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## Interaction of metallic alloys and partially oxidized metals with graphite foil during Spark Plasma Sintering

Dina V. Dudina<sup>1,2\*</sup>, Boris B. Bokhonov<sup>2,3</sup>, Arina V. Ukhina<sup>2</sup>, Vyacheslav I. Mali<sup>1</sup>,  
Alexander G. Anisimov<sup>1</sup>

<sup>1</sup> Lavrentyev Institute of Hydrodynamics SB RAS, Lavrentyev Ave. 15, Novosibirsk, 630090, Russia; <sup>2</sup> Institute of Solid State Chemistry and Mechanochemistry SB RAS, Kutateladze str. 18, Novosibirsk, 630128, Russia; <sup>3</sup> Novosibirsk State University, Pirogova str. 2, Novosibirsk, 630090, Russia

\*Corresponding author: dina1807@gmail.com

### Highlights

- Diffusion of carbon into a Ni-W alloy causes the formation of WC and Ni<sub>2</sub>W<sub>4</sub>C during SPS.
- Reduction of oxide films on metal particles during SPS is due to the presence of carbon.
- During SPS, the presence of carbon affects materials, in which it can dissolve.

### 1. Introduction

In the practice of Spark Plasma Sintering (SPS), tooling and protective foil are normally made of graphite. The influence of carbon on the elemental and phase composition of the sintered materials is an important issue in the SPS processing. Carbon uptake and partial reduction of oxides caused by the presence of carbon can occur within distances comparable to the total thickness of the sintered pellet. Until now, a number of papers have been published that tackle this problem and look into possible mechanisms of carbon accumulation in the sintered specimens (solid-state diffusion and evaporation-condensation at high temperatures) [1-5]. In our work, we used metallic alloys [6-7] and partially oxidized metal powders [8] to study the factors governing the formation of carbide phases and reduction of oxide films during the SPS.

### 2. Methods

SPS of the powders was carried out using a SPS Labox 1575 apparatus (SINTER LAND Inc., Japan). Ni-15at.%W and Cu-15at.%W alloys were prepared by mechanical alloying of the powders in a high-energy planetary ball mill [6]. A Ni+W powder mixture of the same composition as the alloy was used for comparison [7]. Partially oxidized metal powders were obtained by annealing commercially available copper and nickel powders in air [8]. X-ray diffraction, metallographic etching, scanning electron microscopy, energy dispersive spectroscopy and elemental mapping were used to characterize the sintered materials. Microhardness of the compacts sintered from the Ni+W mixture and Ni-W alloy was measured and compared.

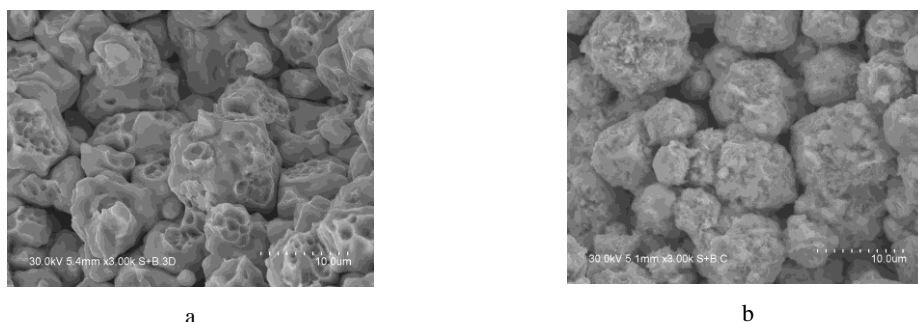
### 3. Results and discussion

In the Ni-W system, tungsten forms stable carbides whereas nickel can dissolve carbon and act as a medium (matrix) for carbon diffusion into the interior of the specimen. During ball milling, a Ni(W) solid solution formed while defects accumulated in the alloy. A highly defect state of the alloy and an expanded lattice of nickel facilitated dissolution of carbon and its inward diffusion. In a compact Spark Plasma Sintered at 900 °C from the mechanically alloyed Ni-W, carbon uptake resulted in the formation of tungsten carbide WC particles ranging from 0.2 μm to 2 μm in the subsurface layers of the compact — within distances 50-100 μm from the interface with the foil [6]. Furthermore, it was not only the subsurface layer of the specimen that was affected by the presence of carbon: particles of Ni<sub>2</sub>W<sub>4</sub>C were found at depths greater than 100 μm from the interface and throughout the rest of the specimen volume (the specimen thickness was 3 mm). The distribution of the submicron WC particles and particles of Ni<sub>2</sub>W<sub>4</sub>C corresponded to a network of boundaries between the Ni-W agglomerates. These boundaries offered paths for faster diffusion of carbon from the foil compared with the volume of the agglomerates. The evolution of the microstructure and phase composition of the compacts was also investigated for a simple mixture of Ni and W powders. For both Ni+W and Ni-W, tungsten carbide WC formed in the layer adjacent to the graphite foil. However, in the case of the mixed powders, the phase composition of the sample's interior remained unaffected by carbon [7].

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A difference in the phase composition resulted in a difference in the microhardness of the compacts: the compacts Spark Plasma Sintered from the mechanically alloyed Ni-W powder were much harder (620 HV) than the compacts produced from the mixed powders (315-370 HV). Experiments with the Cu-W alloy showed that it is not the presence of the carbide-forming element that determines the character of interaction of carbon with the sintered material, but the ability of the matrix metal to dissolve carbon. Indeed, no tungsten carbide-containing layer formed when the Cu-W powder was Spark Plasma Sintered under the same conditions, which was due to the fact that carbon is virtually insoluble in copper.

SPS of the partially oxidized nickel powder in contact with graphite or copper foils indicated that a contact with a source of carbon is necessary for eliminating the oxide films [8]. In compacts sintered from a partially oxidized nickel powder in contact with graphite foil, inter-particle necking was more pronounced than in compacts sintered in contact with copper foil (Figure 1). While NiO was reduced through the compact thickness (3 mm) in the specimen obtained from the partially oxidized nickel powder, reduction of Cu<sub>2</sub>O contained in the partially oxidized copper powder during SPS was limited to a thin layer adjacent to the graphite foil. This result agrees with results obtained for the Ni-W and Cu-W systems in terms of the influence of the nature of the matrix metal on the character of interaction of the sintered material with carbon.



**Figure 1.** Fracture surface of compacts sintered from a partially oxidized nickel powder in contact with graphite foil (a) and in contact with copper foil (b) [8]. SPS temperature 800 °C, pressure 10 MPa. The copper foil acts as a barrier for carbon inward diffusion from the graphite punch.

## 4. Conclusions

Experiments with a Ni+W powder mixture, mechanically alloyed Ni-W and Cu-W powders and partially oxidized nickel and copper powders have shown that the degree of carbon uptake and the degree of reduction of oxides during SPS depend on the ability of the matrix metal (Ni or Cu) to dissolve carbon, which can be enhanced by the defect state of the metal. Under sintering conditions commonly used in the SPS processing of metallic powders, a direct contact with a source of carbon is needed for efficient elimination of oxides from the sintered material.

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## Keywords

Carbon; carbides; microstructure; oxide reduction.