

Effects of heating history on sintering properties of nickel powder compacts

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Abstract

The effects of heating history on the sinterability of nickel powder compacts as a model material are examined from a view point of driving force and flow resistance, that is, the sintering stress and viscosity. Sinter-compression tests were conducted at different constant temperatures for cylindrical specimens, which underwent one-step or two-step heating. In the two-step heating, the specimens were heated up to a higher temperature and cooled down to the test temperatures. After the tests, the microstructure of each specimen was examined and compared with the change in sintering stress and viscosity. For the whole range of test temperatures, viscosity was increased by the two-step heating, which can be explained by the effects of time-hardening. On the other hand, for the lower range of test temperatures, the sintering stress was decreased by the two-step heating. This may be a result of the formation of large pores due to inhomogeneous shrinkage in the unstable state of the powder with small contact in the initial stage of sintering.

Key words : Sintering stress, Viscosity, Two step sintering, Sinter compression test, Pore

1. Introduction

Sintering as a manufacturing process is used to fabricate many things including ceramic parts, metallic machine components of complex shape, and various functional devices with complicated structures. In order to make the sintering process more effective, however, issues such as shrinkage accompanied with densification, and microstructural evolution in elevated temperatures, should be known and controlled to promote high dimensional accuracy as well as good material properties. The shrinkage as well as the microstructure of sintered materials is sometimes significantly affected by the heating history. In the two-step sintering of nanocrystalline ceramic powder, for example, grain growth is suppressed and densification is promoted, where the triple-point dihedral angle of grain or grain boundary/pore junctions is considered to be changed into a stable state by pre-firing (Chen and Wang, 2000; Wang et al., 2006). During the second step of two-step sintering, the mobility of the junctions may be lower than the grain boundary diffusion rate. The effects of the change in grain boundary/pore junctions on the driving force for densification has not yet been revealed, therefore, the effects of two-step sintering should be clarified from the view point of driving force as well as diffusion rate.

Sinter-compression (forging) tests can be used to determine the sintering stress and the viscosity of powder compacts (Venkatachari and Raj, 1986; Rahaman et al., 1986; Zuo et al., 2003a), composites (Bordia and Raj, 1988; Salamone et al., 2003), glass (Ducamp and Raj, 1989), and metal/ceramic mixtures (Shinagawa, 2008, 2009). In these studies, microstructural evolutions, such as, grain growth, were considered, but no experiments have been done for the effects of heating history. Even with non-nanocrystalline powders, some effects regarding the sintering stress and viscosity may be observed for the two-step sintering process and may provide important information to understanding sintering properties and sinterability. In this study, nickel powder with micron-scale metallic particles, which is the same powder used in previous studies as a model material (Shinagawa, 2008, 2009), are examined by sinter-compression tests. The microstructural evolution due to the two-step heating is also checked to clarify the relationship with the change in sintering properties.

2. Experimental methods

2.1 Sinter-compression tests

Nickel powder (4SP-400, NOVAMET, mean size of 12.5 μ m) and binder (Ceruna WK-276, Chukyo Yushi Co., Ltd.) were mixed with a ratio of 1:0.56 in volume, and dried as granules. The granules were formed into cylindrical specimens measuring approximately 4.7mm in diameter and 12mm in height, by uniaxial pressing at 39MPa followed by cold isostatic pressing at 200MPa. The cylindrical specimens were put in a thermomechanical analyzer, and heated to prescribed temperatures at a rate of 20K/min, with an initial load of 0.098N in Ar-20%H₂. Two different loads are needed to determine the sintering properties, but the tests with three loads were conducted to evaluate errors as well. Therefore, the load value was kept, or changed to 0.294N or 0.490N, 20min after reaching the test temperature in the case of one-step heating. The specimens were then measured for changes in length. For the two-step heating, the specimens were cooled by 50K at a rate of 20K/min after 10min at the temperature of the first step. The specimens were then measured for changes in length 10min after the second test temperature, as illustrated in Fig. 1. Six test temperatures for one-step heating were used from 1223K to 1473K at an interval of 50K, as indicated in Table 1. The combinations of the first and the second temperatures in the two-step heating are also shown in Table 1. The interval of the test temperatures is set to be 50K, which was empirically determined by preparatory tests, as a moderate increment to make a difference in measurements but also to avoid an excess change in relative density.

The strain rates were evaluated from the change in height of the specimens, and approximated by the same equations as the previous study (Shinagawa, 2008):

$$\dot{\epsilon}_z = (\sigma_z + S)/E \quad (1)$$

$$S = (1 - 2\nu)\sigma_s \quad (2)$$

$$E = E_0(t + b)^{1-c} \quad (3)$$

where $\dot{\epsilon}_z$ is the strain rate in the direction of loading, σ_z is the external compressive stress by loading, ν is the viscous Poisson ratio, σ_s is the sintering stress, and t is the time, where the time to change the value of load is set to be 0. E_0 is the longitudinal viscosity at $t=1-b$, and b and c are constants determined for each heating condition. Since ν cannot be measured by the present apparatus, an apparent sintering stress S is evaluated instead of σ_s . The errors of E and S are evaluated by the same method studied previously (Shinagawa, 2008). As for E , a value at any time within the range of $t = 0-1800$ s can be displayed, but the initial value $E_s = b^{1-c}$ ($t = 0$) is used for comparison. The relative densities of specimens were evaluated by measuring the weight and the volume of specimens after the tests.

Table 1 Conditions of temperature and holding time before testing.

Heating history	1st step		2nd step	
	Temp. (K)	Time (min)	Temp. (K)	Time (min)
1223K	1223	20	—	—
1273K	1273	20	—	—
1323K	1323	20	—	—
1373K	1373	20	—	—
1423K	1423	20	—	—
1473K	1473	20	—	—
1273-1223K	1273	10	1223	10
1323-1273K	1323	10	1273	10
1373-1323K	1373	10	1323	10
1423-1373K	1423	10	1373	10
1473-1423K	1473	10	1423	10

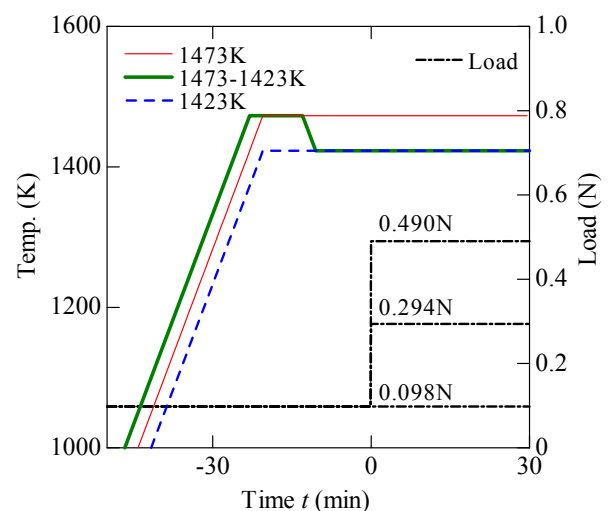


Fig. 1 Example of heating history.

2.2 Microstructure characterization

The different loads are needed for determining the sintering properties, but the microstructures were examined only for the specimens with a load of 0.098N, assuming no influence of the loads used in the present tests. After the sinter-compression tests, the specimens were longitudinally cut and their cross-sections were polished by using VibroMet 2 Vibratory Polisher (BUEHLER). The microstructures of the central parts of the cross-sections were observed by means of FE-SEM/EBSD (electron backscatter diffraction in field emission scanning electron microscopy) and the following two-dimensional, characteristic parameters were evaluated using image processing.

- 1) G : average of crystal grain size, which is the equivalent circle diameter of the grain.
- 2) d : average of pore size, which is the equivalent circle diameter of the pore.
- 3) $A = X/Y$: average of aspect ratio of pore, where X and Y are the maximum width and the corresponding height of the pore, respectively.
- 4) $C = \phi/\pi d$: average of circumferential ratio of pore, where ϕ is the circumference of the pore.

The number of sampling for grain or pore was in the range from 500 to 1400 approximately for each test condition.

Table 2 Constants obtained by sinter-compression tests

Heating history	S (MPa)	E_0 (MPa · s)	b (s)	c
1223K	0.12 ± 0.04	$2.2 \pm 0.2 \times 10^8$	688	0.422
1273K	0.14 ± 0.01	$4.7 \pm 0.3 \times 10^8$	404	0.494
1323K	0.15 ± 0.04	$4.2 \pm 1.2 \times 10^8$	493	0.480
1373K	0.15 ± 0.04	$2.7 \pm 0.7 \times 10^8$	578	0.437
1423K	0.16 ± 0.03	$4.3 \pm 0.9 \times 10^8$	404	0.477
1473K	0.12 ± 0.02	$3.2 \pm 0.6 \times 10^8$	324	0.465
1523K	0.26 ± 0.02	$6.9 \pm 0.4 \times 10^8$	262	0.454
1273-1223K	0.09 ± 0.01	$2.5 \pm 0.2 \times 10^8$	1010	0.448
1323-1273K	0.11 ± 0.00	$3.1 \pm 0.0 \times 10^8$	891	0.454
1373-1323K	0.16 ± 0.05	$4 \pm 1 \times 10^8$	984	0.463
1423-1373K	0.14 ± 0.02	$3.7 \pm 0.5 \times 10^8$	813	0.456
1473-1423K	0.14 ± 0.02	$3.5 \pm 0.4 \times 10^8$	731	0.449
1523-1473K	0.22 ± 0.06	$5 \pm 1 \times 10^8$	546	0.438

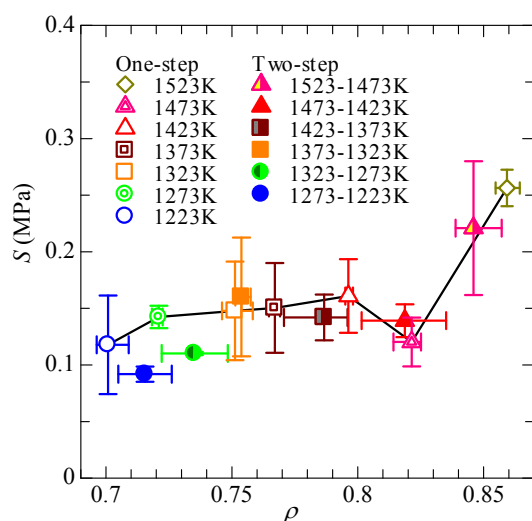


Fig. 2 Variation in sintering stress with heating history.

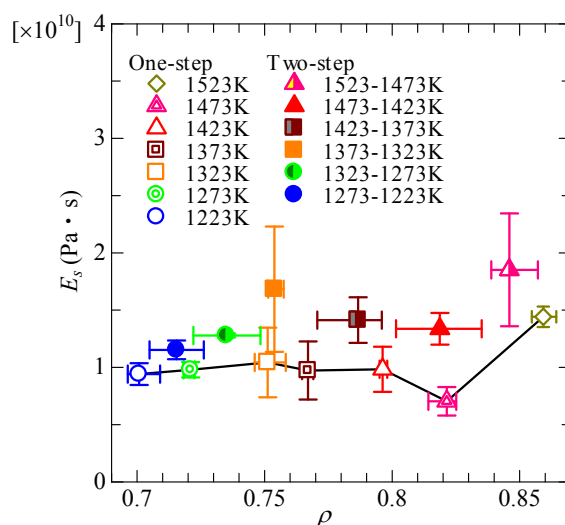


Fig. 3 Variation in viscosity with heating history.

3. Experimental results

3.1 Sintering properties

The material constants and parameters in Equations (1)-(3) obtained from the sinter-compression tests are listed in Table 2. Figs. 2 and 3 show the evaluated S and E_s , which are plotted as a function of the relative density ρ , respectively. Since S and E_s were determined by using the specimens tested with different loads, ρ is the average value, and the difference between the maximum and minimum values is displayed by error bar. This difference was independent of the loads, and mainly stemmed from the variation in the initial relative density by pressing. The data for one-step heating are connected by straight lines, which show fundamental variations in S and E_s , due to the change in test temperature. Both sintering stress and viscosity did not show significant variation within the range of low relative density, but increased in the later stage of sintering, which may be valid results as reported by (Zuo et al., 2003a). The data for two-step heating is superimposed in Fig. 2 and 3. As the test temperature increases, the densification progresses more. Therefore, at higher test temperatures the data is located on the right of the graph. The variations in S and E_s may be fundamentally affected by the change in the temperature as well as the relative density. The effects of heating history on S and E_s can be confirmed by comparing each data point of two-step heating with the point interpolated at the same relative density on the line between the neighboring points of one-step heating.

In Fig. 2, S the lower relative density range (<0.74) or temperature ($<1323\text{K}$) was decreased by two-step heating. In the higher relative density range (>0.74), or higher temperature ($>1323\text{K}$), there seemed to be no significant difference in S between one-step and two-step heating histories. On the other hand, in the lower relative density range, or test temperature, a similar value of E_s was obtained in both heating conditions, but E_s for two-step heating was evidently larger than that for one-step heating. Since the changes in sintering properties against the relative density were small in the range up to 1474K , the error bar for relative density is not significant even if it is large. Thus the influence of heating history was observed.

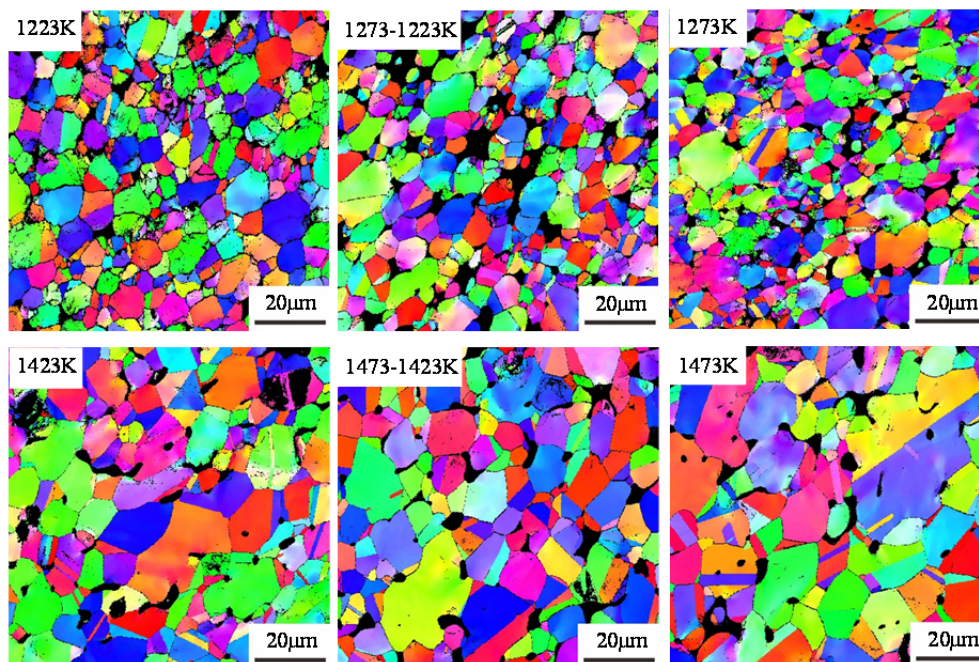


Fig. 4 Examples of EBSD maps for observing grain size. Pore is seen as black region.

3.2 Microstructures

The microstructures of the specimens by two-step heating were compared with those obtained by one-step heating in the range up to 1474K , where the variations in both S and E_s by one-step heating were small. Fig. 4 and 5 display examples of the EBSD maps used to observe crystal grains and the SEM micrographs to characterize pore structures,

respectively, for specimens of one-step heating at high (right) and low (left) temperatures with an interval of 50K, and of two-step heating between them (middle). There seemed to be no significant qualitative difference between one-step and two-step heating on the crystalline structures. On the other hand, large pores were observed in the specimens by two-step heating at lower relative density or temperature.

The average grain G is plotted as a function of relative density ρ in Fig. 6. Note that ρ in the figures for G and the other characteristic parameters d , A , C (Fig. 6-9) has no error bar, because it is a value for each specimen tested with the load of 0.098N, and the data points for one-step heating are connected by straight lines to show fundamental variations with ρ . In general, the grain size of powder compacts does not increase much initially, but does increase later during sintering, because the grain boundary can migrate from the contact area between particles as it grows enough due to densification (Shinagawa et al., 2014). The same grain growth behavior as usual was observed in Fig. 6, even in the specimens for two-step heating.

The change in the average pore size d is demonstrated in Fig. 7. Naturally, d decreased gradually with densification. The difference between one-step and two step heating is not so clear, but the pore size increased by two-step heating in the lower relative density range (<0.74) or temperature ($<1323\text{K}$), which is also confirmed by the pore size distribution. Figs. 8 and 9 show the change in aspect ratio A and circumferential ratio C of pores, respectively. The aspect ratio A represents the anisotropy of pore structure, which may be related to the directional connectivity of pores. A was almost constant through the initial and intermediate stage of sintering and did not seem to be affected by heating history. The circumferential ratio C is affected by the anisotropy of pore structure, but may be a parameter principally to indicate the shape complexity of pores. Since the pores were rounded during sintering, C decreased as the relative density increased. The influence of two-step heating on the pore shape was also not observed.

Although the effect of two-step heating on microstructures was not clear, larger pores were observed in specimens at lower test temperatures shown in Figs. 5 and 7. The pore size distribution was examined and the results are shown in Fig. 10. It was found that there were a larger number of pores 10 μm in diameter in specimens for 1272-1223K and also for 1473-1423K as shown in Fig. 5. The pore size distributions for the specimens at higher test temperatures was not changed much by two-step sintering, as shown in Fig. 10(b). For specimens at low relative density, the sintering rate increases rapidly during the first step of two-step heating, and may cause inhomogeneous shrinkage in unstable particles with small contact. Once the inhomogeneous structure is produced, it may cause internal stress and enhance non-uniform shrinkage.

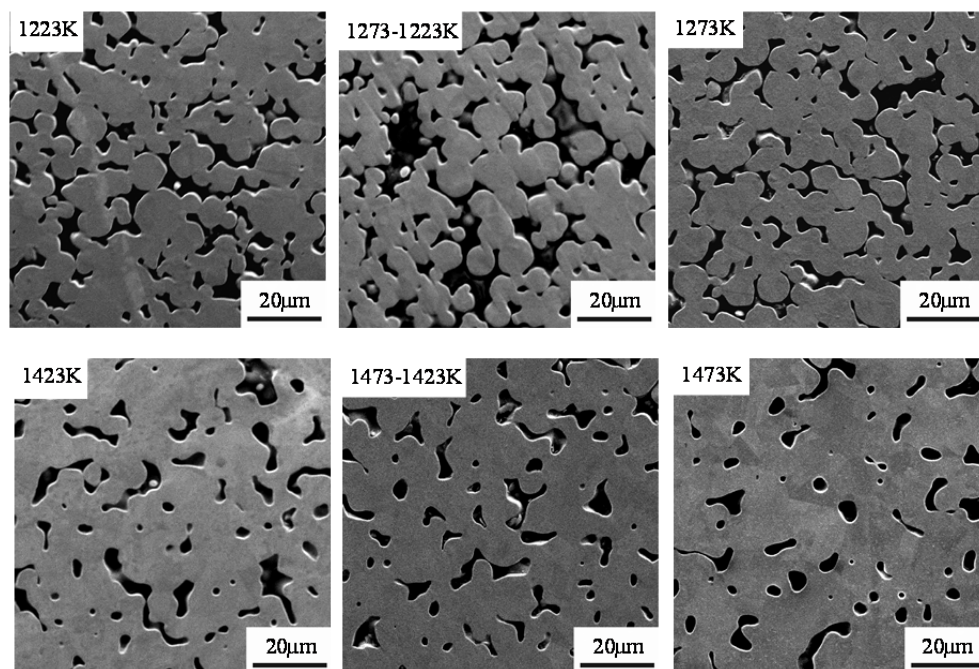


Fig. 5 Examples of SEM micrographs for characterizing pore structures

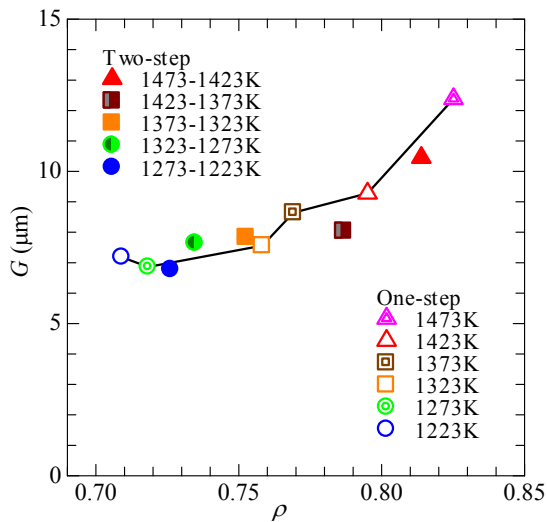


Fig. 6 Variation in average grain size as a function of relative density, plotted with reference data.

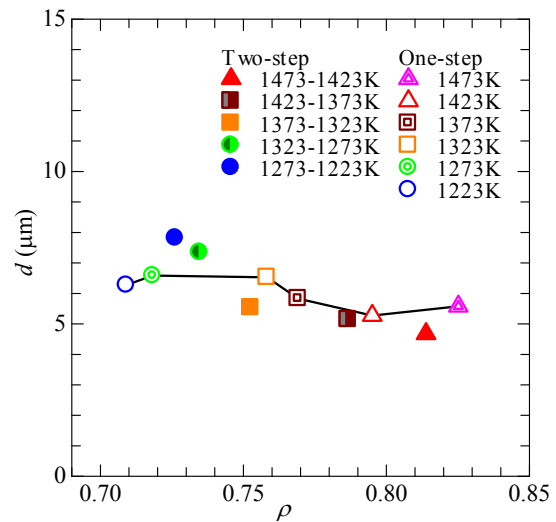


Fig. 7 Variation in average of pore size as a function of relative density.

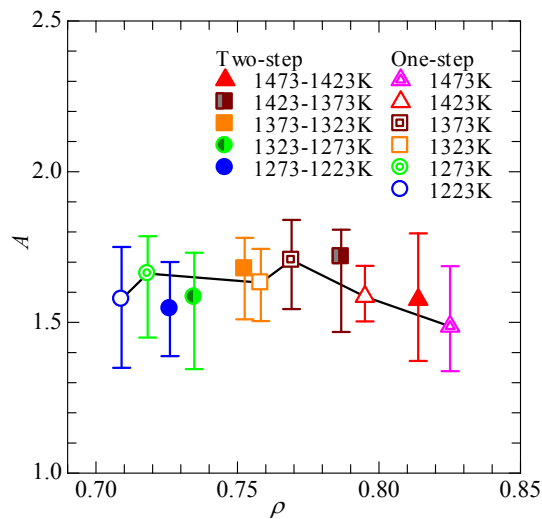


Fig. 8 Variation in average of aspect ratio of pore as a function of relative density.

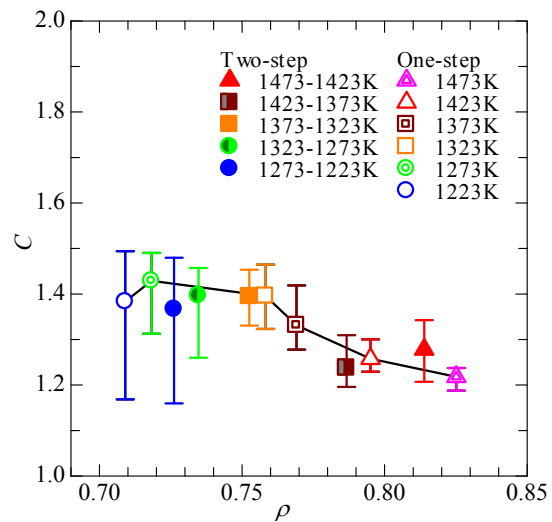
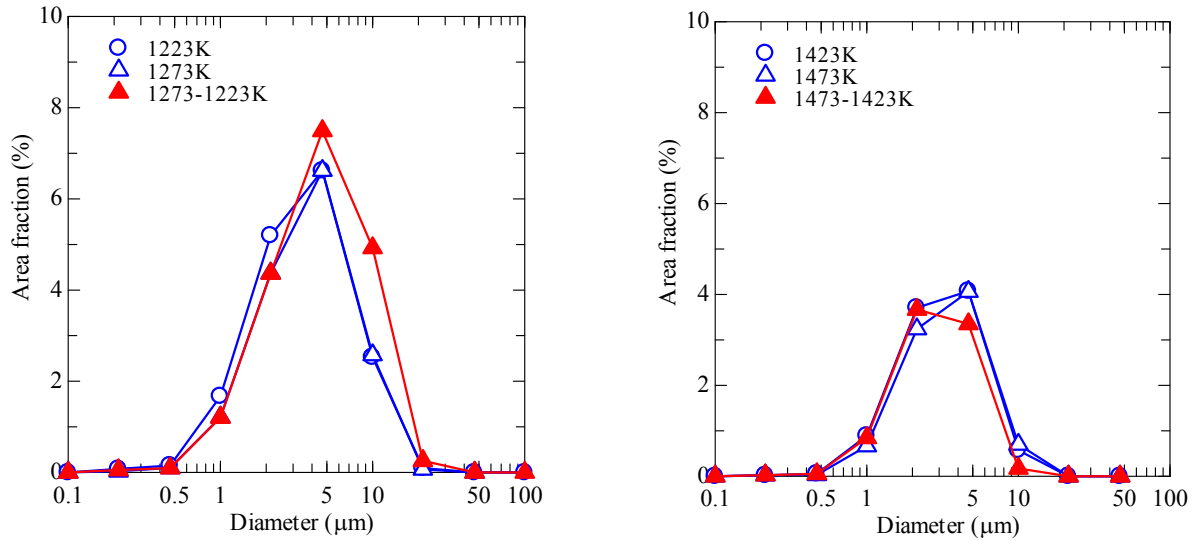


Fig. 9 Variation in average of circumferential ratio of pore as a function of relative density.

4. Discussion

Although the grain growth at elevated temperatures was not suppressed by two-step heating like the nanocrystalline ceramic powder, the sintering properties for the used nickel powder in the current experimental conditions were affected by the heating history. The viscosity was increased by two-step heating except in the case of low relative density. In the previous study (Shinagawa, 2008), it was confirmed that the strain rate of nickel powder compacts during sinter-compressions tests was a function of the time, and Eq. (3) was derived to express the experimental data. The increase in viscosity with the time may be caused by grain growth if the dominant deformation mechanism is grain-boundary diffusion. Combining a well-known grain growth equation $G^m = G_1^m + k t$ and Coble creep law (Coble, 1963) $E = \alpha G^3$ gives



(a) at lower test temperatures (b) at higher test temperatures
Fig. 10 Comparisons of pore size distribution between one-step and two-step heating histories.

$$E = \alpha (kt + G_1^m)^{3/m} \quad (4)$$

where α is a temperature and relative density dependent constant, G_1 is the grain size at $t = 0$, and m is the grain growth exponent. Comparing Eq. (4) with Eq. (3) gives $m = 3/(1-c)$. The m -values calculated from c in Table 2 were almost constant through all test temperatures, and $m = 5.5$ was determined by using the average $c = 0.46$, as indicated in Fig. 11(a). Note that the horizontal axis T is the temperature during the sinter-compression tests. Figure 11(a) may suggest that the grain growth behavior in the specimens for two-step heating is the same as those for one-step heating. In fact, the grain size was not increased by two-step heating, as can be seen in Fig. 6. Since the m -value of 5.5 is greater than the usual range of 2-4, it is considered that m includes the influence of other mechanisms of time-hardening, which may be related to sub-microstructure usually discussed for primary creep (Derby and Ashby, 1987; Ogbonna et al., 1995). Regardless of the mechanisms, parameter b in Eq. (3) for two-step heating was larger than that for one-step heating, roughly by $\Delta b = 420\text{s}$ (7min) as demonstrated in Fig. 11(b) from data in Table 2. In thermally-activated process, deformation for a short time at high temperature is generally equivalent to that for a long time at low temperature. Figure 12 shows a comparison between $E_s(t = 0)$ for two-step heating and E at $t = 420\text{s}$ for one-step. This figure may suggest that the increase in viscosity in two-step heating can be roughly expressed by the shift in time-hardening, i.e., $E - t$ curve for one step heating. As for the lower relative density range (<0.74), E_s for two-step heating seems to be lower than E at $t = 420\text{s}$ for one-step heating, which may be the influence of the formation of large pores, as mentioned above.

The change in pore size may directly affect the sintering stress. The sintering stress is experimentally given by $\sigma_s = \kappa\gamma(1 - \rho)$, where κ is the mean curvature of the pore surface and γ is the surface tension (Gregg and Rhines, 1973; Rahaman et al., 1986). When κ is assumed to be inversely proportional to the average radius of the pore $d/2$, S can be expressed by

$$S = 2\beta\gamma(1 - \nu)(1 - \rho)/d \quad (5)$$

where β is a proportional factor. Equation (5) is too simple to describe the sintering stress precisely, but enough to discuss the effect of pore size. If the measured S and d satisfy Eq. (5) for both one-step and two-step heating histories, common values of β may be obtained. The back calculation of β was conducted by using the data of S , ρ , d as well as $\gamma = 0.905\text{ N/m}$ for pure nickel (Kanetkar et al., 1988). Since the viscous Poisson ratio ν is a function of ρ , an expression $\nu = (25\rho - 7)/(61 - 25\rho)$ from a model for porous metal (Shima and Oyane, 1976), which agrees well with the experimental data obtained from the sinter-compression tests (Zuo et al., 2003b), was used. Figure 13 shows the

results of the back calculation of β . In the lower temperature range (<1323K), there was no difference in β between one-step and two-step heating histories. Therefore, it can be concluded that the decrease in sintering stress by two-step heating was due to the increase in pore size, that is, the formation of large pores.

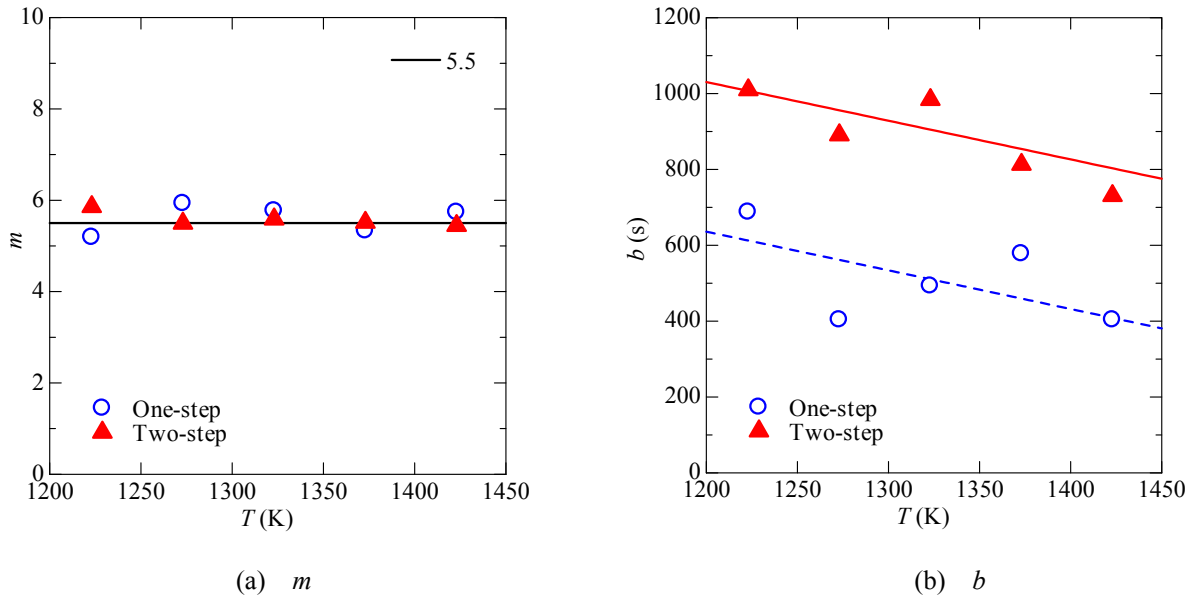


Fig. 11 Comparisons of parameter values related to viscosity between one-step and two-step heating histories.

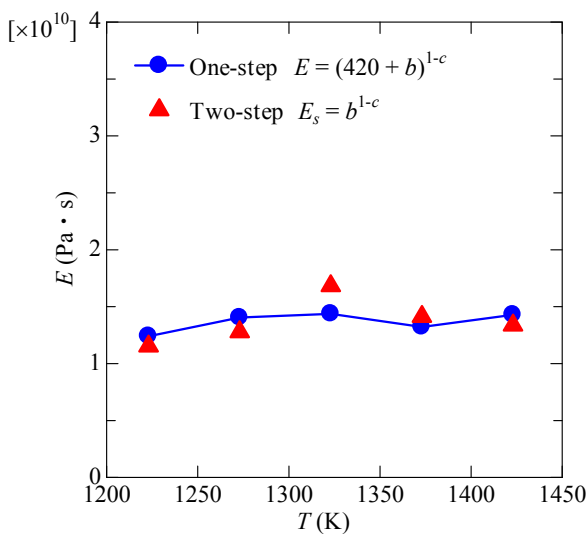


Fig. 12 Comparison between E_s for two-step heating and E at 420s for one-step heating.

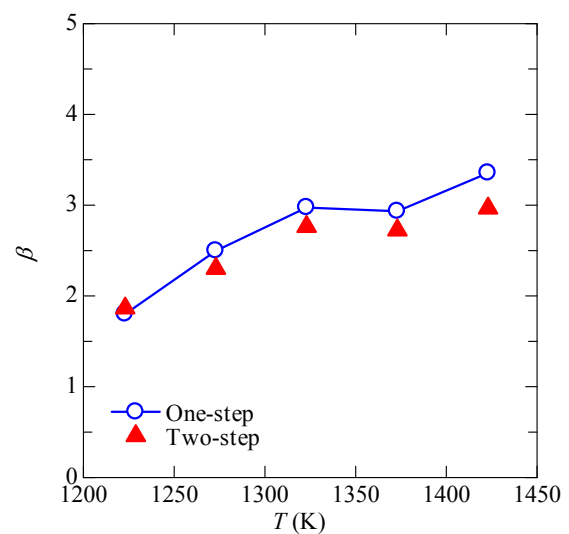


Fig. 13 Comparison of factor in sintering stress between one-step and two-step heating histories.

5. Conclusions

The effects of two-step heating on the sintering properties of nickel powder compacts were examined by using sinter-compression tests. The change in microstructure due to the difference in heating history was also analyzed to discuss the factors influencing the sintering properties. The experimental results showed that the sintering stress was decreased by two-step heating in the lower relative density range or test temperatures. In this range, large pores were

formed by heating at a higher temperature, and may have caused the reduction in driving force for sintering. The viscosity was increased by the two-step heating in the whole range of the relative density or the test temperature. This can be explained by the time-hardening results of the material. There was no drastic change in the sinterability of nickel by two-step heating in the range of the present examination, but the close relationship between sintering properties and the microstructure was confirmed.

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