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Anisotropy of dimensional change and its corresponding improvement by addition of TiH_2 during elemental powder sintering of porous NiTi alloy

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Abstract

The paper deals with the influence of TiH_2 content and sintering conditions (sintering temperature and sintering time) on the dimensional changes and the radial/axial shrinkage (R/A)-ratio of powder compacts. The purpose was to try to find out how to make precision porous products using a conventional powder metallurgical process. It was found that the dimensions of the compact shrink and anisotropy of dimensional change (ADC) occurs during sintering. Addition of TiH_2 markedly minimizes ADC and makes it possible to manufacture the desired final product shape. An R/A-ratio less than 1 is supposed to be attributed to the differences in the degree of mechanical deformation, which occurs on the surface of powder particles parallel to and perpendicular to the direction of pressing during the pressing process. A model of the pore changes during pressing and sintering is proposed.

Keywords: Anisotropy of dimensional changes; Powder sintering; Porous shape memory alloys

1. Introduction

NiTi alloy is widely used for a variety of shape memory applications. Moreover, porous materials as biomaterial have special advantages [1] as compared with nonporous materials. Porous NiTi alloy currently is acknowledged as one of the most promising materials in bone replacement and other applications. Different techniques, which focused on compact NiTi alloys, have been used for production of NiTi alloy [2–9], and among these methods powder metallurgy, as a means of fabricating NiTi alloy, offers the ability to produce a variety of component shapes with a controllable porous structure, whilst eliminating machining operations and avoiding the problems of casting defects due to segregation. However, it has often been stated that during sintering of metal powder compacts dimensional changes and its corresponding anisotropy may occur [10–16]. Therefore, it is important to control the dimensional change during sintering in order to gain the desired shape of porous products. Several studies [10,11,17] have previously referred to dimensional changes during the sintering of compact equiatomic NiTi alloys, in which it was observed that during sintering anisotropy of dimensional change (ADC) occurred with expansion in the radial and contraction in the axial direction. Igharo and Wood [17] attributes these phenomena to the different diffusion rates of Ti and Ni, along with the large discrepancy in powder sizes which results in significant powder aggregation during uniaxial pressing. Another explanation given by Majama and Sohama [10] is that the contracting phenomenon in the axial direction is attributed to the appearance of thick layers of intermetallic compounds, whilst the expanding phenomenon is due to the reaction between the eutectic liquid and intermetallic compounds. However, in our study ADC also occurred during sintering, but with contraction in all directions, which can not be explained by the former two mechanisms. Our study deals with the influence of TiH_2 content and sintering conditions (sintering temperature

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and sintering time) on the dimensional changes and the radial/axial shrinkage-ratio (R/A-ratio) of powder compacts. The purpose was try to find how to make precise porous products in a conventional powder metallurgical process. In the present study, the authors used TiH_2 powder as the reactant and pore-forming agent in producing porous NiTi alloy. Meanwhile, as the oxide film on Ti powder greatly affects the sintering behavior [18], it was thought that the substitution of Ti powder by TiH_2 powder, which is oxide free, would improve ADC so as to give the desired shape and final porous products of near net shapes. A model of the pore changes during pressing and sintering is proposed.

2. Experimental

Elemental Ti powder (− 74 μm), Ni powder (− 74 μm) and TiH_2 powder (− 44 μm), all with a purity of 99%, were used in the present study. To evaluate the influence of TiH_2 on the dimensional changes as well as the R/A-ratio, four equiatomic NiTi blended powders with different TiH_2 content were designed. Table 1 shows the nominal composition of the blended powders, which were mixed by ball-milling in a steel chamber for 2 h in an argon atmosphere. The blended powder was cold pressed into cylindrical compacts with a diameter of 11.5 mm and a typical height of 10.3 mm, and this operation was performed in a uniaxial die press under 70 MPa for 2 min on a DCS-10t tension machine. Three specimens were prepared for each test condition and the dimensional value was the average of these three specimens. The compacts were isochronally sintered at various temperatures for 1 h or isothermally sintered at 1223 K for various times in a silicon–carbon tube furnace under a vacuum of 1.33×10^{-2} Pa. Two heating rates were used during sintering: a slow heating rate of 4 K min^{-1} to 773 K followed by a fast heating rate of 30 K min^{-1} to the final sintering temperature. The R/A-ratio is used to express the degree of ADC, if the anisotropy is serious then the R/A-ratio has a large deviation from 1, where R is the linear shrinkage in the direction perpendicular to that of pressing, and A is the linear shrinkage parallel to the direction of pressing.

Table 1
Chemical composition of the experimental blended powders

Sample No.	TiH_2 (wt.%)	Ti (wt.%)	Ni (wt.%)
1	0	44.9	Balance
2	9.3	35.8	Balance
3	27.8	17.8	Balance
4	45.9	0	Balance

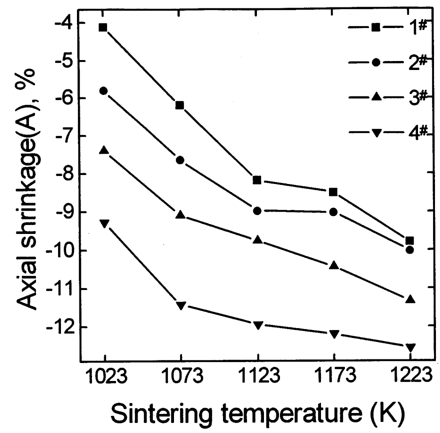

Fig. 1. Effects of sintering temperature on axial shrinkage percentage for a sintering time of 1 h.

3. Results

3.1. Dimensional changes

Unlike the study of Igharo and Wood [17] in which serious deformation and shape loss of the compact occurred, in the present study the compact retained its designed cylindrical shape although dimensional changes appeared during sintering. The dimensional changes with sintering temperature, sintering time and/or TiH_2 content are given in Figs. 1–4, respectively. The salient features are as follows:

1. The dimensions of all the compacts shrank during sintering. The magnitude of the shrinkage increased rapidly with increasing temperature from 1023 to 1073 K for 1 h, followed by a gradual increment with a further increase in temperature (Figs. 1 and 2). It also followed a similar pattern for the sintering time at 1223 K (Figs. 3 and 4).
2. Dimensional shrinkage increased rapidly with increasing TiH_2 content.

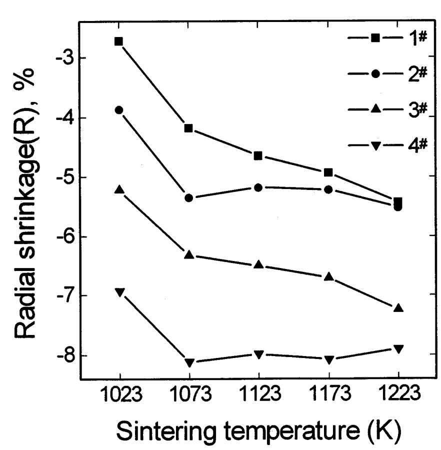

Fig. 2. Effects of sintering temperature on radial shrinkage for a sintering time of 1 h.

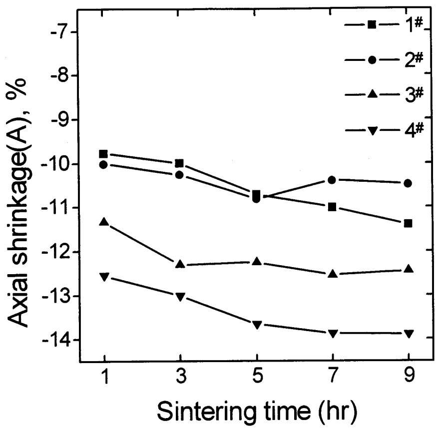

Fig. 3. Effect of sintering time at 1223 K on axial shrinkage.

3. The magnitude of shrinkage was much greater in the axial direction than in the radial direction.

3.2. *R*/*A*-ratio

It was found that the *R*/*A*-ratio depends upon the experimental parameters. The influence of sintering temperature on the *R*/*A*-ratio is shown in Fig. 5. As can be seen, the *R*/*A*-ratio decreases linearly with increasing sintering temperature. The influence of sintering time at 1223 K on the *R*/*A*-ratio is shown in Fig. 6. It is clear that the *R*/*A*-ratio of sample 1 with no TiH_2 shows no change with increasing sintering time. By comparison, the *R*/*A*-ratio of the other samples increases with increasing sintering time, and the upward trend of the *R*/*A*-ratio mirrors the increasing TiH_2 content. As a result, the *R*/*A*-ratio of sample 4, with TiH_2 completely substituted for Ti, is the greatest, but increases only slightly with increasing sintering time. In addition, with increasing TiH_2 content, the *R*/*A*-ratio increases.

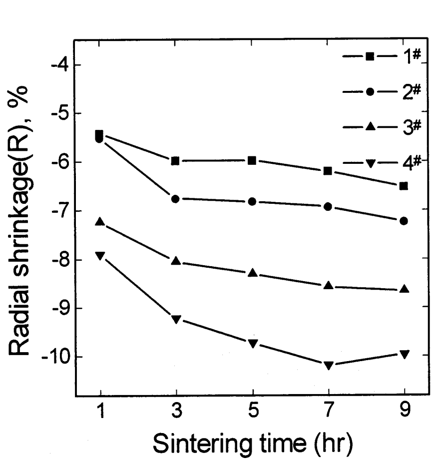

Fig. 4. Effect of sintering time at 1223 K on radial shrinkage.

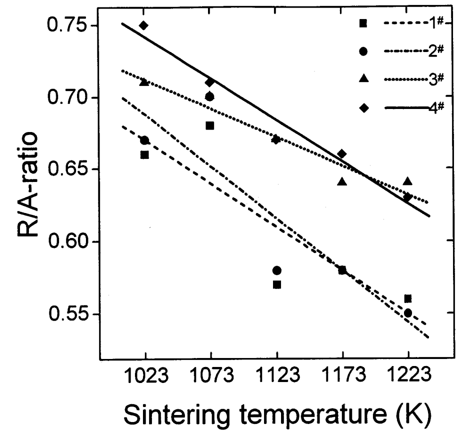

Fig. 5. Effect of sintering temperature on the *R*/*A*-ratio for a sintering time of 1 h.

4. Discussion

The shrinkage of the dimensions observed in this study is mainly related to the following phenomena:

1. Shrinkage of the original pores in the green compact.
2. The alloying effect. The difference in the theoretical densities between the blended powder and the intermetallic compounds leads to a shrinkage in the dimensions [8]. With increasing TiH_2 content this shrinkage effect is more apparent due to the low density of TiH_2 powder.
3. The decomposition of TiH_2. Under the present sintering conditions, TiH_2 decomposes above 773 K. As this decomposition is an extensively exothermic reaction, and the decomposed new-born Ti is more active, the addition of TiH_2 accelerates the contraction.
4. The Kirkendall effect. The different diffusion rates of Ti and Ni, e.g. at 1023 K the bulk diffusion rates of Ti and Ni are 7.0×10^{-12} and 5.5×10^{-15} cm^{-2} s^{-1} respectively, leads to the creation of an unbal-

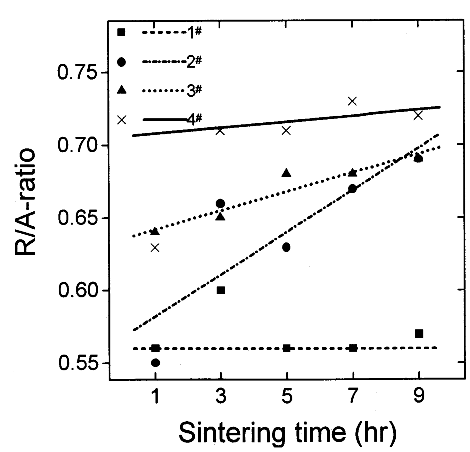

Fig. 6. Effect of sintering time at 1223 K on the *R*/*A*-ratio.

anced mass transfer and results in pore formation [19].

The expansion as a result of (4) will partly counteract the contraction due to (1–3), however, the actual phenomena observed were different from that observed by Igharo and Wood [17], and also different from that observed by Majama and Sohama [10]. In the present study, the samples shrink in all directions. According to the calculations, the alloying effect attributes less than 30% to the whole volumetric shrinkage, thus the dimensional shrinkage is supposed to be mainly due to the effect of (1) for the higher heating rate above 773 K. This is because a higher heating rate generates more heat, which results in greater shrinkage of the original pores due to the exothermic intermetallic formation reactions. At the same time, with increasing sintering temperature or sintering time, the shrinkage due to (1) will further increase, along with the shrinkage increment as a result of (3), if the samples have TiH_2 added.

In the present study, the R/A-ratio is smaller than 1, which indicates that ADC has occurred, but with the addition of TiH_2 this anisotropy is greatly improved. A possible model of changes in pore profile is proposed and illustrated in Fig. 7. Before pressing the powder particle surfaces are not deformed and, to simplify the problem, all the pores are assumed to be similar and near-globose (Fig. 7(a)). During pressing, due to both the great affinity of Ti with oxygen [6,18,20] and work hardening from the ball-milling technique used before pressing [7], the blended powder is hard and more easily deformed by shearing rather than by pressing as the pressing pressure is low. At the same time, the friction between the die wall and the powder particles also causes greater deformation in those particle surfaces perpendicular to the axial direction and, as a result, the pores in the green compact appear elliptical with their longer axes parallel to the axial direction (Fig. 7(b)). However, the more the particle surface deforms during pressing, the less will it shrink during the sintering stage due to release of the deformed stress [16]. Therefore, the shrinkage will be of greater value in the axial rather than in the radial direction (Fig. 7(c)), and the R/A-ratio will be less than 1.

It is observed that the R/A-ratio depends greatly on the sintering conditions. With increasing sintering temperature, the effect of deformation leads to much greater shrinkage in the axial rather than in the radial direction and as a result the R/A-ratio becomes even smaller. However, after sintering at 1223 K for 1 h, it is supposed that this effect vanishes and the pores tend to be near-globulose. Thus with the increment of sintering time at 1223 K, greater shrinkage occurs in the radial direction and the R/A-ratio increases. This is assumed to be attributable to the surface-tension forces, which favor radial more than axial shrinkage as the sintering process continues and also to the fact that the diameter of the samples is greater than the height. In addition,

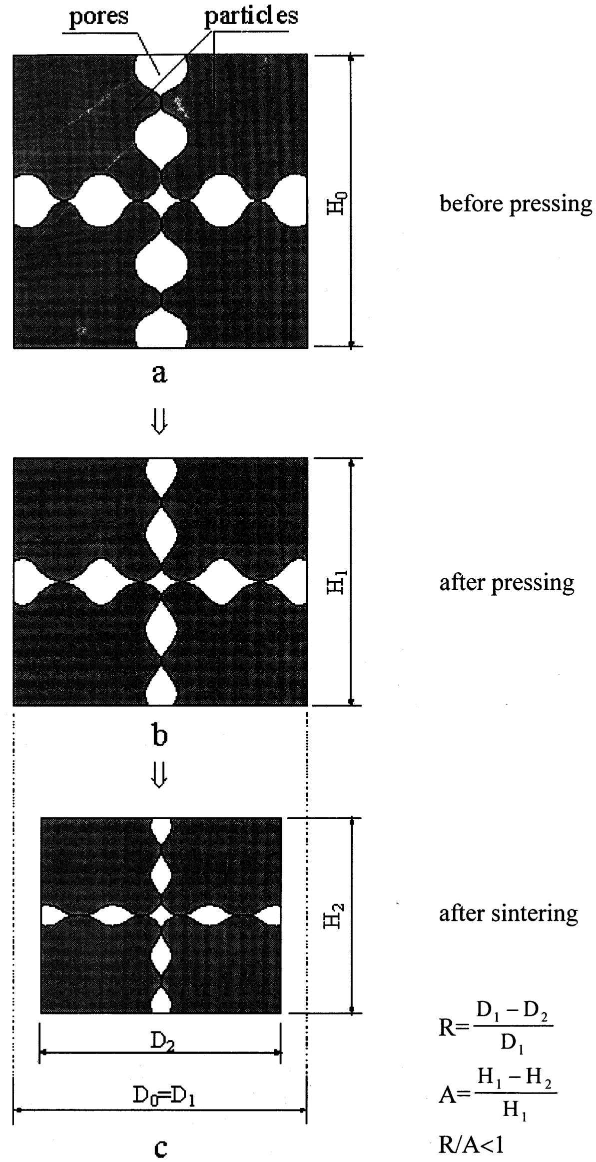

Fig. 7. The model of the changes in pore profile during pressing and sintering.

with increasing TiH_2 content, the R/A-ratio also increases. The reason for this phenomenon is based on two aspects: first, the addition of TiH_2 decreases oxygen contamination and improves the compactibility of the blended powders, which minimizes the deformation difference in the powder particle surfaces during pressing; and secondly, the smaller size of the TiH_2 powder gives a finer distribution of pores and allows the particles to rearrange themselves during sintering.

5. Conclusion

The dimensional changes during sintering with contraction in the axial and radial directions are found to be anisotropic, however, it can be controlled by the addition of TiH_2. Because of the shrinkage of the original pores, the R/A-ratio is less than 1 and decreases with increasing sintering temperature. With increasing sintering time at 1223 K, the R/A-ratio of some samples increases which is largely related to the addition of TiH_2. The observed R/A-ratio less than 1 is assumed to be attributed to the ball-milling and the affinity of Ti for oxygen. The affinity of Ti and Ni for oxygen makes the blended powder hard and results in differences in mechanical deformation, which occurs on the surface of powder particles parallel to and perpendicular to the direction of pressing during the pressing process.

The addition of TiH_2 has given new perspectives to the manufacturing of porous NiTi alloy because it has markedly decreased the anisotropy of dimensional change. A conspicuous increase in the R/A-ratio can be obtained with Ti completely replaced by TiH_2. It is proposed that the desired final product with close dimensional tolerance can be produced by selecting certain materials and sintering conditions.

Acknowledgements

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