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Original Research Paper

Elimination of oxide films during Spark Plasma Sintering of metallic powders: A case study using partially oxidized nickel

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ABSTRACT

We present a case study addressing the issue of surface cleaning of the particles of metallic powders from oxide films during Spark Plasma Sintering (SPS). Based on the results obtained using an intentionally oxidized powder of carbonyl nickel (O/Ni(at.) = 0.2), we show that when the powder is heated in the SPS chamber but is not in direct contact with graphite foil commonly used in the SPS practice, the reduction of the oxide is limited to the surface layers of the powder bed. Comparative sintering experiments with graphite and copper foils indicate that a direct contact with a source of carbon is critical for the elimination of the oxide from the sintered compact. Compacts/regions of the compacts, in which nickel oxide NiO was reduced, showed more pronounced inter-particle necking than the regions maintaining the initial oxide concentration.

1. Introduction

Surface cleaning of powder particles from oxides and contaminants is widely accepted in the sintering community as one of the advantages of Spark Plasma Sintering [1]. Although this effect can be easily put forward, experimental evidence of material purification in the form of detected compositional changes of the sintered state relative to the powder state is reported only in a limited number of studies. Model in-situ experiments in a transmission electron microscope were conducted by Bonifacio et al. [2], who observed the formation of oxygen-free metallic necks between nickel nanoparticles covered with a layer of an oxide 2 nm thick subjected to electric bias. Partial reduction during SPS can lead to the formation of oxygen vacancies in oxide materials, as was pointed out by Jiang and Mukherjee [3]. Evidence of reduction of tungsten oxides in the environment of the SPS chamber was obtained as the formation of fine metallic particles on the surface of larger tungsten grains [4] and tungsten wires [5]. Isobe et al. [6] showed that nickel nanoparticles form in a matrix of alumina during SPS of co-precipitated Al_2O_3 and NiO oxides through a reduction reaction in the SPS chamber.

In the present article, we address the issue of cleaning of metallic powders from oxide films during SPS on the scale of the size of the sintered compact, i.e. in the material volumes comparable in size to the sintered object. For this case study, we used an intentionally oxidized carbonyl nickel powder. SPS of nickel powders of different sizes and subjected to different pretreatment procedures before sintering has been addressed in a number of studies [7–11]. The purpose of studies presented in Refs. [7,8,11] was reaching densification while maintaining a fine crystallite size and mechanical property enhancement. Metallic nickel was also studied as a model system to elaborate the features of the microstructure development during SPS as a function of the die dimensions [10]. Powders of a nickel-based alloy were used to investigate the influence of the SPS parameters and particle size on the densification behavior of the material [9]. The issue of the interaction of carbon of the graphite tooling or foil with nickel powders and that of the oxygen content dynamics were not covered in those publications. In the present work, SPS of partially oxidized nickel and characterization of the compacts (composition, microstructure) were carried out for the first time. We showed that for a substantial reduction of the oxygen content in the oxidized Ni powder, direct contact of the compact with graphite foil during SPS is necessary.

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2. Materials and methods

The carbonyl Ni powder (99.9% purity, <20 μm, Norilsk Nickel, Russia) was annealed in air at 400 °C for 30 min. Sintering experiments were also conducted using an ultrafine Ni powder produced by wire electric explosion (WEE) [12] at High Voltage Research Institute, Tomsk Polytechnic University, Russia. Spark Plasma Sintering was carried out using a SPS Labox 1575 apparatus (SINTER LAND, Inc., Japan). The heating rate was 70 °C min^{-1}, the holding time at the maximum temperature was 3 min. A graphite die with an inner diameter of 20 mm and graphite punches were used. The temperature during the SPS was measured by a thermocouple inserted in a hole in the die wall located at its mid-plane (for a temperature of 600 °C) and by a pyrometer focused on a hole in the die wall (for a temperature of 800 °C). The die/punch assemblies used in the present work are shown in Fig. 1. Sintering under pressure in contact with graphite foil at the flat ends and along the cylindrical surface of the sample was conducted using an assembly schematically presented in Fig. 1(a). The sintering pressure was 10 and 40 MPa. In all experiments, the die wall was lined with graphite foil 250 μm thick. Circles of graphite foil 250 μm thick or copper foil 10 μm thick were placed between the punch and the sample. Annealing of the powder without direct contact with carbon was carried out on the flat end of the lower punch, which was coated with a layer of hexagonal boron nitride (Fig. 1(b)). Sintering under pressure in contact with copper foil at the flat ends of the compact and graphite foil along the cylindrical surface was conducted using as assembly shown in Fig. 1(c). The phase composition of the oxidized powder and sintered compacts was studied by X-ray diffraction (XRD) using a D8 ADVANCE diffractometer (Bruker AXS, Germany) with Cu Ka radiation. Scanning Electron Microscopy (SEM) was carried out using a Hitachi-3400S Scanning Electron Microscope working at 30 kV (Hitachi, Japan) and equipped with an Energy-Dispersive Spectroscopy (EDS) unit (NORAN Spectral System 7, Thermo Fisher Scientific Inc., USA). EDS was used to determine the O/Ni ratio in the powders and sintered materials.

3. Results and discussion

The O/Ni atomic ratio in the initial (non-oxidized) nickel powder was determined to be 0.05 (Table 1). The SEM image, XRD pattern and EDS of the oxidized nickel powder are presented in Fig. 2. The XRD pattern of the powder (Fig. 2(b)) shows reflections of the NiO phase. The O/Ni atomic ratio in the oxidized powder increased to 0.20 (Table 1). The oxidized powder has a black color, as can be seen from Fig. 3(a), while the non-oxidized carbonyl nickel powder is gray. A change of color[1] of the powder annealed in the SPS chamber at 800 °C using an assembly without the upper punch can be seen from Fig. 3(a). In this experiment, a layer of the powder about 1 mm thick was placed on the flat end of the lower punch coated with a boron nitride layer. After annealing in the SPS chamber, the surface of the powder layer turned gray. When the central part of the sample was stirred with a glass rod, the powder of black color was revealed (Fig. 3(a)). The O/Ni measured on the gray surface was 0.02, which is even lower than in the initial non-oxidized powder, while that measured on the black regions was 0.07 (Table 1). The surface morphology of the particles in the black areas is different from that of the particles found in the gray areas: the former show fine grains of the oxide phase covering the surface (Fig. 4(a and b)), while the latter have smooth surfaces (Fig. 4(c and d)). This experiment shows that when the powder is heated in the SPS chamber but is not in direct contact with

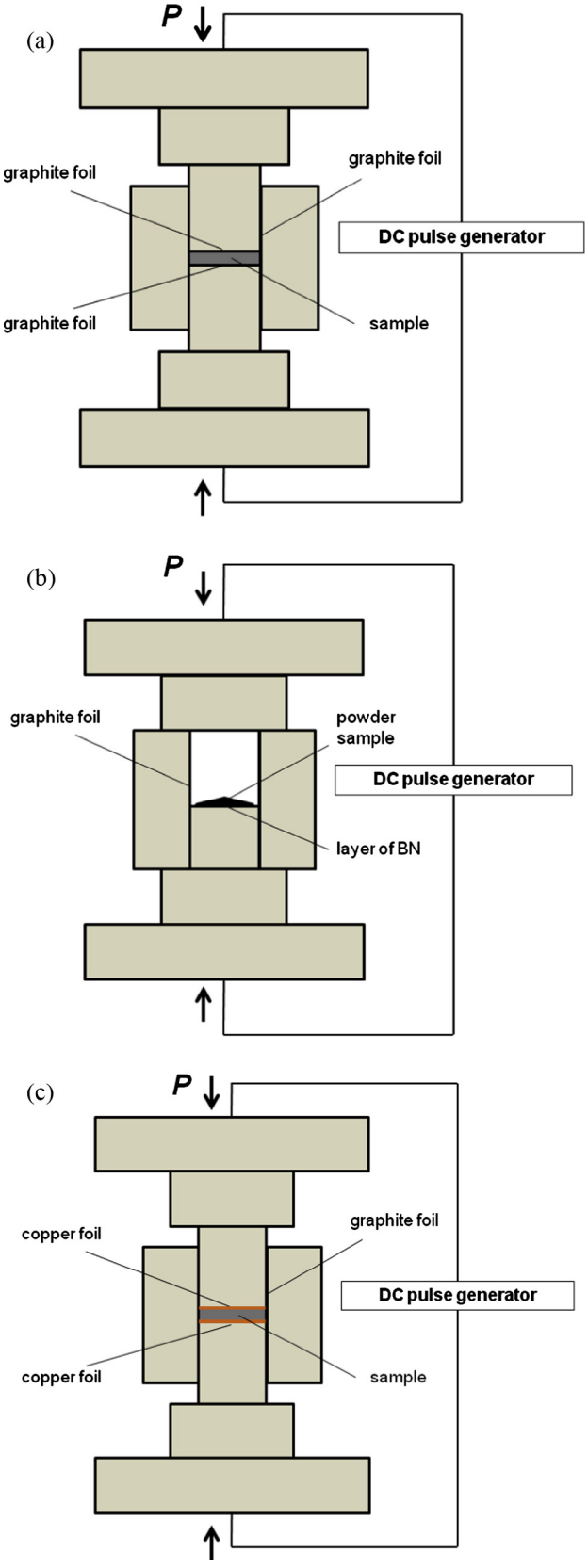

Fig. 1. Sintering and annealing of the partially oxidized nickel powder using a SPS die/punch assembly: (a) sintering under pressure in contact with graphite foil at the flat ends and along the cylindrical surface of the compact, (b) annealing on the flat end of the lower punch, (c) sintering under pressure in contact with copper foil at the flat ends of the compact and graphite foil along the cylindrical surface.

[1] For interpretation of color in Figs. 1–4 and 6, the reader is referred to the web version of this article.