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PROCEEDINGS OF THE SYMPOSIUM ON SPARK PLASMA SYNTHESIS AND SINTERING

Effect of pulsed DC current on atomic diffusion of Nb–C diffusion couple

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Abstract The effect of pulsed DC current on the atomic diffusion of an Nb–C system using Spark Plasma Sintering (SPS) was investigated. In all experiments, a current density of approximately 723 A/cm^2 was applied to the specimen and used in a temperature range of 1,673–1,973 K. From the results of X-ray diffraction analysis, the product phases formed between Nb and C were found to be Nb_2C and NbC. The growth of product layers significantly increased in the presence of current. However, the thickness of the product layer did not change in the current direction in the SPS. The activation energies for the formation of the Nb_2C and NbC layers were calculated to be 298 ± 4 kJ/mol and 282 ± 3 kJ/mol in the presence of current, which were similar values compared to the activation energies of 300 ± 5 kJ/mol and 285 ± 2 kJ/mol in the absence of current, respectively.

Introduction

The Spark Plasma Sintering (SPS) process, which is also known as pulsed electric current sintering or plasma activated sintering, makes it possible to consolidate metal and ceramic powders at relatively low temperature and in a short time. This process is extensively investigated and utilized in the fabrication of functionally graded materials, intermetallic compounds, and nano-crystalline materials [1, 2]. In this process, low-voltage and high-intensity pulsed DC current can be directly applied to the specimen through graphite die with external pressure. Therefore, the sinterability of powders is improved in the initial part of the sintering cycle by a local spark-discharge process in the vicinity of the contacting particles [3]. Moreover, the cleaning effect of the powder surface (i.e., the elimination of surface oxide films and impurities) by spark or plasma generated between particles also enhanced the sinterability [3]. In addition, grain-boundary diffusion is enhanced by the electrical field originating from the current [4]. But the occurrence of spark or plasma has not been evidently demonstrated yet.

The characteristic role of the current, which is known as electromigration in metal and intermetallic systems, can provide an added driving force to the chemical potential for mass transfer; atomic flux species J_i can be expressed as [5]:

$$J_i = -\frac{D_i C_i}{RT}\left[\frac{RT\partial \ln C_i}{\partial x} + F z^* E\right], \quad (1)$$

where J_i is the flux of the diffusing ith species, D_i is the diffusivity of the species, C_i is the concentration of the species, F is Faraday's constant, z^* is the effective charge on the diffusing species, E is the electric field ($E = \rho j$, ρ is resistivity, and j is current density), R is the gas constant, and T is the temperature. Indeed, investigation of the effect of the current (electromigration) on the Sn–Ag and Sn–Cu diffusion couple was performed, and the mass transfer, which accelerated by passing the current through the sample, was indicated [6–10]. For the investigation of the electromigration effect in an Al–Au multiplayer, the effect of the current on reactivity and diffusivity shows a considerable enhancement of growth rate, nucleation kinetics,

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and point defect mobility [11]. However, under SPS the temperature and current are dependent parameters, and thus the thermal effect of the current (Joule heating) cannot be clearly separated from its intrinsic role.

Recently, the neck growth between copper spheres and plates was investigated under the influence of the current using two different systems (with/without pulsed DC current) due to varying temperature and current parameters independently [12]. The current showed a significant effect on the neck growth between the spheres and the plates, and the enhancement of neck growth under the presence of the current was attributed to electromigration. The effect of the current on diffusion kinetics using the diffusion couple of Mo–Si was also investigated by SPS apparatus [13, 14]. The growth of the product phase formed between Mo and Si showed a strong dependence on the current. The results were explained in terms of the current-induced changes in the growth mechanism arising from changes in the concentration of point defect and mobility. Moreover, for sintering and consolidation, the influence of the current on sintering during SPS was investigated by constitutive modeling using conductive materials such as aluminum [15]. It was suggested that electromigration-related material flux is a considerable component of current-accelerated diffusion. Therefore, the role of the current has been understood in metals and intermetallic compounds, which have a metallic bond. However, the influence of the current on mass transfer and sintering has been barely investigated in cases of electrically conductive ceramics with a comparatively strong covalent bond, even though SPS can consolidate carbide ceramics with a high melting point at a lower sintering temperature for a shorter holding time. As indicated above, it is difficult to separate the thermal influence from the intrinsic role of the current due to the consolidation of carbide ceramics with high melting point, which generally requires heat treatment at high temperature. In this work, the effect of pulsed DC current on the atomic diffusion of the Nb–C system was investigated by diffusion couple at temperatures ranging from 1,673 to 1,973 K.

Experimental procedure

Square Nb (10 mm × 10 mm) and C (10 mm × 10 mm) plates were cut from Nb plate with 99.9% purity obtained from Nilako Co. Ltd., Japan, and C plate with a purity of >98% obtained from SGL CARBON Co. Ltd., Germany. The thickness of each Nb and C plate was 100 μm and 1.0 mm, respectively. The samples consisted of three layers with a single Nb plate sandwiched between two C plates. The three-layer assembly provides both C–Nb and Nb–C interface to investigate the influence of current direction on atomic diffusion. Before assembling each sample, the Nb and C plates were polished with a 2000-grit SiC abrasive paper, rinsed in distilled water, and ultrasonically cleaned by acetone.

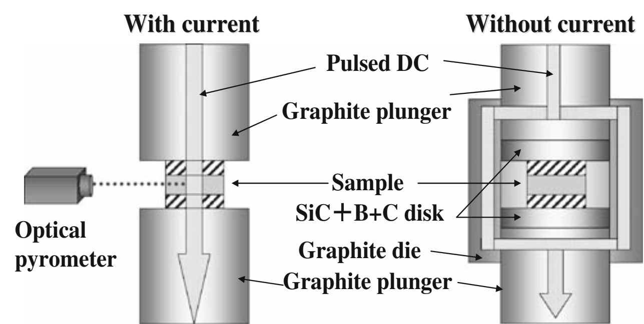


Fig. 1 Scheme of SPS apparatus with current and without current

All experiments were carried out in the SPS apparatus (Model 1050, Sumitomo Coal and Mining Co.). The pulsed cycle of the DC current was 12:2, i.e., 12 pulsed of 3 ms on and 2 pulsed of 3 ms off. Figure 1 shows the scheme of the SPS apparatus and the local setting around the sample: (a) with pulsed DC current and (b) without pulsed DC current. In order to make the current through only the specimen, the graphite die was not used in the presence of the current, as shown in Fig. 1a. In the absence of current, an additional layer as insulator (silicon carbide with boron and carbon: SiC + B + C-disk: 3 mm, φ: 20 mm) was placed on the top and the bottom of the sample to ensure that the current passes through only the graphite die, not the specimen, as shown in Fig. 1b. The SPS program (annealing temperature: 1,673–1,973 K, heating rate: 100 K/min, annealing time: 180–1,800 s) was set, and then the temperature of the diffusion couple was controlled by an optical pyrometer focused on the center of the specimen coated by graphite powders. In all experiments, pressure of 10 MPa was applied to ensure good electrical contact in the whole system. All samples were heat-treated using SPS under vacuum conditions less than 5.0 Pa and cooled to room temperature by turning off the power.

To observe the product layer formed between Nb and C layers, all samples prepared by SPS were sectioned and mounted in conductive epoxy resin. Then 3000-grit SiC abrasive paper and 1-μm diamond paste were used to polish the specimens. Consecutively, all samples were rinsed in distilled water and ultrasonically cleaned by acetone. The layer thickness was measured from backscattered electron images (BEI) taken by scanning electron microscopy equipped with energy dispersive X-ray spectroscopy (EDS) (JSM-5410, JEOL, Tokyo Japan) to calculate the growth rate constant of the product layer and the activation energy for its formation. X-ray diffraction (RINT2500, CuKa radiation operated at 100 mA and

40 kV, RIGAKU, Tokyo) was used as an identification method of the product phase.

Results and discussion

Identification of the product phase

Figure 2a and b shows the BEI micrographs of the product layers formed at 1,973 K for 1,800 s in the presence and absence of the current, respectively. Two different contrasts were clearly found, as can be seen from Fig. 2a and b. Thus, XRD measurement was carried out to identify the product phase. Figure 3a and b shows the XRD patterns of the product layer annealed by SPS at 1,973 K for 600 s in the presence and absence of the current, respectively. In both cases, the product phases formed between Nb and C layers were Nb_2C and NbC. Moreover, the concentration gradient between the Nb and product layers was confirmed by EDS analysis. These results agree with those reported in the literature for growth in the absence of the current [16, 17], and the composition of these phases also corresponded with the Nb–C phase diagram. Thus, in this work, the product phases formed between Nb and C layers were determined by Nb_2C and NbC, which are the stable phases at temperature ranging from 1,673 to 1,973 K.

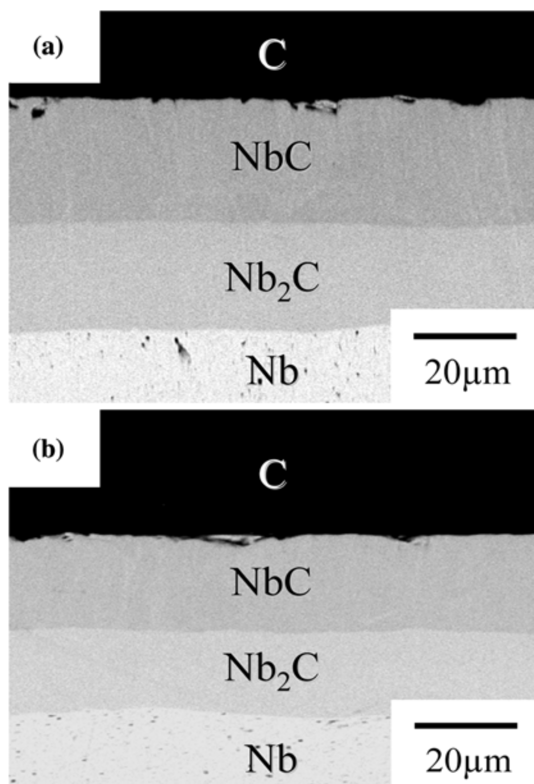
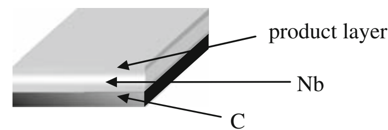


Fig. 2 Back-scattered electron images of the product layer at 1,973 K for 1,800 s (**a**) with current and (**b**) without current



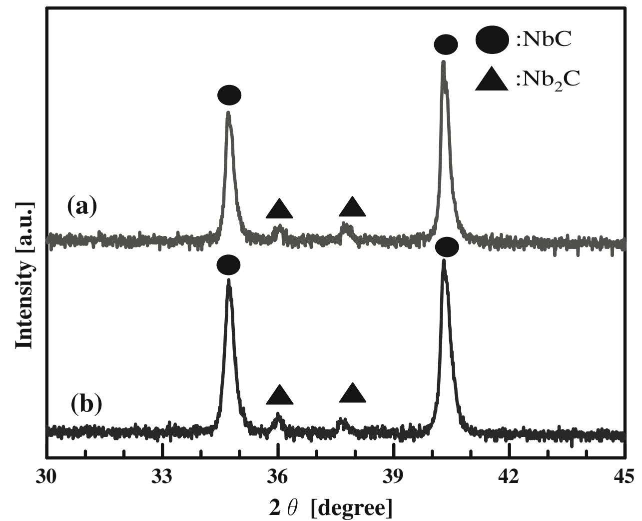


Fig. 3 XRD patterns of Nb–C diffusion couple annealed at 1,973 K for 600 s (**a**) with current and (**b**) without current

The influence of current direction on the product layer thickness

To investigate the current direction on the product layer thickness during SPS, we carried out two different systems (with/without pulsed DC current). In all experimental conditions, the growth of the product layers, which paralleled the interfaces between Nb and C layers, was observed. Since two different layers were found from the XRD analysis results, the thickness of the product layers was measured by BEI. When the specimen was annealed at 1,973 K for 1,800 s in the presence of the current, the thicknesses of the Nb_2C and NbC layers were 18.2 ± 0.5 and 22.3 ± 0.8 μm, respectively. On the other hand, in the absence of the current, the thicknesses of the Nb_2C and NbC layers were approximately 14.7 ± 0.4 and 16.4 ± 0.9 μm, respectively. Regardless of annealing time and temperature, the product layers annealed in the presence of the current were constantly much thicker than those in the absence of the current. The enhancement of product layer thickness was only clearly observed in the presence of the current. Moreover, for metals and intermetallics, accelerated atomic diffusion is asymmetric based on the electron wind force caused by electron movement from cathode to anode [6–8]. In an Sn–Ni diffusion couple system, the thickness of the product layers formed between the Sn and Ni layers was dependent on the direction of the electron transfer [7]. These phenomena have confirmed that the atomic diffusion in the specimen is accelerated due to the

momentum transfer from electron with high energy to metal ion by passing the current through the specimen. In other words, passing the current can provide an added driving force to the chemical potential for diffusion. The electrical force proposed by Huntington is

$$F_{\rm em} = Z^{*}eE = \left(Z^{*}_{\rm el} + Z^{*}_{\rm wd}\right)eE, \quad (2)$$

where e is the charge of an electron and E is the electric field ($E = \rho j$, ρ is resistivity, and j is current density). $Z_{\rm el}^{*}$ can be regarded as the effective valence of the diffusing ion in the metal when the dynamic screening effect is ignored; it is responsible for the field effect, and $Z^{*}_{\rm el}eE$ is the direct force. $Z^{*}_{\rm wd}$ is the charge number representing the momentum exchange effect, and $Z^{*}_{\rm wd}eE$ is the electron wind force and is generally found in the order of 10 for a good conductor; thus, the electron wind force is much greater than the direct force for electromigration in metals [5]. In this work, the influence of current direction on the thickness of the product layer was investigated by varying annealing time and temperature. However, the thickness of the product layer, as measured at the two Nb–C interfaces in the Nb–C diffusion couple, was independent of the current direction, as seen in Fig. 4. This result agrees with recent observations on the growth of intermetallic layers in the presence of the current [11–14, 18]. If the acceleration of atomic diffusion in the presence of the current is dominantly caused by the electron wind force, i.e., the term on the right hand side of Eq. 2, the bottom layer thickness in the Nb–C diffusion couple should be higher than the top layer thickness due to the electron transfer from the bottom to the top electrodes in SPS. In contrast, the direct force,

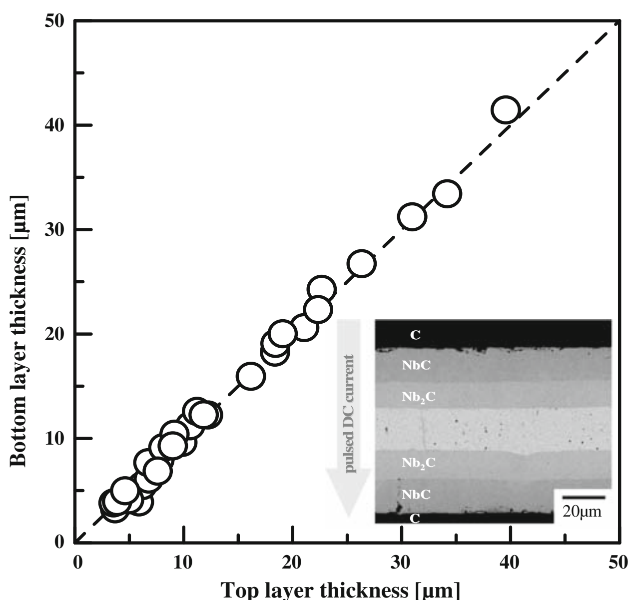


Fig. 4 Comparison between total layer thickness at the two (Nb–C and C–Nb) interface to the direction of the current

i.e., the term on the left hand side of Eq. 2, depends on the intrinsic effective valence of the specimen, and the sign of the effective valance of the C solid-dissolved in Nb is also positive in the presence of the current [19]. In other words, the direction of the diffusion of C dissolved in Nb under the presence of the current is the opposite of the direction of the electron by the influence of the electric field. However, in this work, the difference between bottom and top layer thickness was negligible, which usually results in the intricate diffusion of C and Nb while maintaining the structures of each compound of Nb_2C and NbC. Moreover, according to Munir and co-workers, since the effect of current direction on the growth of intermetallic layers was ignored, the current takes a role for increasing concentration of point defect and enhancing defect mobility [11–14, 18]. Thus, we considered that the current did not influence the direction of the atomic diffusion, but the presence of high dense current enhanced the concentration of point defect and the defect mobility in the layers.

The influence of pulsed DC current on the growth of product layer

The effect of pulsed DC current on the growth rate constant of Nb_2C and NbC was investigated by varying the annealing time and the temperature. In both cases of the system with/without pulsed DC current, the thickness of the product layer increased with the annealing time and the temperature. To calculate the growth rate constant, we used Eq. 3:

$$x^2 = kt, \quad (3)$$

where x^2 is the square of the product layer thickness, k is the growth rate constant, and t is the annealing time.

Figure 5 shows the growth rate constant of Nb_2C and NbC at different temperatures in the presence and absence of the current. In both cases, the growth rate constant of Nb_2C and NbC increased with annealing temperature. When the current passes through the sample, a significant increase in the growth rate constant is observed compared with the absence of the current. The current density applied to the sample in this case was approximately 723 A/cm^2. The growth rate of the product layer was accelerated by passing the current through the sample, and the mass transfer clearly showed a dependence on the current in the Nb–C systems.

To calculate the activation energy for the formation of the product layer, we used an Arrhenius Eq. 4:

$$\ln k = \ln A - \left(\frac{Ea}{RT}\right), \quad (4)$$

where Ea is the activation energy for the formation of the product layer, k is the growth rate constant, A is the

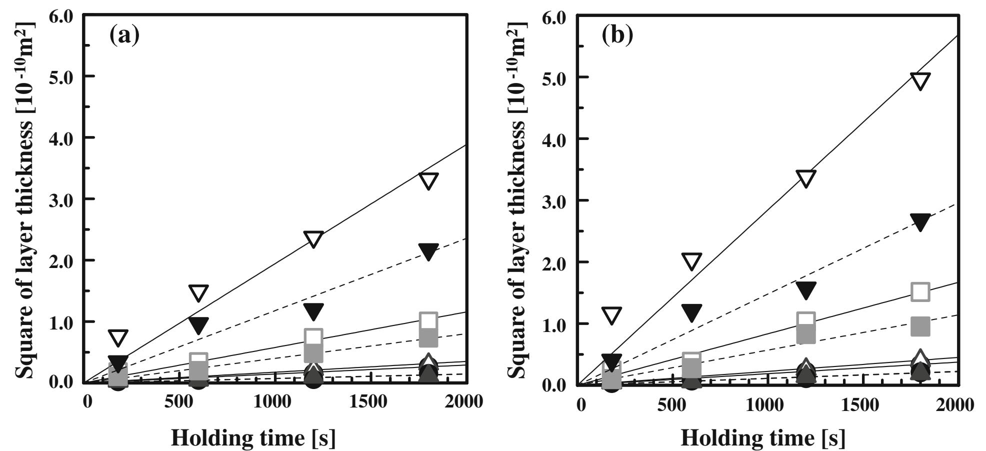


Fig. 5 Product layer thickness of (**a**) Nb_2C versus time and (**b**) NbC versus time for samples reacted at various temperature in Nb–C diffusion couple with current (opened dot) and without current (closed dot)

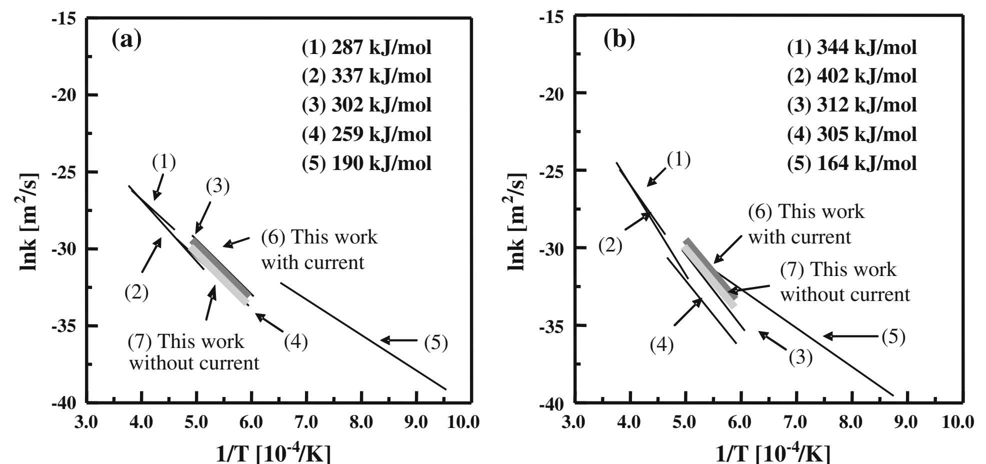


Fig. 6 Temperature dependence of (**a**) Nb_2C and (**b**) NbC growth rate constant as obtained by various investigators [16]

constant, R is the gas constant, and T is the annealing temperature. The temperature dependence of the growth rate constant is shown in Fig. 6 with Refs [1–5] in the literature for activation energy in the absence of the current [16]. In the presence of the current, the activation energies for the formation of Nb_2C and NbC were calculated to be 298 ± 4 kJ/mol and 282 ± 3 kJ/mol, respectively. In the absence of the current, the activation energies for the formation of Nb_2C and NbC were calculated to be 300 ± 5 kJ/mol and 285 ± 2 kJ/mol, which were similar values compared to the activation energies in the presence of the current, and agreed with those reported in literature for the activation energy in the absence of the current [16]. A significant difference in those activation energies was not observed between the two cases, as seen from Fig. 6. These results are in good agreement with Anselmi-Tamburini et al. [14], who investigated the effect of electromigration in a Mo-Si diffusion couple during SPS in which a difference of activation energy for the formation of the product layer between the presence and the absence of the current was not observed. The effect of current on the growth rate constant was significan; however, that on the difference of activation energy was relatively small. In contrast, Garay et al. [20] investigated the effect of electromigration in the Ni–Ti multilayer in which the activation energy for the formation of the product layer decreased drastically with high current density (higher than 1,500 A/cm^2). However, in Nb–C system, the current density was approximately 723 A/cm^2. Therefore, the effect of current on activation energy in the Nb–C diffusion couple system is, probably, observed by increasing the current density. Furthermore, a more recent positron annihilation study on Ni_3Ti indicated that enhanced mobility is the primary effect of the current [21]. That is, the high current enhances the mobility of the generated point defect. Asoka-Kumar et al. [22] provided direct evidence for an increase in vacancy concentration as a result of current treatment. Utilizing positron annihilation spectroscopy, they found that with a current density of 8.0×10^{-4} A/cm^2, the vacancy concentration in Al–Cu was clearly increased compared with the absence of the current . Hence, the growth of the product layers of Nb_2C and NbC increased in the presence of the current as a result of the enhanced defect mobility and the concentration of the point defect.

Conclusion

The effect of pulsed DC current on the atomic diffusion of an Nb–C system during SPS was investigated by diffusion couples at a temperature ranging from 1,673 to 1,973 K. A significant increase in the growth rate constant of Nb_2C and NbC in the presence of the current was observed compared to the absence of the current. The thickness of the produced phase showed the independence on the current direction. The activation energies for the formation of the Nb_2C and NbC layers were calculated to be 298 ± 4 kJ/mol and 282 ± 3 kJ/mol in the presence of the current, which are similar values compared to the activation energies of 300 ± 5 kJ/mol and 285 ± 2 kJ/mol in the absence of the current, respectively. The growth of the product layers of Nb_2C and NbC increased in the presence of the current as a result of the enhanced defect mobility and the concentration of the point defect.

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