

## Study on Reaction Diffusion Behavior in NG-Al/CG-Cu Diffusion Couple

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**Abstract:** A novel technique has been developed to produce nanostructure-grained (NG) Al coatings on Cu plate by means of surface mechanical attrition treatment (SMAT). The reaction diffusion behavior in nanostructure-grained (NG) Al/course-grained (CG) Cu diffusion couple was investigated by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The experimental results showed that the aluminizing kinetics of NG coating on Cu plate was obviously enhanced, and the temperature to form compound layer was also greatly reduced with respect to the coarse-grained (CG) Al/course-grained (CG) Cu diffusion couple. The activation energy for compound layer growth in the NG-Al/CG-Cu diffusion couple was calculated from the temperature dependence of compound layer thickness, the obtained values being about  $97.85 \text{ kJ/mol}$ , which is much smaller than that in the previous report for Al diffusion in the CG Cu ( $136 \text{ kJ/mol}$ ).

**Keywords:** Reaction diffusion, nanostructure, aluminizing, surface mechanical attrition treatment

### 1 Introduction

Nanostructure-grained (NG) materials have been widely researched in the past years. Experimental results show that NG materials have unique mechanical and physical properties which are derived from their unique microstructures. For example, the yield strength of NG Cu is several times higher than coarse-grained (CG) Cu [Valiev, Alexandrov, Zhu, and Lowe (2002)]; NG Ti has better corrosion resistance than CG Ti [Balyanov, Amirkhanova, Stolyarov, Lowe, Valiev, and Zhu (2004)]. Moreover, it has been recognized that NG materials exhibit superior diffusion properties. Especially in NG surface layer, it can provide a new way to improve the surface properties of materials.

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Recently, the reaction diffusion behavior of nanostructured surface layer has been studied by means of SMAT. It is found that a large number of grain boundaries in NG materials may act as fast atomic diffusion channels [Lu (1996)], and the numerous stored energy in grain boundaries facilitates chemical reactions. For example, Wang et al. measured the chromium diffusion in SMAT Fe and low carbon steel with a grain size of about 30 nm. The result shows that the diffusivity of Cr in SMAT Fe is 2-4 orders of magnitude higher than that in the CG Fe. [Wang, Tao, Tong, Lu, and Lu (2003); Wang, Lu, and Lu (2005)]. Tong et al reported that nitriding temperature of SMAT Fe in pure ammonia can be reduced to 300°C, which is at least 200°C below the conventional nitriding temperature [Tong, He, He, and Zuo (2006)]. A pack processes for simultaneous deposition of Al and Fe by SMAT has been researched, which indicates that the aluminizing temperature is at least 200°C below the conventional aluminizing temperature [Zhan, He, Wang, and Gao (2006)].

Though the researchers above have paid much attention to the reaction diffusion behavior of foreign atoms in the NG surface layers, the interdiffusion behavior between NG and CG materials is rarely reported. In this work, a NG-Al/CG-Cu diffusion couple was prepared by means of SMAT, and the kinetics of compound layer growth during annealing at low temperature was investigated. An interesting phenomenon has been found that the growth rate of interdiffusion layers was enhanced not only in the NG-Al side but also in the CG-Cu side, and the reaction diffusion behaviors was analyzed in detail.

## 2 The coating technique by SMAT

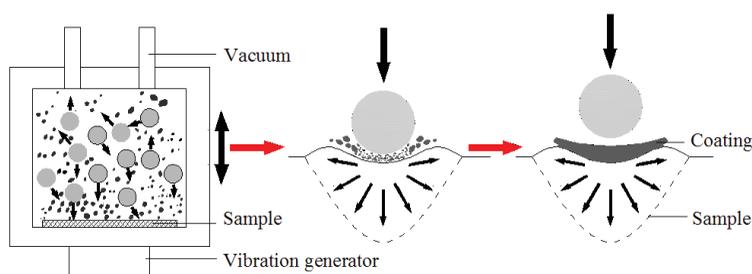


Figure 1: Schematic illustration of the formation of aluminum coating on the copper surface by milling

Figure 1 illustrates the experimental set-up for the NG coating. The stainless steel balls and pure aluminum powder were mixed at a certain ball-to-powder weight ra-

tio, and then placed in a reflecting chamber that is vibrated by a vibration generator. The vibration frequency of the chamber is in the range  $50\text{Hz} \sim 20\text{kHz}$ . When the balls are resonated, the velocity of the balls is about  $1 - 20\text{m/s}$ , depending upon the vibration frequency, the ball size and the distance between the sample surface and the ball. The impact directions of the ball on the sample surface are rather random due to the random flying directions of the balls inside the vibration chamber. In order to prevent oxidation, the vibration was performed in a high-purity argon atmosphere or vacuum pumping during SMAT.

During the SMAT, the pure aluminum powder will form a coating on the Cu matrix in two steps: (1) Through continuous plastic deformation, fracture and cold welding in an inert atmosphere, and the Al particles are adhered onto the Cu plate. (2) With further milling, the size of Al particle decreases from micrometer scale to sub-micrometer scale and then to nanostructure scale.

### 3 Experimental Procedure

#### 3.1 The NG-Al/CG-Cu diffusion couple preparation

The materials used to prepare the NG-Al/CG-Cu diffusion couples were pure aluminum powder (99.99 wt%) and copper plate (99.97 wt %). Before the SMAT, the sample was annealed at  $600^\circ\text{C}$  for 120 min to eliminate the effect of mechanical polishing on the surface structure and to obtain homogeneous grains of Cu phase.

The copper plate ( $60 \times 100 \times 100\text{mm}^3$  in size) was fixed on one side of the retort, and then the stainless steel balls (6mm diameter) and pure aluminum powder were mixed at the ball-to-powder weight ratio of 8/1. After the treatment for 2 hours in 50 Hz, the copper plate with Al coating were taken out and cut to  $7\text{mm} \times 7\text{mm} \times 5\text{mm}$  in size.

#### 3.2 The CG-Al/CG-Cu diffusion couple preparation

For comparison, a similar CG-Al/CG-Cu diffusion couple was prepared. The bonding face of copper ( $7\text{mm} \times 7\text{mm} \times 1\text{mm}$ ) and aluminum(99.99 wt %) plate ( $7\text{mm} \times 7\text{mm} \times 1\text{mm}$ ) were polished and cleared, and then the copper plate and aluminum plate were clamped by an iron clamp.

All samples above were sealed in evacuated silica capsules and then heated at  $350 \sim 420^\circ\text{C}$  from 2 to 72 hours. The temperature was controlled to within  $\pm 1^\circ\text{C}$  in all experiments. The microstructure of the specimens was characterized by using a LEXT OLS3100 laser scanning microscope, a SSX-550 scanning electron microscopy (SEM) and a Philips EM420 transmission electron microscope (TEM) with an operating voltage of 120 kV.

#### 4 Results and Discussion

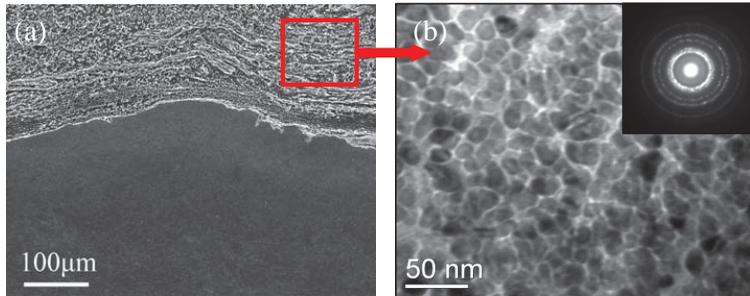


Figure 2: Micrograph of (a) the NG-Al/CG-Cu diffusion couple, and (b) TEM of the coating

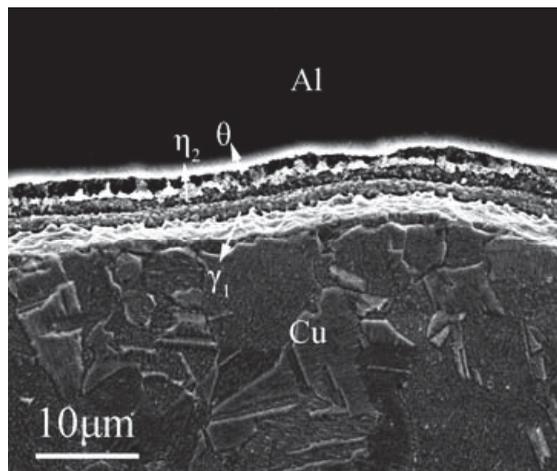


Figure 3: SEM observation of the NG-Al/CG-Cu diffusion couple annealing at 350°C for 2h

SEM observations found that a continuous Al coating layer can be formed on the copper plate surface for SMAT sample, which was caused by severe plastic deformation during coating process, as shown in figure 2 (a). TEM micrograph combined with the electron diffraction (see Fig 2 (b)) showed that the coating layer contained a large number of the nanostructured Al particles, and their average size is about 15 nm. Underneath the Al coating was an obvious severe deformation layer

with very fine Cu grains (less than 200nm) on the top surface of matrix. When the sample was subjected to annealing at 350°C for 2h, the ultrafine Cu grains became coarse (about 5 ~ 10 $\mu$ m), and a continue diffusion layers was formed, as shown in figure 3. According to the equilibrium phase diagram of Al-Cu system [Nagasaki and Hirabayashi (2001)] and energy dispersion spectrometer (EDS) analysis (Table 1), there are three intermediate phase in coarse-grained sample, i.e.  $\theta$  (Al<sub>2</sub>Cu),  $\eta_2$  (AlCu) and  $\gamma_1$  (Cu<sub>9</sub>Al<sub>4</sub>). Unexpectedly, nanostructured Al particle in coating layer had a low growth rate, and the average size still retained less than 100nm during the annealing. This is attributed to the formation of an amorphous Al<sub>2</sub>O<sub>3</sub> shell surrounding the particle, which prevent the Al crystal growth at higher temperature [Mei, Wang, Cong, Jin, and Lu (2005)]. Therefore, the NG-Al/CG-Cu diffusion couple can be obtained by means of SMAT and annealing treatment.

Table 1: EDS results of chemical compositions for  $\eta_2$ ,  $\gamma_1$  and  $\theta$  compound in nanostructure Al/Cu diffusion couples

	$\eta_2$	$\gamma_1$	$\theta$
Al	48.01	33.07	63.98
Cu	51.99	66.93	36.02

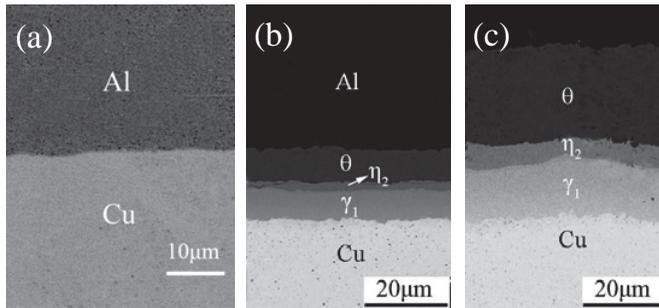


Figure 4: Micrograph of (a), (b) for the CG-Al/CG-Cu and (c) for the NG-Al/CG-Cu diffusion couple: (a) Annealing at 420°C for 2h, (b) and (c) annealing at 420°C for 24h

Micrographs of the intermediate layers at the CG-Al/CG-Cu diffusion couples annealed at 420°C for 2h can be seen in figure 4 (a), which shows that the interface of the CG-Al/CG-Cu bonding very well. However, no diffusion layers can be found in this case. This indicates that the diffusion time is too short for the CG-Al/CG-Cu diffusion couple to form the intermetallic layers. In order to compare the growth

rate of intermetallic layers of the NG-Al/CG-Cu and the CG-Al/CG-Cu diffusion couples, the annealing time for diffusion was increased. Figure 4 (b) and (c) show the diffusion layers for the NG-Al/CG-Cu and the CG-Al/CG-Cu diffusion couple annealed at  $420^{\circ}\text{C}$  for 24h. Diffusion layer thickness of  $\theta$ ,  $\eta_2$  and  $\gamma_1$  were measured to be about  $24.56\mu\text{m}$ ,  $5.21\mu\text{m}$  and  $13.63\mu\text{m}$  respectively in the NG-Al/CG-Cu sample after the treatment, which is apparently thicker than that in the CG-Al/CG-Cu counterpart. In the CG-Al/CG-Cu sample the thickness of  $\theta$ ,  $\eta_2$  and  $\gamma_1$  are  $8.53\mu\text{m}$ ,  $1.74\mu\text{m}$  and  $8.68\mu\text{m}$ , respectively.

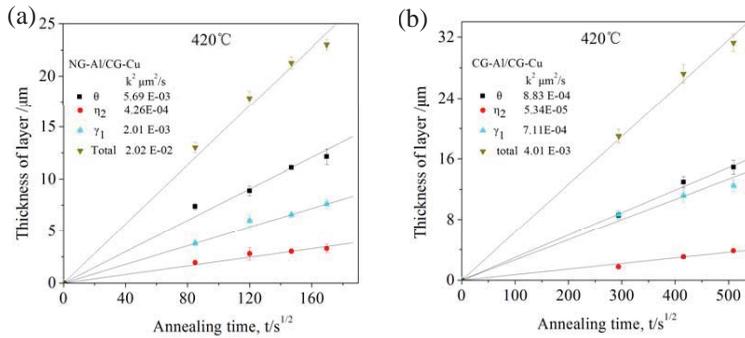


Figure 5: Intermetallic layer thickness with various times annealing at  $420^{\circ}\text{C}$ .: (a) the NG-Al/CG-Cu and (b) the CG-Al/CG-Cu diffusion couple.

In order to investigate the diffusion kinetic of the NG-Al/CG-Cu and the CG-Al/CG-Cu diffusion couple, the thickness of the compound layer for each sample was measured. Figure 5 shows the growth curves of compound layers in the NG-Al/CG-Cu and the CG-Al/CG-Cu diffusion couple at  $420^{\circ}\text{C}$ . It is found that the thickness  $l_i$  of the compound layers monotonically increases with increasing annealing time  $t$  at given temperature, and the plotted point for each layer lies well on a straight line. This means that the thickness  $l_i$  of the compound layers can be expressed as the following equation [Li, Dong, Zeng, Lu, Ding, and Ren (2007)]:

$$l_i = kt^{1/2} \quad (1)$$

Here,  $l_i$  is the thickness of the intermediate phase layer,  $t$  is the diffusion time and  $k$  is the growth rate constant. It is obvious that parabolic rate law is still obeyed for the growth of the diffusion layers in the NG-Al/CG-Cu diffusion couple when annealed at different temperatures. The calculated values of growth rate constant  $k$  for  $\theta$ ,  $\eta_2$  and  $\gamma_1$  at annealing temperature of  $420^{\circ}\text{C}$  as defined in Eq. (1) is shown in figure 5.

Assuming that the growth rate  $k$  in each layer follows the Arrhenius law in the lower temperature range, Eq. (1) can be expressed as:

$$l_i = k_0 \cdot \exp(-Q/RT)t^{1/2} \quad (2)$$

Where  $k_0$  is the pre-exponential factor,  $Q$  is the activation energy, and  $R$  is the gas constant. According to Eq. (2), the temperature dependence of compound layer growth can be deduced (as shown in figure 6), and the activation energy  $Q$  for diffusion layer growth in each compound can be calculated.

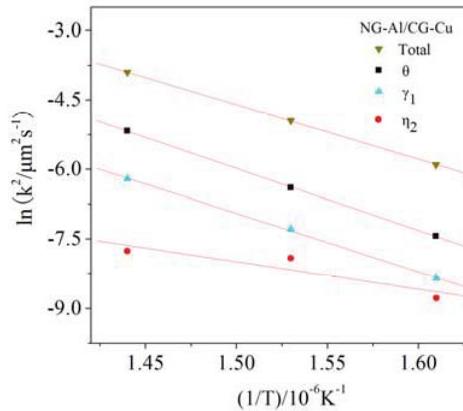


Figure 6: Temperature dependence of the growth rate ( $k$ ) in the NG-Al/CG-Cu diffusion couples

Table 2:  $k_0$  and  $Q$  for phase growth in the NG-Al/CG-Cu diffusion couple

Type	Phase	$k_0(cm^2s^{-1})$	$Q/(kJ/mol)$
NG-Al/CG-Cu	$\theta$	1.30E-03	111.16
	$\gamma_1$	2.35E-09	104.93
	$\eta_2$	1.60E-04	49.06
	Total	4.65E-04	97.85

The obtained value of apparent diffusion activation energy  $Q$  in the nanostructure sample is  $97.85kJ/mol$  which is much smaller than that reported in the literature ( $136kJ/mol$ ) [Dolgoplov, Rodin, Simanov, and Gontar (2008)] for the diffusion of Al in Cu. The results show that the ultrafine-grained structure possesses lower diffusion activation energy and higher diffusion coefficient.

According to the experimental results, the ultrafine grain Cu grows rapidly at 350°C for 2 hours, which indicates that the aluminizing kinetic was affected by the ultrafine grain Cu at the early stage. The characteristic of the ultrafine Cu in diffusion will disappear with time. In contrast, the low growth rate of Al particle was observed in our experiments. The NG Al coating may play a key role in enhancing the aluminizing kinetic for the NG-Al/CG-Cu diffusion couples. In order to study the influence of NG Al on the growth of compound layers, the rate values were calculated to be  $k_{NG}^{\theta}/k_{CG}^{\theta} = 2.53$  and  $k_{NG}^{\gamma_1}/k_{CG}^{\gamma_1} = 1.68$ . Where  $k_{NG}^{\theta}$  and  $k_{CG}^{\theta}$  are the growth rates for  $\theta$  layer in the NG-Al/CG-Cu and the CG-Al/CG-Cu diffusion couple, respectively, and  $k_{NG}^{\gamma_1}$  and  $k_{CG}^{\gamma_1}$  are the growth rates for  $\gamma_1$  phase in the NG-Al/CG-Cu and the CG-Al/CG-Cu diffusion couples, respectively. The result shows that the growth rate of  $\theta$  and  $\gamma_1$  phase layers are larger than those in the CG-Al/CG-Cu diffusion couple. In general, reaction diffusion of the solid Al/solid Cu can be described as follows: the Al and Cu atoms migration in the opposite direction to form Al-Cu solid solution in the mixing region. When the concentrations of Al and Cu reach certain values in the mixing region, the Al and Cu will react to form a new compound layers. Its growth rate depends on the migration of Cu and Al atoms. Therefore, the simultaneous increase of  $\theta$  and  $\gamma_1$  phase growth rate indicates that NG Al coating enhance diffusion process not only in the NG-Al side but also in the CG-Cu side.

According to the coating structure, large numbers of grain boundaries exist, which may serve as numerous fast diffusion “channels” for Cu atoms diffusion into NG Al layer. The high density of dislocation, extrinsic defects and high stored energy also affect the diffusion behaviors [Wang, Tao, Tong, Lu, and Lu (2003); Wang, Lu, and Lu (2005)]. On the other hand, the influence of NG Al coating on Al atoms diffusion into CG Cu must be considered in the NG-Al/CG-Cu diffusion couple. During the penetration process of the Al atoms into the Cu matrix, the chemical potential exerts a direct influence on the diffusion phenomena. As for the ultrafine grains in pure metal, the increase of chemical potential is given by  $\Delta\mu = 4\gamma\Omega/D$  ( $\Delta\mu$  is the change of chemical potential,  $\gamma$  is the interface energy,  $\Omega$  is atomic volume, and  $D$  is the diameter of crystal) [Lu and Sui (1993)]. According to the formula:  $J_i = -M_i C_i (\partial\mu_i/\partial x)$  (where  $J_i$  is  $i$  atoms diffusion flux,  $M_i$  is the proportional factor,  $C_i$  is the solution concentration and  $(\partial\mu_i/\partial x)$  is the chemical potential gradient) [Yu (2006)], the high chemical potential gradient of ultrafine grain Al is one of the reason for the increase of diffusion layer thickness.

The experiment results also show that the activation energy of compound layers in the NG-Al/CG-Cu diffusion couples (97.85kJ/mol) is lower than that in the CG-Al/CG-Cu counterpart (136kJ/mol) [Dolgopolov, Rodin, Simanov, and Gontar (2008)]. Similar results were previously obtained in NG metals [Kolobov,

Grabovetskaya, Ivanov, Zhilyaev, and Valiev (2001)]. This indicates that the barrier of migration for Al and Cu atoms is decreased greatly by the higher stored energy in the nanostructure sample, which may contribute to the enhanced formation kinetics of diffusion layers at low temperature in the NG-Al/CG-Cu diffusion couple.

## 5 Conclusions

The Cu plates were coated with Al powder by SMAT. The average grain size of Al particle in the coating is about 15 nm. During the 2 hours annealing at 420°C, the size of nanometer Al particle become coarse in local region in our experiment. The growth rate of compound layer in the NG-Al/CG-Cu diffusion couples is about one times higher than in the CG-Al/CG-Cu counterpart. The activation energy of compound layer in the NG-Al/CG-Cu diffusion couples is 97.85kJ/mol, which is much smaller than the value reported in the literature for CG Al diffusion in Cu. The significantly enhanced aluminizing and significant decreasing the aluminizing temperature can be attributed to the high stored energy and high volume fraction of grain boundary in the nanostructure sample.

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