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Field-assisted sintering of Ni nanopowders

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Abstract

Ni nanopowders were sintered by a field-assisted sintering technique (FAST). The influence of heating rate from 90 to 1100 °C/min on densification and final grain structure of sintered Ni was studied. A moderate heating rate was found to be beneficial for the densification of Ni nanopowders, whereas a high heating rate was conducive to a lower final density. Very high heating rates resulted in non-uniform densification of the samples and formation of cracks during sintering. Electric field activation and possible densification mechanisms are discussed.

Keywords: Nanopowder; Sintering; Densification; Grain; Cracks

1. Introduction

The large surface area of nanopowders provides a strong driving force for both sintering and grain coarsening. Consolidation of nanopowders has been extensively studied using different techniques to preserve the nanoscale structure in the fully sintered product [1]. Generally, it is difficult for conventional sintering techniques to restrain grain growth, due to the long dwell time at high temperature.

The densification mechanisms during conventional sintering of Ni are well established. It was reported that the particle size of the initial powder is critical to determine the dominant mass transport mechanisms during sintering [2]. When the powder size decreases from 10 to 0.1 μm, the combined effects of surface and grain boundary diffusion prevail over volume diffusion. An essential part of Ni powder sintering is the degassing and NiO thermal dissociation (in a neutral atmosphere) or reduction (in a reducing atmosphere such as hydrogen) from the surface of the powders. For coarse powders, degassing starts before the densification, whereas for nanopowders, it coincides with the densification onset. This is due to the lower sintering temperature often required for nanoscale materials [1,2]. The low values of activation energy of degassing suggest that the gases on the surface of Ni nanopowders are mostly H_2, CO, and N_2 [2]. Based on thermogravimetric and dilatometric analysis, Arsentyeva et al. came to the conclusion that dissociation of NiO on the surface of the Ni nanopowders activates the mass transport during sintering [2].

Beyond shifts in the magnitude of the mass transport mechanisms, the sintering behavior of nanoparticles may be governed by alternative mechanisms. For instance, Andrievski suggests interparticle gliding as a possible densification mechanism during the initial stages of sintering nanopowders [3]. The experimental parameters for Ni densification up to 600–700 °C are in good agreement with the calculations based on interparticle gliding theory [4]. The contribution of the interparticle gliding mechanism to densification was evaluated to be close to 80%, with the balance due to grain boundary and volume diffusion [3].

During conventional pressureless sintering, the high rate of grain boundary migration of the Ni nanopowders leads to anomalous grain growth with grain sizes reaching up to 100 μm [2]. Attempts to suppress the grain growth led to the development of non-isothermal sintering with rapid heating rates. This was done to avoid the low temperature range where coarsening due to surface diffusion dominates densification [5–7]. Skorokhod and Ragulya have shown that in nano-Ni

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densification, the heating rate and heating pattern are critical in determining which of the three mechanisms of pore evolution will occur: coalescence of pores, pore shrinkage, or local pore elimination [8]. To reach high density-levels, it is necessary to avoid the pore coarsening process, which is the main obstacle for achieving full densification. Using non-agglomerated powders to generate a large array of small and uniform pores is the most common method to avoid pore coarsening [1].

The purpose of the present work is to study the influence of an electric field on the densification of Ni nanopowders using a newly developed field-activated sintering technique (FAST). This method has been successfully used for the consolidation of nanopowder systems with limited coarsening of the microstructure [9–12].

2. Experimental

Ni nanopowders produced by microwave plasma synthesis from Materials Modification, Inc. (Fairfax, VA) were used. This powder had a nominal reported particle size of 50–80 nm. Sintering was performed using a Spark Plasma Sintering machine (SPS – Sumitomo, Japan) with pulsed DC voltage (2–4 V; pulsing cycle: 12 pulses on/2 pulses off, pulse duration 3 ms). Constant amounts of powders were loaded into a graphite die-punch unit to sinter disc-shaped samples. The current is transferred to the metal powders by of the upper and lower graphite plungers. All experiments were conducted in a vacuum with a pressure of 3 Pa (22 mtorr) and an applied uniaxial pressure of 45 MPa. The powders were also sintered without vacuum using the Plasma Pressure Compaction (P^2C) at the Army Research Laboratory. In this machine, a pulsed current of 1000 A was applied for 10 min, then a constant DC current of 2000 A and 40 MPa of pressure were applied to achieve consolidation.

Using both consolidation methods, samples were sintered at temperatures ranging from 520 to 1000 °C with heating rates ranging from 90 to 1100 °C/min. The temperature was measured by a thermocouple inserted into an opening in the die wall to a depth of 1/2 of the wall thickness. The variation of heating rates was achieved by using current intensities between 600 and 4000 A.

The SPS-sintered samples were discs with a diameter of 19 mm and thickness 5 mm. The specimen sintered in the P^2C machine was 25 mm in diameter. The density of sintered samples was measured using Archimedes' method. Structural analysis of the powders was performed using a conventional TEM (Philips CM 12 operating at 100 kV with a spatial resolution of 3.5 Å). X-ray diffraction (XRD) analysis was performed on an Automated Scintag X-ray diffractometer. The structure of sintered samples was analyzed using a TEM (JEOL 002B) microscope running at 200 kV with spatial resolution 1–4 Å. The samples for TEM analysis were prepared by electropolishing in 10% perchloric acid, 15% acetic acid, 75% methanol electrolyte with the following parameters: temperature 20 °C, voltage 30 V, and current 0.6 A. To analyze the structure of the fracture surface, the samples were cooled in liquid nitrogen and then fractured. The microstructures of fractured samples were studied using an ISI DS130 SEM microscope at a voltage of 20 kV.

3. Results

TEM analysis of initial Ni powders showed that the individual particles are spherical in shape and loosely agglomerated (Fig. 1). The particle diameter is in the range 7–230 nm, with an average size of 70 nm and a standard deviation of 45 nm [13]. The XRD revealed a small quantity of NiO phase in the powder (Fig. 2).

The evolution of FAST densification as a function of time and temperature is shown in Fig. 3. Densification starts at relatively low temperature, i.e. around 230 °C (at 90 °C/min), and proceeds with a high rate from the very beginning (Fig. 3a). The densification rate in the initial stage of sintering decreases when heating rate increases (Fig. 3b) Densification is complete when a temperature of 520 °C is reached for both heating rates. The final densities and grain sizes of FAST-sintered Ni

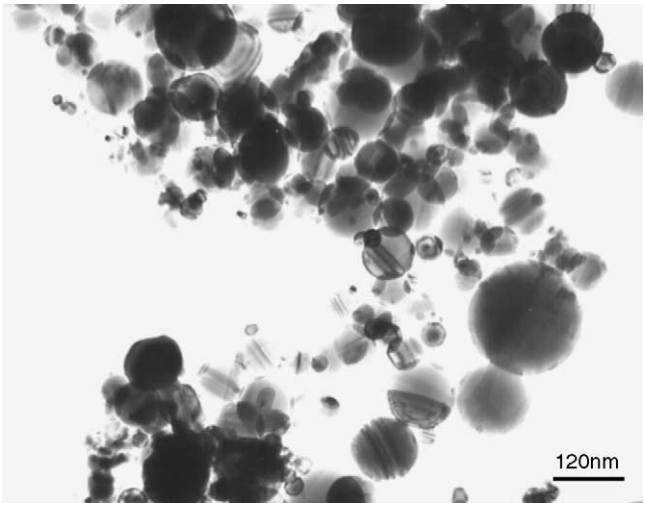

Fig. 1. TEM image of Ni nanopowders.

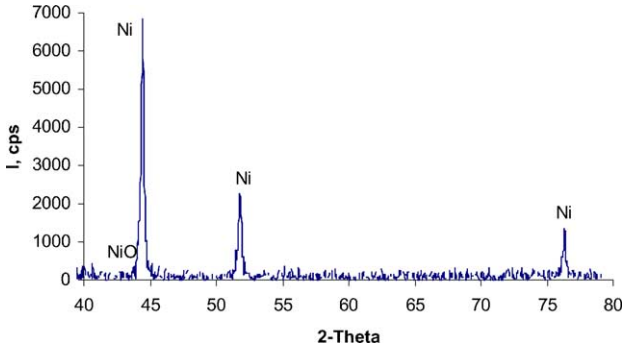

Fig. 2. XRD pattern of Ni nanopowder.

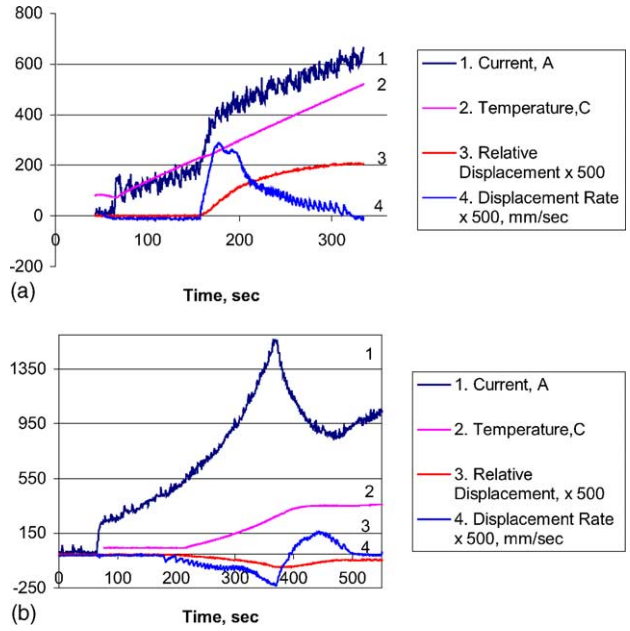

Fig. 3. Current (1), temperature (2), shrinkage (3) and shrinkage rate (4) during FAST sintering of Ni nanopowders: (a) heating rate 90 °C/min, (b) step heating rate variation 210 °C/min (temperature range 145–350 °C), 50 °C/min (temperature range 350–520 °C).

Table 1
Densities and grain sizes of sintered Ni as a function of temperature and heating rate

Temperature (°C)	Current (A)	Heating rate (°C/min)	Final density (%)	Grain size (nm)
520	600	90	95.0	150
	1450	210	91.3	100
	4000	1100	90.0	100
700	1600	50	96.0	250
1000*	2000	210	92.2	2000

* P^2C machine used; the other specimens were sintered using SPS machine.

are shown in Table 1. The grain size of the samples sintered at 520 °C is in the range 100–150 nm (Fig. 4). The higher sintering temperatures induce grain growth. For the samples sintered at 1000 °C, the grain size reaches 2 μm.

The analysis of the cryogenic fracture surface shows that the samples undergo intergranular fracture revealing grains with randomly scattered pores mostly on the grain boundaries (Fig. 5). In the samples sintered at high heating rate**,** some melting of the small grains was observed, and large cracks in the form of semicircles were distributed from the edges to the center of the samples.

4. Discussion

Generally, in the sintering of powdered metals, the surface free energy may be decreased by either decreasing the pore volume or changing the pore curvature while the pore volume remains constant. To achieve a high sintered density**,** the first

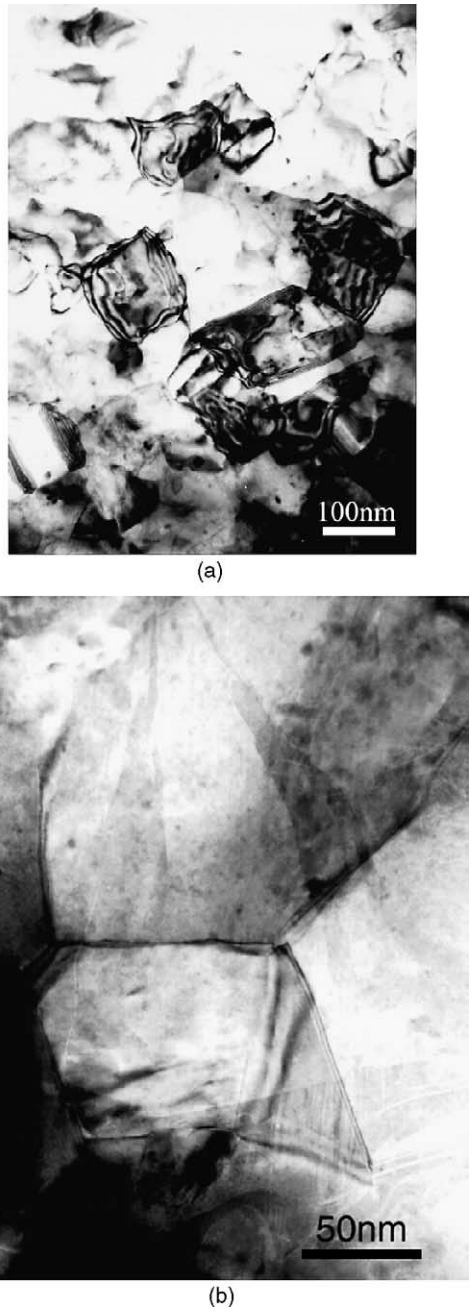

Fig. 4. TEM micrograph of the FAST sintered Ni samples at temperature 520 °C and heating rate (a) 90 °C/min, (b) 210 °C/min.

process should be enhanced while the second is suppressed. In conventional sintering**,** grain growth is suppressed due to grain boundary pinning by open pores. Growth of large pores at the expense of the small pores diminishes the pinning effect and grain growth is usually observed beyond the intermediate stage. Therefore, intense grain coarsening is usually observed in the late sintering stages.

During non-isothermal sintering of spherical particles, Skorokhod and Ragulya calculated the surface area change resulting from volume and grain boundary mass transport during the pore coalescence and densification stages [8]. Pore

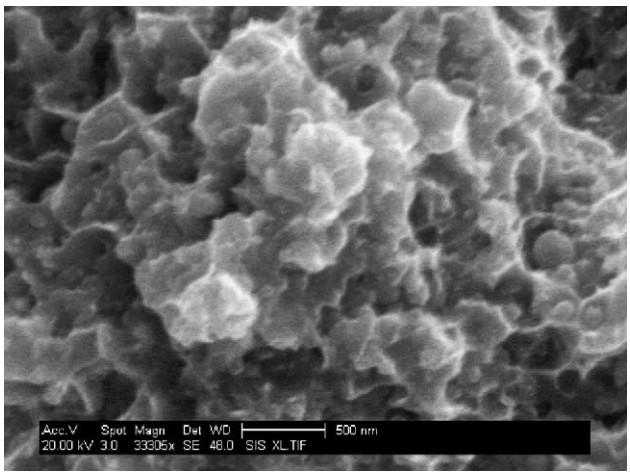

Fig. 5. Fracture surface of Ni sintered at 520 °C at a heating rate of 1100 °C/min.

coarsening dominates at low temperature and results in slow surface area reduction. At high temperature, the densification mechanisms are the main contributors to the surface area reduction of the pores. They confirmed this behavior during conventional sintering of Ni nanopowders and found that the heating rate is an important factor. At slow heating rates, the surface diffusion and, consequently, pore coalescence are predominant. To suppress pore coalescence at low temperature, they suggested that Ni nanopowders be sintered with a heating rate of at least 48 °C/min or higher. Above this heating rate, the densification mechanisms prevail. The small pore size and absence of large grains in the microstructure of FAST sintered Ni at 50 and 210 °C/min suggest the favorable influence of electric field sintering on the shrinkage of large pores. In addition to a fast heating rate due to direct current application, Raichenko showed that when an external electrical current is applied, a temperature gradient exists in the vicinity of small and large pores during the intermediate and late stages of sintering [14]. This temperature gradient is a result of a higher electrical current density next to a large pore as compared to a small one. The large pores shrink due to vacancy diffusion from large to small pores. This is contrary to conventional sintering, in which an increase in the large pore volume is observed [8].

At low temperatures (520 °C) minimum coarsening is observed in FAST sintered samples. As expected, an increase of sintering temperature intensifies grain growth. Similar to conventional sintering, grain growth and densification by FAST sintering occur concurrently. The fast heating rates specific to field-activated sintering proved to be an effective means to further favor densification over grain growth in coarsening sensitive ceramics (i.e., with higher activation energy for densification than coarsening, such as Al_2O_3 [15]). In the case of Ni powders, an increase of the heating rate resulted in a slightly smaller grain size (Table 1). Grain growth occurred at higher temperatures and the resulting density of specimens is low (e.g., 92.2% at 1000 °C) as compared to the expected trend observed at lower temperatures. The wide particle size distribution of the initial powders may have also contributed to grain growth. The high heating rate due to application of high currents may also cause local temperature gradients and local inhomogeneous densification. In conventional sintering of nanopowders with high heating rates, Skorokhod and Ragulya observed different rates of local and integral densification due to local temperature gradients [8]. For FAST sintering of electroconductive materials, an important issue is the uniformity of the electrical current [16]. In the early stages, when the relative density of the powder is low, the amount of interparticle contacts varies significantly. As a result, concentration of the current along discrete favorable paths is possible. The efficiency in powder packing is reduced for nanometer size powders, thus increasing the possibility of non-uniform conducting paths. Usually, this unfavorable localization of the electric current in the compact is effectively eliminated by the application of pressure. The combination of these unfavorable conditions — inefficient powder packing, high heating rates with shorter times for particle rearrangement, early start of sintering, and insufficient pressure (as will be shown later) — may collectively contribute to the low sintered densities and specimen cracking at high heating rates (210 °C/min).

Arsentyeva et al. [2] showed that the linear shrinkage of the Ni nanopowder samples coincides with the end of the thermal dissociation of NiO films on the particle surface (at 290 °C) during conventional sintering. Sparking and a possible plasma formation in the initial stages of FAST sintering may result in surface oxide decomposition and cleaning of the powder surface [9]. The fast heating rates may be favorable for interparticle gliding during sintering of Ni nanopowders. As already shown, Andrievski attributed the accelerated densification kinetics of Ni nanopowders during conventional sintering to interparticle gliding [3]. In FAST sintering with a reasonable heating rate, the interparticle bonding is weak, and the particles may be easily re-arranged by the applied pressure. At high heating rates (i.e., higher current application), high-density electrical discharges may lead to welding of the particles, thus preventing particle gliding. This may account for a lower degree of densification at the beginning of sintering and a shift of most densification events to higher temperatures. At temperatures higher than 350 °C, the diffusion-governed mechanisms become not only active but also more intense local creep at particle contact areas and Joule heat generation may contribute to higher densification rates (Fig. 3). Recent studies showed that the applied current enhances solid-state diffusion by increasing vacancy mobility [17]. This enhanced mass transport during FAST sintering results in powder densification before a dwell temperature is reached. In contrast, conventional sintering of Ni nanopowders takes 2 h of isothermal holding at 1100 °C [2]. This long dwell time at high temperature leads to an exaggerated grain growth of up to 100 μm.

The microstructure formed in the initial stages of sintering is critical for achieving a high final density. Dense packing

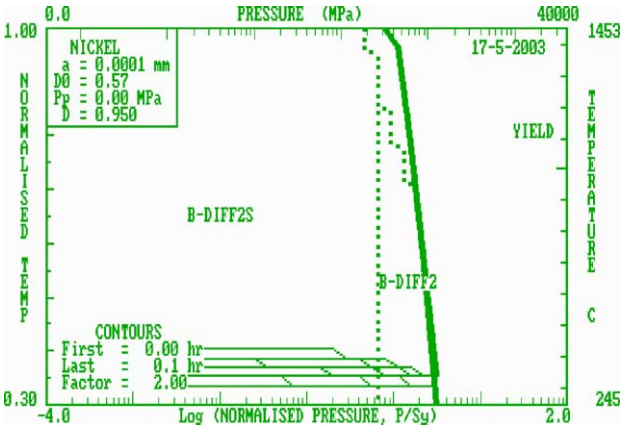

Fig. 6. Densification map of Ni powder with a particle size of l00 nm.

due to interparticle gliding leads to high initial densities and microstructures with a more narrow distribution of pore sizes. On the other hand, the microstructure of the powder system with limited gliding is highly irregular, with larger pores that are difficult to eliminate in the late stages of sintering. This may account for the lowest final density of FAST sintered Ni samples at highest heating rates (1100 °C/min).

To evaluate the pressure contribution on densification of Ni nanopowders, an Ashby densification map was built using the parameters used in the FAST experiments and initial particle size of 100 nm (Fig. 6) [18]. This map shows little influence of the applied pressure (45 MPa) on Ni densification, which is controlled primarily by surface tension-driven diffusion along interparticle boundaries, regardless of sintering temperature. In this case, the applied pressure role in FAST may have been mostly in avoiding an unfavorable localization of the electric current through the densifying nanopowders.

5. Conclusions

FAST sintering was shown to enhance the densification rate of Ni nanopowders. In the initial stage, the current application may generate sparks at particle-to-particle contacts, thus enhancing the dissociation of oxide films. This dissociation activates the surface of the particles and accelerates interparticle bonding, but seems to hinder particle rearrangement and gliding. In intermediate and late sintering stages, enhanced mass transport and favorable temperature gradients result in faster elimination of large pores than in conventional sintering. This way, FAST densification may be completed at relatively low temperatures.

The heating rate was found to be critical for the process of interparticle gliding. At high heating rates, the intense current application hinders particles gliding, thus decreasing the rate of densification. The grain size of the Ni sintered at low temperature (520 °C) remains close to that of the initial powders. When the sintering temperature is increased to 1100 °C, considerable coarsening of the microstructure is observed.

Acknowledgments

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