*Journal of Alloys and Compounds, 190* (1992) 31–33
*JALCOM 436*

# Effects of cold isostatic pressure on the sintering behaviour of nickel ultrafine powders

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(Received May 21, 1992)

## Abstract

The sintering characteristics of two kinds of nickel ultrafine powder (UFP) in a hydrogen atmosphere were examined. A decrease in the sintered density after the maximum value was observed on increase in the cold isostatic pressure. This phenomenon was explained by the inhomogeneous packing due to the strong agglomeration of the UFPs.

## 1. Introduction

Herring's [1] scaling law and traditional sintering theories [2] predict that, the finer the particle size, the lower is the sintering temperature and the shorter is the sintering time. In fact, sintering shrinkage of compacts made of clean ultrafine powders (UFPs) occurs at lower temperatures [3, 4]. However, it is difficult to obtain dense products by sintering UFPs because of their tendency to agglomerate strongly [5] and evolution of large amounts of gases [4].

Metal UFPs are so reactive that exposure to open air is accompanied by appreciable oxidation, by adsorption of various gases and by formation of hydroxide-like and carbonate-like compounds [6]. Therefore an increase in the oxide phase is observed during heating in vacuum or inert gases [6]. To avoid this, metal UFPs must be treated in a controlled atmosphere or the surface oxide phase of the UFPs exposed to air must be reduced before or during sintering the UFPs.

The present author [7] reported that an increase in the consolidation pressures of copper and iron UFPs, which were contaminated by various gases owing to exposure to air, resulted in a decrease in the densities after sintering in a stream of hydrogen. This phenomenon is explained by the evolution of gases in the closed pores and inhomogeneous packing due to the strong agglomeration of the UFPs. Since the reduction temperature of the surface oxide of the nickel UFPs is low [4], the effects of the oxide phase and gas evolution (mainly $H_2O$) on the sintered density of the nickel UFPs are expected to be small compared with those for the iron and copper UFPs [8]. Therefore the hindrance of sintering due to the agglomeration may become clearer in the sintering of the nickel UFPs.

In the present study, two types of Ni UFP were cold isostatically pressed into pellets and the effects of the cold isostatic pressure on the green density and sintered density were examined.

## 2. Experimental details

Two kinds of nickel UFP were prepared by a gas evaporation technique [9]. The particle shape of these UFPs is nearly spherical as shown in Fig. 1. The formation of strong bonds between the particles is seen in both UFPs. Here, the large nickel UFPs are referred to as L-Ni and the small nickel UFPs as S-Ni. They were subjected to a slow oxidation treatment [10] followed by exposure to air. The slow oxidation treatment is generally conducted by flowing gases containing a small amount of oxygen gas to avoid fast oxidation [10]. The oxygen impurity contents of the L-Ni and S-Ni were 1.3 wt.% and 9.0 wt.% respectively. The specific

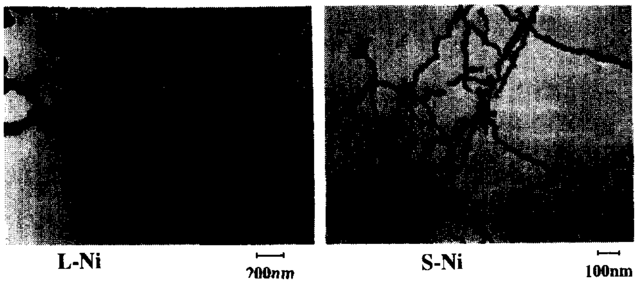

Fig. 1. Particle shape of UFPs.

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surface areas of L-Ni and S-Ni, measured after outgassing at room temperature, were 5.0 $m^2 g^{-1}$ and 40 $m^2 g^{-1}$. X-ray diffraction measurements of the two kinds of as-received nickel UFP showed that L-Ni and S-Ni contained the NiO phase and that S-Ni contained an additional small amount of the $Ni(OH)_2$ phase.

The powders were isostatically pressed under a pressure of 30–400 MPa into a disc of approximately 10 mm diameter and 4 mm thick. The continual change in the dimensions of the pellets was measured using a dilatometer in a stream of hydrogen (flow rate, 800 ml $min^{-1}$). Thermogravimetry (TG) and differential analysis (DTA) were also performed to examine the sintering characteristics.

## 3. Results and discussion

Figure 2 shows the linear shrinkage of the two compacts, which were pressed under 50 MPa, at a heating rate of 5 K $min^{-1}$ in a stream of hydrogen. The green densities of the compacts of S-Ni and L-Ni were 1.94 g $cm^{-3}$ and 3.86 g $cm^{-3}$ respectively. TG and DTA measurements revealed that the reduction reaction, which was accompanied by a small endothermic reaction, occurred in the temperature range 400–450 K. This result suggests that the shrinkage of both pellets at around 423 K is related to the reduction of the surface oxide of nickel UFPs. This shrinkage was not observed for a sample of clean nickel UFPs [4]. The volumetric shrinkage is much larger than the amount of surface oxides. Therefore this shrinkage seems to be due to the rearrangement accompanying the reduction reaction as in the case of sintering of iron [11], copper [12], and cobalt [13] UFPs in a hydrogen atmosphere. The different shrinkages of L-Ni and S-Ni in this range are due to the different green densities, the different amounts of surface oxide and the different particle sizes. Lower green densities, larger amount of oxides and smaller particle sizes might result in larger shrinkage of the compacts. S-Ni shrank again and the shrinkage was saturated at temperature above 773 K. On the contrary, L-Ni shrank at higher temperatures in comparison with S-Ni mainly because the particle size of L-Ni is larger than that of S-Ni.

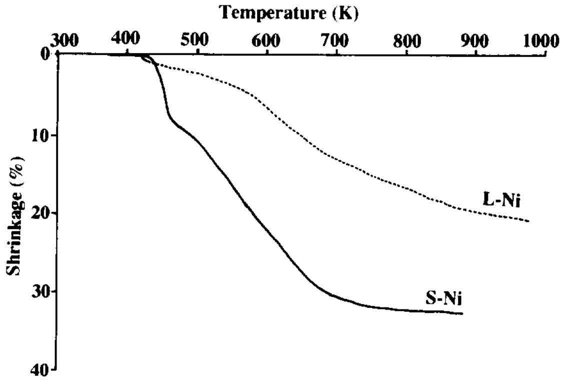

Fig. 2. Linear shrinkage of the two compacts, which were pressed under 50 MPa, at a heating rate of 5 K $min^{-1}$ in a hydrogen stream.

The green densities of both UFPs increase with increase in cold isostatic pressure as is seen in Fig. 3. The data for L-Ni cold isostatically pressed above 300 MPa could not be obtained because the green bodies of L-Ni cold isostatically pressed above 300 MPa were broken into pieces. The theoretical limit of dense packing for monosized spherical particles is 74%. One of the main causes of the extremely low densities of the UFPs might be their strong agglomeration [14]. Figure 3 also shows the sintered densities of L-Ni heated at 973 K and S-Ni heated at 773 K for 1 h in a stream of hydrogen. Usually an increase in the green density results in an increase in the sintered density. Although the sintered density of S-Ni cold isostatically pressed under 60 MPa and that of L-Ni under a 200 MPa increase with cold isostatic pressure, that of S-Ni decreases on increase in cold isostatic pressure above 60 MPa. This decrease in density is due to gas evolution and/or inhomogeneous packing as reported before [7].

Figure 4 shows the effect of the cold isostatic pressure on the density curves of S-Ni during heating at 5 K $min^{-1}$. The densities are calculated from the linear shrinkage. The density before the reduction reaction is shown on the left-hand side (referred to as the apparent density), and that after the reduction reaction at around 450 K is shown on the right-hand side, where the mass loss due to the reduction reaction is taken into consideration in the calculation of the density. The density of the S-Ni cold isostatically pressed at 400 MPa is saturated at around 700 K, but that cold isostatically pressed at 50 MPa increases above 700 K.

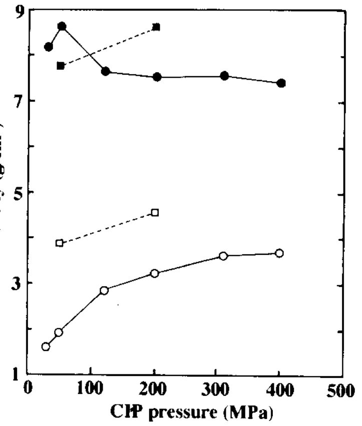

Fig. 3. Green densities (open symbols) and sintered densities (closed symbols) of L-Ni (■, □) after heating at 973 K for 1 h and those of S-Ni (●, ○) after heating at 773 K for 1 h in a stream of hydrogen as a function of cold isostatic pressure.

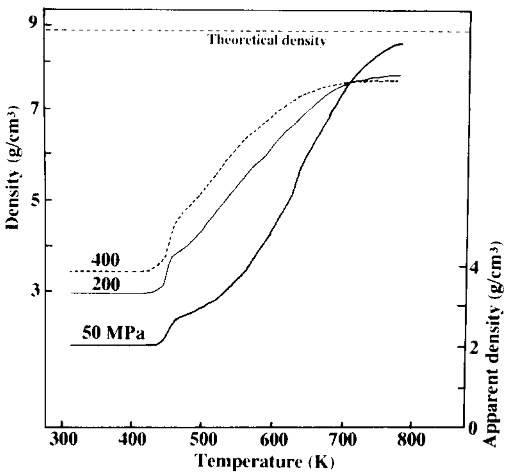

Fig. 4. Effect of cold isostatic pressure on the density curves of S–Ni during heating at 5 K $\min^{-1}$.

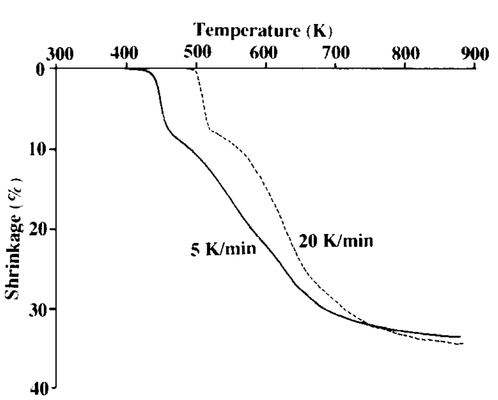

Fig. 5. Effect of the heating rate on the shrinkage curves of S–Ni cold isostatically pressed at 50 MPa.

Figure 5 shows the effect of heating rate on the sintering of the first shrinkage due to the rearrangement accompanying with the reduction reaction shifts to higher temperature at a higher heating rate, the final sintering shrinkage at 873 K is nearly equal. Similar results were obtained for the compacts of S-Ni cold isostatically pressed at 200 and 400 MPa. These results suggest that the depression of sintering shrinkage due to the gas evolution is not significant in the sintering of nickel UFPs in comparison with the sintering of copper and iron UFPs [7].

The effects preventing the densification process of agglomerated powder compacts were discussed by Lange [15]. He concluded that grain growth and rearrangement processes were the two phenomena which controlled their densification, and that the following type of rearrangement process was detrimental to densification: interconnecting packing units that have more contacts per unit volume than the average shrink faster than the compact as a whole to produce fissures [15]. This difference in shrinkage may tend to increase with increasing packing pressure. This type of effect of inhomogeneous packing may be one of the main causes of the lower sintered density after compacting at higher pressures in the sintering of UFPs.

## Acknowledgments

The author thanks R. Konno for his help with part of the experiments. He also acknowledges the helpful suggestings of Y. Muramatsu, S. Ohno, K. Halada and T. Uchikoshi.

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