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Interdiffusion between copper and nickel powders and sintering map development during spark plasma sintering

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An investigation into spark plasma sintering was performed using Cu–Ni powder blends. Pucks were sintered between 700 and 900 °C. Isolated copper particles were analyzed by energy-dispersive spectroscopy. Compositional maps and diffusion coefficients showed that diffusion was uniform in all directions, while activation energies demonstrated an increase in diffusion efficiency. A solution to the diffusion equation was used to model sintering times to obtain homogeneous components, given various powder blend compositions, and the results were experimentally validated.

Keywords: Spark plasma sintering; Copper; Nickel; Diffusion

Sintering is based on the phenomenon of atomic diffusion. Various non-conventional sintering techniques are currently being investigated in order to reduce sintering time and cost. One such technique is spark plasma sintering (SPS), which uses a pulsed DC current to induce joule heating between powder particles while simultaneously applying a uniaxial compressive force against the powder bed [1]. In order to consolidate metal powders into solid components, atoms of adjacent particles must diffuse through each particle's boundary layer to develop necks which evolve into grain boundaries. In a crystal lattice, diffusion can occur by various processes, one of which is vacancy diffusion, whereby an atom will move to occupy an adjacent empty site denoted as a vacancy [2]. In a two-component system, the existence of a concentration gradient will drive atoms of both species to diffuse from areas of high concentration to areas of low concentration, and diffusion will cease when chemical equilibrium throughout the material is reached [2]. Mixtures of powders of different types are called powder blends and are currently used as a cost-effective alternative to pre-alloyed powders. The Cu–Ni system is a model system for diffusion studies because the two form a complete solid solution while diffusing through vacancies [3]. Previously, the effect of the pulsed DC current in SPS on 1-D Cu–Ni binary diffusion had been studied and it was shown that below 950 °C the current had no effect on the diffusion distance or rate of the species [4]. However, the diffusion kinetics differ in a 3-D system (powder blend), where atoms are free to diffuse throughout a volume, compared to a 1-D system, where diffusion occurs along a line [5]. Therefore, in order to properly assess the diffusional mechanisms of SPS, diffusion between powder particles must be analyzed.

Few studies have been performed on sintering powder blends with SPS and, as such, the relations between the diffusion kinetics and the processing parameters are still not well understood, precluding inhomogeneous microstructures and partial diffusion-based phase transformations. Sun et al. studied SPS of Ti–Al powder blends by employing a two-step annealing program [6]. The effects of current on the phase transformations and microstructure were studied, whereas the current effect on atomic movement was not addressed [6]. Murakami et al. showed that inhomogeneous microstructures developed during short SPS trial times using a Nb–Al powder blend, while no investigation into the diffusion mechanisms was presented [7].

This study will bridge the gap between diffusional mechanisms in SPS of powder blends using the Cu–Ni system. A blend consisting of 10% copper was used in order to observe the diffusion of a single copper particle in a nickel matrix. Experiments performed at various temperatures akin to sintering yielded concentration maps used to assess diffusion coefficients and activation energies, permitting a better interpretation of diffusion progression during SPS. The results were used to develop SPS sintering predictions for Cu–Ni powder blends using a conventional diffusion model.

Spherical −100 + 325 mesh 99.9% pure copper powder and 99.8% pure nickel powder obtained from Alfa Aesar were blended to obtain a powder mix of 10 wt.% Cu and 90 wt.% Ni. Using a Thermal-Technology 10-3 SPS press, the powder blend was sintered into 20 mm diameter pucks

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with a thickness of 5 mm. Experiments were performed at 700, 800 and 900 °C for 30 min. The pucks were then cross-sectioned and polished down to a 1 μm finish using standard metallographic procedures. A Hitachi SU3500 scanning electron microscope was used for chemical analysis. Energy-dispersive spectroscopy (EDS) was used to obtain chemical composition maps of the area containing the copper particle. Intensities were obtained in terms of number of counts from the EDS detector, and the Horny and Gauvin method was used to obtain the corresponding weight fractions of copper [8]. This method employs a Monte Carlo simulation of the electrons' interactions with the material to obtain a correction curve. This curve is then applied to the relative intensities to obtain the appropriate weight percentages [8]. The weight percentages of copper were plotted as a 2-D map to show the area of copper diffusion. Diffusion coefficients were obtained parallel and perpendicular to the applied current, from low to high copper concentrations through the Sauer–Freise den Broeder method [9]. These concentration dependent diffusion coefficients were calculated through the following equation:

$$D(C') = \frac{1}{2t\left(\frac{dC}{dx}\right)_{x'}}\left[(1-\psi)\int_{x'}^{\infty}(C'-C_R)dx + \psi\int_{-\infty}^{x'}(C_L-C')dx\right] \quad (1)$$

Here, $\psi = \frac{C'-C_R}{C_L-C_R}$, C' is the concentration at which the diffusion coefficient is to be calculated, and C_L and C_R are the concentrations at the extremities. Activation energies were obtained by the Arrhenius plot of the diffusion coefficients. Finally, the time to obtain a fully homogenized component was calculated using the homogenization model solution to the diffusion equation. In order to validate the results of the model, X-ray diffraction (XRD) with a silicon standard was performed using a Bruker D8 X-ray diffractometer with a copper source. Spectra were obtained for both the pure copper and nickel powders, and a powder blend of 50 wt.% Cu, sintered at 900 °C for 5 and 30 min. Lattice parameters were subsequently calculated from the XRD data. Vegard's law was applied to calculate, from the starting powders, the linear change in lattice parameter with composition [10]. The lattice parameters of the sintered pucks were compared to the linear fit in order to determine whether the elements were uniformly distributed.

Representative contour maps of copper concentrations under all conditions are shown in Figure 1.

Given that diffusion is a thermally activated process [2], as the sintering temperature increases, the greater diffusion area causes a larger change in particle shape. The circularity of the particle decreases at each temperature while the diffusion area increases. Under all conditions, diffusion is uniform from the center of the original copper particle outward. The homogeneous copper concentration rings surrounding the particle suggest that there is no high diffusion path in any specific direction, and hence no directional effect of the electric field. Studies performed using electric discharge sintering, a form of field-assisted sintering, showed that necking occurred more quickly parallel to the current than perpendicular to it [11,12]. This sintering method uses high voltages and current densities on the order of 10^7 A/cm^2 in order to create a discharge that induces melting, particle wetting and electromigration [11,12]. Current densities attained in SPS for the temperatures used in this experiment are 250 A/cm^2 on average, which are too low to incite any electromigration effects [13,4]. Without such high current and high voltage conditions, there is also no melting, and mass transport occurs only through solid-state diffusion [11].

Diffusion coefficients were calculated from the center of the copper particle outward in directions parallel and perpendicular to the current. The results are shown in Figure 2.

Diffusion coefficients parallel and perpendicular to the applied current are similar at 700 and 800 °C. The small difference between the diffusion coefficients in the two

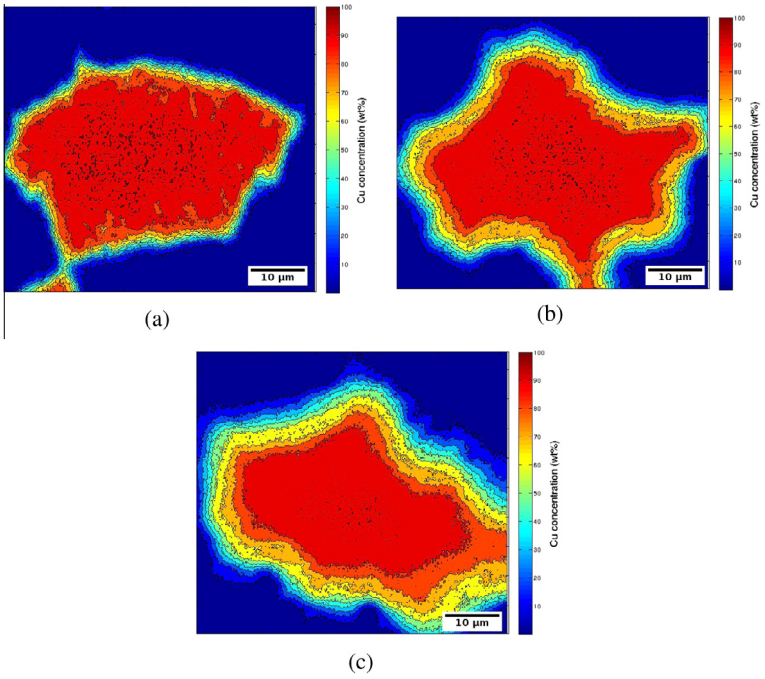

Figure 1. Copper concentration by area for compacts sintered for 30 min at (a) 700 °C, (b) 800 °C and (c) 900 °C.