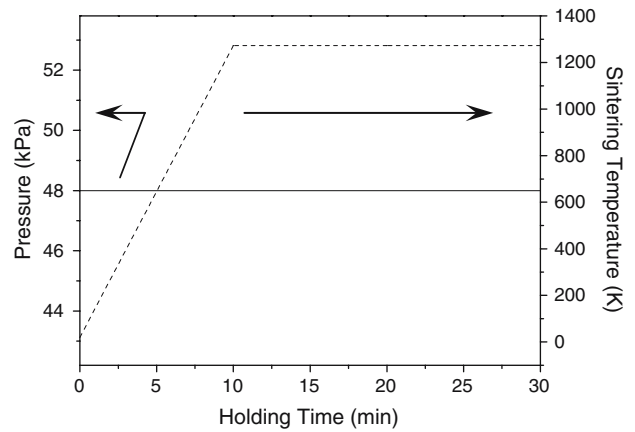
Results and discussion

Porosity measurement

Apparent porosity measurement was based on Archimedean principal method. Figure 3 shows that the porous metals fabricated via SPS exhibited an enhanced densification in comparison with HP. To attain the similar porosity, the SPS temperature is lower than the HP temperature, and the holding time of SPS is much shorter than that of HP.

The changes in the relative porosity of the spark plasma sintered specimens with holding time are shown in Fig. 4. Apparent porosity decreased with increasing holding time from 5 min to 20 min. When the specimens were sintered at the same condition, porosity of the specimens from 0.5 mm particles was lower than that of the specimens from 1 mm particles. Effect of holding
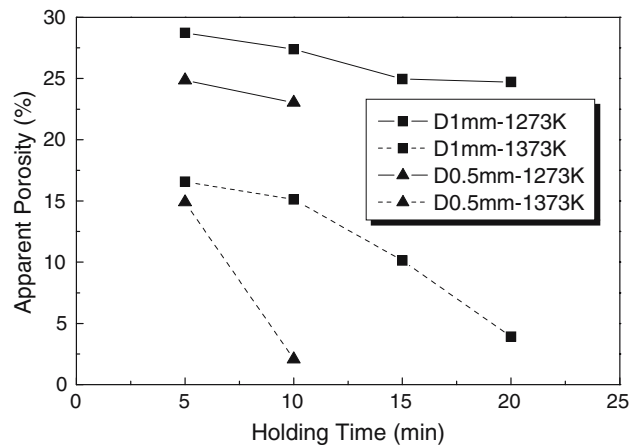

Fig. 2 Pattern of sintering temperature and pressure with holding time during the SPS process
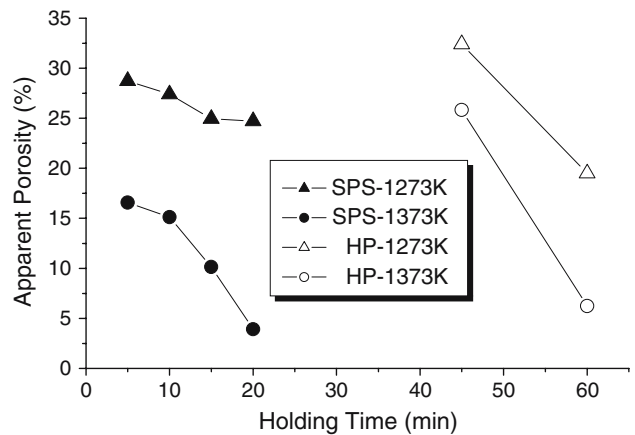
Fig. 3 Apparent porosity of the specimens from 1 mm particles under different sintering condition

Fig. 1 Schematic of the apparatus used for the spark plasma sintering

Fig. 4 Apparent porosity of SPS specimens as a function of holding time

time on porosity tends bigger with increasing sintering temperature and decreasing particle size.

Calculation of diffusion coefficients

In order to compare the diffusion coefficient of SPS process with that of HP process, a sintering model, which considered the fact of this experiment, was established based on the existent theories about sintering as shown in Fig. 5.
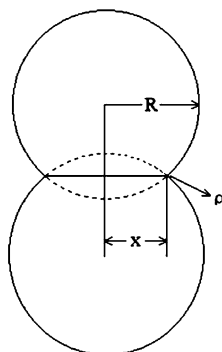
For the sintering process of spherical particles, the relationship between sintering temperature and holding time can be approximatively expressed by Kuczynski's sintering model [6]; that is:

$$t = \frac{R^3 \xi^5 KT}{80\sigma\delta^3 D} \qquad (1)$$

where t is the sintering holding time; R the radius of raw particles; ξ the relative sintering neck $(\frac{x}{R})$; x the radius of sintering neck; D the self-diffusion coefficient; σ the surface tension coefficient, $\sigma_{Fe} = 1.880$ N/m; δ the lattice parameter, $\delta_{Fe} = 3.640 \times 10^{-10}$ m; K the Boltzmann's constant, K = 1.38×10^{-23} J/K; T the absolute sintering temperature.

During sintering, the growth of sintering neck was enhanced. Figure 5 shows the double-sphere model of the earlier sintering process [7].

The distance between the centers of the two spheres decreased with the growing of the sintering neck. Suppose the radius of sintering neck formed in earlier sintering process was small, and there was no change on the radius of particles, the linear shrinkage [8] can be calculated by the geometrical relations on Figure 5.

$$\frac{\Delta l}{l_0} = -\frac{x^2}{4R^2} \qquad (2)$$

$$\frac{\Delta V}{V_0} = 3 \cdot \frac{\Delta l}{l_0} \qquad (3)$$

Under the assumption that all the specimens put into the graphite die showed similar packing configuration, the relationship between the volume and porosity can be described by these formulas.

$$V_b = \frac{V_S}{1 - \varepsilon_b} \qquad (4)$$

$$V_a = \frac{V_S}{1 - \varepsilon_a} \qquad (5)$$

where ε_b the porosity of the specimens before sintering; ε_a the porosity of the specimens after sintering; V_b the volume of the specimens before sintering; V_a the volume of the specimens after sintering; V_S the total volume of all the solid particles, a changeless constant ; and the other symbols mean the same as Eq. (2).

From the expression pattern of Eqs. (2), (3), (4) and (5), the value of $\frac{x}{R}$ can be calculated.

$$\frac{x}{R} \approx \sqrt{\frac{4(\varepsilon_b - \varepsilon_a)}{3(1 - \varepsilon_a)}} \qquad (6)$$

Substituting the data of $\frac{x}{R}$ into equation (1) to reckon the value of diffusion coefficients under different sintering conditions. The results are shown in Table 1.

According to Table 1, diffusion coefficients increase with increasing sintering temperature. At the same

ρ - the curvature radius of sintering neck;

R –the radius of raw particles;

x — the radius of sintering neck;

Fig. 5 Double-sphere sintering models

Table 1 Diffusion coefficients under different sintering conditions

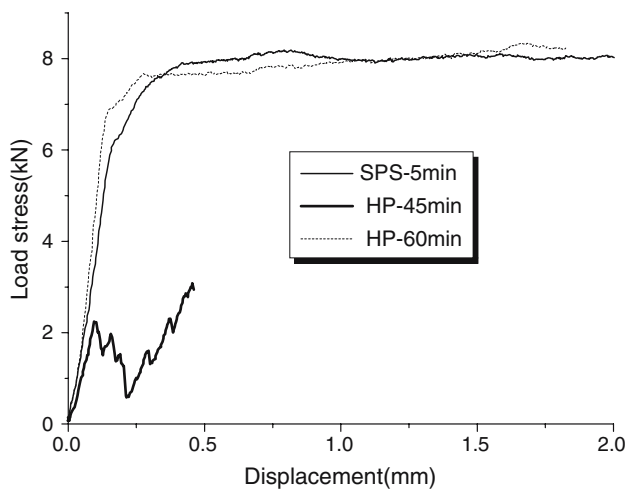| Sintering technique	Sintering temperature (K)	Holding time (s)	$\frac{x}{R}$	D($10^{-8}m^2 \cdot s^{-1}$)
SPS	1273	300	0.595	3.564
		600	0.610	
		900	0.635	
		1200	0.637	
	1373	300	0.705	9.239
		600	0.715	
		900	0.750	
		1200	0.780	
HP	1273	2700	0.548	1.111
		3600	0.683	
	1373	2700	0.626	2.142
		3600	0.767	

sintering temperature, the diffusion coefficient during the SPS process is larger than that of HP, so atom diffusion under SPS is quicker than under HP. The reason might be that there are other drives in the process of SPS, besides the atom diffusion drive caused by conditions under radiation heating, which are caused by electric and magnetic fields and regional temperature grads under pulse current. As a result, the chemical potential energy grade of SPS process is lager than that of HP process. Based on the thermodynamic expression of Fick's theory on atom diffusion, the diffusion flux under SPS is larger than that under HP, which makes atom diffusion quicker under SPS.
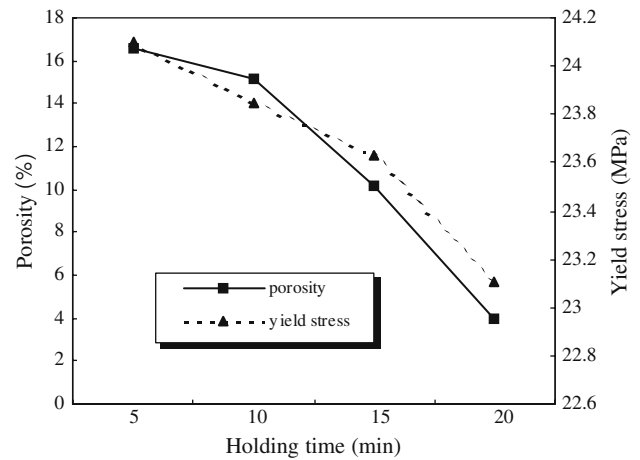
Compression tests

The specimens were cylindrical with nominal dimensions of 20 mm in length and 10 mm in diameter for compression tests. All of the tests were performed at room temperature. The tests were performed at a ramp rate about 2.0 mm/min.

Figure 6 shows the compressive load stress–displacement curve of the SPS specimens and the HP specimens. To attain the similar max load stress, the holding time of SPS process was much shorter than HP.

Figure 7 shows a change in porosity and yield stress of the SPS specimens with holding time, which was changed from 5 min to 20 min. It can reveal that the yield stress increased with the increase of the porosity. As can be seen in figure, longer holding time brought a lower porosity 3.92% (20 min) compare with 16.57% (5 min) in spite of same sintering temperatures and yield stresses from 23.102 MPa (20 min) to 24.105 MPa

Fig. 7 Change of porosity and yield stress as a function of holding time (Particle size: D = 1 mm; SPS Temperature: 1373 K; SPS Pressure: 48 kPa)

(5 min). This is considered that notable increase in porosity (322.7%) compare with tiny change of yield stress (4.34%) results from greater effect of holding time on porosity than on yield stress. It is also the evidence that SPS is capable of sintering at shorter sintering holding time.

Microscopy observation

Some of the sintered materials were cross-sectioned perpendicular to the flat surface, polished and examined by scanning electron microscopy (SEM). Figure 8 shows the result of SEM analysis of sintering neck of the SPS specimens at the sintering temperature of 1000°C. As can be seen, there are necks formed at the contacts between particles. The forms of the pores are regular.

Figure 9 shows the spark occurs during the SPS sintering. It is also one of the evidences that the pulse electric current in SPS process makes the particles surface active in sintering. Reference [9] believed that the spark effect is one of the reasons for the sintering activity.

Fig. 6 Compressive load stress–displacement curve under different heating mode (Particle size: D = 1 mm; SPS Temperature: 1373 K; SPS Pressure: 48 kPa)

Conclusion

(1) To attain the similar porosity, the sintering temperature of SPS process is lower than the HP process, and the holding time of SPS is shorter than HP. Effect of holding time on porosity tends bigger with increasing sintering temperature and decreasing particle size.

Fig. 8 SEM of sintering neck (SPS Temperature: 1373 K; SPS Pressure: 48 kPa; Holding time: 10 min)

(a)D=1mm (b)D=3mm
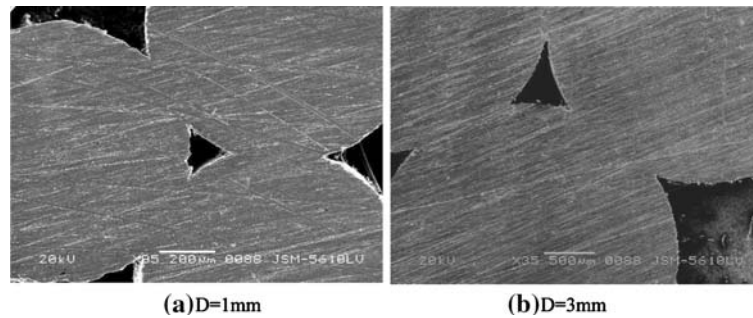
Fig. 9 Spark occurs during sintering (SEM) (SPS Temperature: 1373 K; SPS Pressure: 48 kPa; Holding time: 10 min)
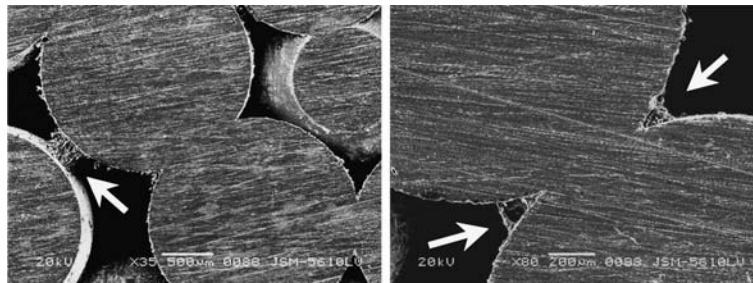
(2) The diffusion coefficient increased with the increasing of the sintering temperature. The diffusion coefficient during the SPS process are larger than that of HP, so atom diffusion under SPS is quicker than under HP.

(3) To attain the similar max load stress, the holding time of SPS process is shorter than that of HP. In addition, there is notable increase in porosity compared with tiny change of yield stress, with the variations of holding time in SPS.

(4) Spark occurs during the SPS sintering, which might be one of the reasons for the sintering activity.

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