The growth kinetic behaviors of the intermetallics at W/Co interface under the current of spark plasma sintering

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Abstract
The interdiffusion behaviors of elements at the W/Co interface under the application of current during SPS were investigated. It is found that Co₇W₆ and Co₃W are formed at the W/Co bonding interface. The growth of the Co₃W layer is apparently improved by the high current during SPS. The growth rate constant of the Co₃W layer under current is 1.73–3.03 times faster than that without current. The research shows that the growth rate is increased with the current density. The growth activation energy of the Co₃W layer is calculated to be 229.51 ± 27 kJ mol⁻¹ under current, which is smaller than that without current (279.38 ± 11 kJ mol⁻¹). Moreover, the growth activation energy of the Co₃W layer is decreased with the increase of the current density. The mechanism of current-improved growth of the Co₃W layer is suggested to be the fact that the current lowers the nucleation barrier of intermetallic layer, which accordingly promotes chemical reactions.

1. Introduction

Due to the coupling of strong electric current, pressure and temperature, spark plasma sintering (SPS) was known of the advantage for low sintering temperature and high sintering speed and high efficiency, which has been wildly used for the preparation of powder metallurgical materials [1]. As a typical rapid sintering technique, the sintering mechanisms during SPS have been disputed for a long time. In recent years, the rapid densification of metallic powder during SPS has been proved to be related to the improved mass transportation by the high electric current [2–4]. Li et al [5] reported that the interdiffusion coefficient of elements at the Fe/Al interface under the electric current is almost 46 times higher than that treated without current. Anselmi-Tamburini [6] investigated the interdiffusion behaviors of Mo–Si system, finding that the diffusion layer at Mo/Si interface is increased obviously by current during SPS. There have been quite a lot of such reports around these years. Nevertheless, so far, there has been no scientific consensus for the mechanisms of current-improved mass transportation. Asoka-Kumar [7] and Kondo [8] thought that the current increases the vacancy concentration and mobility, and subsequently promote atomic diffusion. However, some researchers attributed the current-promoted atomic diffusion to electromigration, which lead to higher diffusivity along the direction of current flow [9–11]. Our previous work found that different types of diffusion systems show different diffusion kinetic behaviors [9]. That is, the mechanisms of current-improved different systems may well be different. Therefore, the study of diffusion behaviors of metals during SPS considering the current effect is regarded as a necessary issue.

In the present work, to enable the understanding of sintering mechanisms and diffusion behaviors of materials during SPS, the W-Co system was chosen as the research object. The growth kinetic behaviors of the intermetallic phase at the bonding interface were investigated. And the current-induced improved growth effect of intermetallics at the interface was discussed.
2. Experimental procedure

In this research, the W (99.95% pure) flakes were processed into the disk of 2 mm in thickness and 20 mm in diameter, the Co (99.95% pure) foil (0.3 mm in thickness) was processed into a disk with a diameter of 20 mm. Before assembling, the W plates were polished with 2000-grit abrasive paper, rinsed with distilled water, and ultrasonically cleaned by alcohol. After surface polishing, the W flakes and Co foil were superimposed with a sandwich structure (W/Co/W) and then placed in a graphite die, as shown in figure 1. The sample-die assembly was then put into the vacuum chamber of the SPS apparatus (HP D25, FCT Systeme GmbH, Rauenstein, Germany). The sintering parameters were set as follows: temperature 1100 °C–1300 °C, heating rate 100 °C min\(^{-1}\), annealing time 1800–3600 s, axial pressure 16 MPa. For comparison, the W-Co interdiffusion experiments were also carried out in a conventional tubular atmosphere furnace (heating rate 10 °C min\(^{-1}\), dwelling time 60–180 min, atmosphere Ar) at the temperature range of 1000 °C–1200 °C. Before traditional annealing, the polished W and Co plates were pre-soldered by hot pressing equipment (heating rate 50 °C min\(^{-1}\), temperature 900 °C) for 1 min.

The W/Co bonding samples were sectioned perpendicular to the diffusion interface and polished using standard metallographic procedures. The layer thickness and element distribution were measured by scanning electron microscopy (SEM, Zeiss Sigma, German) with energy dispersive x-ray spectroscopy (EDS, X-Max SDD, Oxford Instruments Ltd., UK). The electron back scattering diffraction (EBSD, Oxford Aztec HKL Standard NordlysMax2, UK) was used to characterize the orientation of intermetallic grains at the interface.

3. Results and discussion

3.1. The microscopic morphology of W/Co diffusion interface

Figures 2(a), (b) show the microstructures at the W/Co/W interface which is annealed at 1200 °C for 60 min by SPS. It is obvious that two different diffusion layers can be observed: layer I and layer II. The concentration distribution curve of W at the interface was depicted in figure 3. It's apparent that the W element has a long diffusion distance at Co side, but the diffusion distance of the Co element at W side is very short, implying that the diffusion flux from W to Co is greater than that of Co to W side. The concentration of W drops dramatically likes a bluff at the bonding interface, indicating that intermetallics are generated at the interface. The concentration of W at layer I is around 34%, improving that layer I is a typical intermetallic layer. Layer II is suggested to be the solution-diffusion layer because the content of the W element changes continuously in layer II, as shown in figure 3. Moreover, as shown in figure 2(b), there are two distinct types of intermetallic layers in reaction layer I. According to the W–Co binary phase diagram [12], there are only two kinds of intermetallic phases between W and Co: Co\(_7 W_6\) and Co\(_3 W\). The EDS analysis of reaction layer I was conducted to determine the chemical compositions of the intermetallic phases, as shown in figure 4. For the thicker intermetallic phase layer, the atomic ratio between Co and W is close to 3:1. But for the thinner intermetallic phase layer, the atomic ratio between Co and W is close to 7:6. Obviously, it is not difficult to judge that the thinner one is the Co\(_7 W_6\) layer, while the thicker one is the Co\(_3 W\) layer. The thickness of Co\(_3 W\) layer is larger than that of Co\(_7 W_6\), indicating a higher growth rate of Co\(_3 W\) compared with Co\(_7 W_6\).

Additionally, the morphology of the intermetallic layer at the W/Co interface annealed without current is different from that treated by SPS. Unlike the interface bonded by SPS, many Kirkendall Voids exist at the
interface for the sample processed by conventional heating, as shown in figure 2(c). This is because that there is no pressure during the traditional annealing. To compare the growth behaviors of the intermetallics between SPS and traditional heating, the EBSD was used to characterize the size and morphology of the intermetallic grains. Figure 5 shows the band contrast map, phase distribution and crystallographic orientation of intermetallic phase layer annealed by SPS and conventional heating technique. The Co3W grains were generally coarse and equiaxed when annealing without current (figures 5(a), (c), (e)). But for W/Co diffusion couple that annealed with high current, the Co3W grains were almost columnar, which is significantly different from that treated by the traditional method. Moreover, the Co3W grains have a current direction-grown effect during SPS, which is suggested to be related to the electromigration effect. The resistance anisotropy of Co3W grains under the electromigration effect results in the different current densities in different orientations, leading to the anisotropic atomic diffusion in different orientations. The atomic diffusion coefficient is maximum in the
direction of least resistance, ultimately inducing the preferential growth in this direction. The directional growth behaviors and their mechanisms were studied in depth in our previous work [11].

3.2. The growth kinetics of Co3W layer at the W/Co interface
The above research shows that the high current during SPS leads to a unique growth morphology of intermetallic grains, which is significantly different from that processed by the conventional heating method. To investigate the effects of current on the growth kinetics of the intermetallics at the W/Co interface qualitatively, the Co3W layer was selected as the research object. The growth kinetics of the reaction layer obeys a parabolic rate law as follows [8]:

Figure 4. The EDS spectra of reaction layer: (a) SEM morphology; (b) spectrum of boxed region (the thicker layer); (c) spectrum of point A (the thinner layer).

Figure 5. (a), (b) The band contrast map of the diffusion layer that acquired by different heating techniques; (c), (d) The phase distribution of the W/Co diffusion layer that processed by conventional heating method and SPS; (e), (f) The orientations of the intermetallic grains at W/Co interface that annealed by conventional heating method and SPS.
where \( x \) is the thickness of the Co3W layer, \( D \) is the growth rate constant and \( t \) is the time. Therefore, the relation of the square thickness of the diffusion layer and time obeys a linear rate law. The \( D \) can be calculated from the slope of the line obtained by plotting \( x^2 \) and \( t \). The plot of the square thickness of the diffusion layer against reaction time is depicted in figure 6, and the obtained growth rate constant of the Co3W layer for different anneal conditions are listed in table 1.

Obviously, for the same conditions, the growth rate constant of the Co3W layer under current is 1.73–3.03 times higher than that without current, indicating that the growth of Co3W layer is promoted by the high current. The conventional thermal-activated atomic diffusion obeys the Arrhenius relation:

\[
x^2 = Dt \tag{1}
\]

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\[
D = D_0 \exp \left( -\frac{Q}{RT} \right) \tag{2}
\]

where \( Q \) is the activation energy for the formation of the growth layer, \( R \) is the gas constant, \( D_0 \) is the frequency factor, and \( T \) is the temperature. Equation (2) is rewritten in a logarithmic form as:

\[
\ln D = \ln D_0 - \frac{Q}{RT} \tag{3}
\]

The value of \( Q \) can be calculated by plotting \( \ln D \) versus \( 1/T \) based on equation (3). Figure 7 shows the Arrhenius plots of the temperature dependence of \( D \), from which the growth activation energies of Co3W layer for SPS and traditional heating are calculated to be 229 ± 27 kJ mol⁻¹ and 279.38 ± 11 kJ mol⁻¹, respectively. Obviously, the activation energy is decreased by a high current during SPS.

### 3.3. The influence of current density on the growth kinetics of Co3W

To study the influence of current density on the growth behaviors of Co3W, the method reported in our previous work was applied to control the current density during the annealing of SPS [9, 13]. Figure 8(a) shows the growth rate constant of Co3W layer under different current densities, in which a significant positively correlation between current density and growth rate constant can be observed. Figure 8(b) shows the obtained lines of \( \ln D \) versus \( 1/T \), by which the growth activation energies were calculated to be 292.00, 275.34 and 252.14 kJ mol⁻¹ for 255, 306 and 371 A cm⁻², respectively. It appears that the activation energy decreases with the increase of current density.

![Figure 6. Square of Co3W layer thickness versus time for samples reacted at various temperatures in W/Co diffusion couple with current (a) and without current (b).](image-url)

| Temperature/°C | SPS | Conventional |
|---------------|-----|--------------|
| 1000          | /   | 2.60 × 10⁻⁴  |
| 1100          | 5.33 × 10⁻³ | 1.76 × 10⁻³ |
| 1200          | 1.61 × 10⁻² | 9.3 × 10⁻³  |
| 1300          | 6.95 × 10⁻² | /            |

Table 1. Growth rate constant of Co3W for different sintering techniques.
From the above studies, the growth activation energy of the Co₃W layer under the influence of current is obviously lower than that without current. Moreover, the growth rate constant of Co₃W layer increases with the current density, but the activation energy decreases with the increase of current density. This phenomenon agrees well with the growth kinetic behaviors of the intermetallic layer reported in Ni−Ti [14], Cu−Ti [3], Ni−Ni₃Al and Ti−TiAl [15] system, which also were processed by high current density. However, unlike the above reaction-diffusion system, the diffusion activation energy of the solution-diffusion systems, such as W−Ti [9] and Cu−Ni [16], is unchanged with the increase of current. Hence, the physical mechanisms of current-improved diffusion for reaction-diffusion system and solution-diffusion are different. For solution-diffusion, it has been reported that a significant electromigration effect is observed in the W−Ti [9] and Cu−Ni [16, 17] systems, which are bonded with high electric current. Therefore, the mechanism of current-enhanced atomic diffusion for solution-diffusion system is suggested to be electromigration. However, as for reaction-diffusion system, there are different views. Some researchers concluded that the presence of current does not alter the mechanism of interdiffusion in the reaction-diffusion systems, and the enhanced diffusion coefficient observed in the case with a current is likely to be related to the enhanced mobility or the change in defect concentration. The enhanced mobility of defects or the increase of defect concentration subsequently improves the diffusion at the interface and finally increases the growth of the intermetallic phase [7, 18]. Asoka-Kumar et al [7] investigated the effect of current on Al−Cu diffusion systems, finding that the concentrations of vacancy at the interface are increased by the current, which is different from that without current. Garay et al [18] provided direct evidence for an increase of defect mobility in the formed Ni₃Ti layer between Ni and Ti under the high current. Hence, the current increases the point defect and enhances the defect mobility in the product layers, providing an excellent kinetics condition for the atomic diffusion. In order to clarify the mechanisms of
current-induced improvement of Co3W layer at W/Co system, the W/Co/W diffusion couple with a sandwich structure (as shown in figure 1) was applied to investigate the effect of current direction on the diffusion rate. The results are depicted in figure 9. It can be observed that the thickness of the Co3W layer at W/Co interface and Co/W interface are almost equal, indicating that the current direction has no impact on the growth rate of the Co3W layer. That is, no electromigration effect was observed in W/Co system under the high current during SPS. Hence, the current-induced improved growth of the Co3W layer should not be attributed to electromigration.

Sun [19] reported that the effective Gibbs nucleation barrier of intermetallics (ΔG) is related to the current density when the nucleation is under the influence of current and can be written as:

\[
\Delta G = -kT \ln \left( \frac{C}{C_{eq}} \right) + 4\pi n_0^2 \gamma \cdot n^{2/3} - \frac{Z^* \sigma C_j}{5\pi C_{eq}} \cdot n^{5/3}
\]

The above equation shows a significant negative correlation of ΔG with current density J. The higher current density will lead to a lower effective Gibbs nucleation barrier. Sun’s thermodynamic computation shows that the Gibbs nucleation barrier of TiAl2 is significantly lowered by the current despite the fact that the formation of the intermetallic phase of Ti/TiAl2 is not affected by the current. That is, the nuclear energy of the intermetallic phase may well be decreased by the current. Therefore, for W−Co, Ni−Ti, Ni−Al, and other reaction-diffusion systems, the current-induced improved growth of the intermetallic phase layer should be attributed to the fact that the high current lowers the nucleation barrier of intermetallics, which accordingly promotes chemical reactions. This explains the growth kinetic behaviors of the Co3W layer at W/Co interface during SPS. The high current increases the concentration of defects at the interface. Meanwhile, the current lowers the nucleation barrier of Co3W layer.

4. Conclusions

(1) Two diffusion layers can be observed at the W/Co interface: solution-diffusion layer and reaction-diffusion layer. Two intermetallic phases are formed at the reaction-diffusion layer: Co7W6 and Co3W. The growth rate of Co3W than that of Co7W6.

(2) The growth rate constant of the Co3W layer undercurrent is 1.73–3.03 times faster than that without current. Moreover, the growth activation energy of the Co3W layer is 229.51 ± 27 kJ mol⁻¹ undercurrent, which is smaller than that without current (296.46 ± 56 kJ mol⁻¹). The growth activation energy of the Co3W layer decreases with the increase of current density, indicating that the current reduces the growth activation energy during SPS.

(3) The growth rate constant of Co3W layer increases with the current density, but the activation energy declines with the increase of current density. It is suggested that, for the reaction-diffusion system, the current lowers the nucleation barrier of the intermetallic layer, which accordingly promotes chemical reactions.
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Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files). Data will be available from 30 September 2021.

Conflict of interest statement

The data that support the findings of this study are available upon reasonable request from the authors.

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