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ScienceDirect
Trans. Nonferrous Met. Soc. China 23(2013) 2460−2464
Transactions of Nonferrous Metals Society of China
www.tnmsc.cn

Atomic interdiffusion in Ni−Cu system under high magnetic field

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Received 20 June 2012; accepted 20 November 2012

Abstract: The effect of high magnetic field on the atomic interdiffusion in Ni−Cu system was studied using the Cu/Ni/Cu diffusion couples. During the atomic interdiffusion in Ni−Cu system, it was found that the interdiffusion coefficients increased with the increase of molar fraction of Ni atoms in the interdiffusion zones when the couples were annealed with or without the magnetic field. It was noted that all corresponding interdiffusion coefficients under the magnetic field are smaller than those without the magnetic field. The results demonstrate that the magnetic field retards the atomic interdiffusion in Ni−Cu system. This retardation is achieved through reducing the frequency factors but not changing the interdiffusion activation energies.
Key words: Ni−Cu system; high magnetic field; atomic interdiffusion; diffusion couple

1 Introduction

Enormous amounts of magnetization energy can be transferred to a material at atomic scale without any contact when the material is placed in a high magnetic field. As a result, the thermodynamic state is changed obviously and thus the arrangement, matching, migration and other behaviors of atoms and molecules of the material are affected [1−9]. Therefore, the high magnetic field can result in enormous and profound influence on the microstructure and mechanical properties of materials.

Diffusion is one of the most important fundamental scientific problems in material science. Many processes and phenomena are closely related to the diffusion. Consequently, it is beneficial to investigate the atomic diffusion under the high magnetic field for exploring the physical nature of new phenomena in a high magnetic field and revealing intrinsic mechanisms of processes. It would lay a theoretical foundation for preparing new materials and developing new technologies. However, it is so lack in the research on the effect of high magnetic field on the atomic diffusion, and only several alloy systems have been studied by far. For example, YOUDELIS et al [10], LI et al [11] and REN et al [12] investigated Al−Cu, Mg−Al and Ni−Al systems, respectively. It was found that high magnetic field can retard the atomic diffusion. ZUO et al [13] also found that the thickness of compound layer was reduced by the high magnetic field during reactive diffusion between solid Cu and liquid Al. However, NAKAJIMA et al [14] did not find any effect of the magnetic field on the diffusion of nickel in titanium with the application of a 4 T magnetic field. In order to prove the availability of the above law, it is necessary to enlarge the range of study of the alloy system.

In this work, Ni−Cu system is firstly used to research the effect of high magnetic field on the atomic diffusion. It provides a new and powerful evidence for the retardation of high magnetic field on the atomic diffusion.

2 Experimental

The materials used to prepare the Cu/Ni/Cu diffusion couples were cold-rolled pure Ni plate (99.95%, mass fraction) and cold-rolled Cu plate (99.90%, mass fraction). Ni and Cu plates were cut to specimens in dimensions of 55 mm × 55 mm × 2 mm and 55 mm ×

Foundation item: Project (2011CB012803) supported by the National Basic Research Program of China; Project (NCET-10-0278) supported by Program for New Century Excellent Talents in University, China
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DOI: 10.1016/S1003-6326(13)62755-7

55 mm × 1.5 mm, respectively. Prior to clamping the couple halves, on one hand, the slices were mechanically ground with alumina waterproof abrasive papers up to 1500 grits; on the other hand, particles of zirconium dioxide (ZrO_2) were introduced as fiducial (inert) markers at the contact interface between the initial end-members. The oxide powder with particle size of ~1 μm was dispersed in acetone and then applied to the bonding faces of the couple halves. After this step, the couple halves were clamped at the sequence of Cu/Ni/Cu as a couple, and then wrapped with aluminium foil several times. The aluminium foil was used to prevent the couple halves from oxidation. In addition, it could avoid the relative movement among the couple halves. Finally, the clamped Cu/Ni/Cu couple was prepared by solid state diffusion bonding using a hot-pressing equipment. The parameters for diffusion bonding were (350 °C, 2 h, 10 MPa). The pressure was removed when the temperature was below 300 °C. The couple was taken out and cooled down in the air. At last, the couple was cut into rectangular prisms with dimensions of 10 mm× 5 mm × 5 mm. They were then subjected to diffusion annealing according to the heat treatment process shown in Table 1. Temperature was controlled by a programming thermometer with a Pt−Rh type thermocouple, which allows the temperature within ±2 °C of the expected value. The temperature rising and decreasing were controlled at a rate of 10 °C/min. The magnetic field apparatus used was illustrated in Ref. [15]. The schematic diagram of the annealing treatment process and applying magnetic field are illustrated in Fig. 1. Prior to annealing with a magnetic field, the vacuum inside the heating system was kept below 0.1 Pa. The corresponding annealing treatment without the magnetic field was conducted in a resistance furnace in the air.

Table 1 Annealing treatment process for diffusion couples

B/T	Temperature/°C	Time/h
0	600	8−40
	650	8−32
	700	8−32
	750	8−32
10	600	8−32
	650	8−32
	700	8−32
	750	8−32

During the annealing under the magnetic field, the specimens were placed with their interfaces parallel or perpendicular to the field direction. Figure 2 shows the field direction (***B***), where interface PN means that the field direction goes along the Cu/Ni interface. In contrast, interface TNU means that the field direction goes from Ni side to Cu side, and interface TND denotes that the field direction goes from Cu side to Ni side.

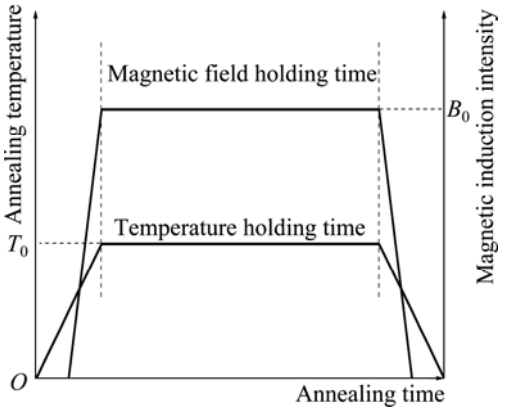

Fig. 1 Schematic diagram of annealing treatment process and applying magnetic field process

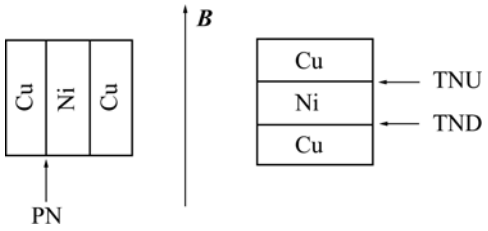

Fig. 2 Schematic diagram of relationship between diffuse interface and field direction

After standard metallographic preparation, cross-sections of the annealed diffusion couples were examined by optical microscopy. Distance—concentration profiles across the interdiffusion zones were measured using an EPMA-1600 electron probe microanalyzer (EPMA) under the following conditions: accelerating voltage 15 kV; specimen current 15 nA; beam spot diameter 1 μm; scanning step 1−5 μm. The interdiffusion coefficient was determined by Boltzmann−Matano method [16]. The distance—concentration profiles for specimens with the magnetic field were obtained from the interface TNU.

3 Results

After annealing with or without the magnetic field, interdiffusion took place across the Ni/Cu interface, then the interdiffusion zone formed. A back-scattered electron (BSE) micrograph of a typical specimen after annealing at 600 °C for 32 h with 10 T magnetic field is shown in Fig. 3. As can be seen in Fig. 3, a fine grain region occurs between the Cu and Ni phases, which is called diffusion-induced recrystallization (DIR) region. The dark particles between the Cu phase and DIR region are the inert makers (ZrO_2). It is useful for determining the original Ni/Cu interface. The distance—concentration

profiles across the interdiffusion zones were measured from Cu phase to Ni phase along the dashed line as shown in Fig. 3.

Figure 4 shows the distance—concentration profiles of Ni atoms in diffusion couples annealed at 750 °C with and without the 10 T magnetic field and the site of Matano plane. The scatter points are the molar fraction of Ni atoms measured by EPMA, and the solid lines are the fitted curves by the least-squares method based on the experimental values. If the lattice constant doesn't change with the molar fraction of Ni atoms and the vacancy keeps an equilibrium concentration, the Matano plane would coincide with the original Ni/Cu interface. As can be seen from Fig. 4, however, the distance—concentration profiles are not symmetric with the Matano plane. It suggests that the interdiffusion coefficients are related to the molar fraction of Ni atoms.

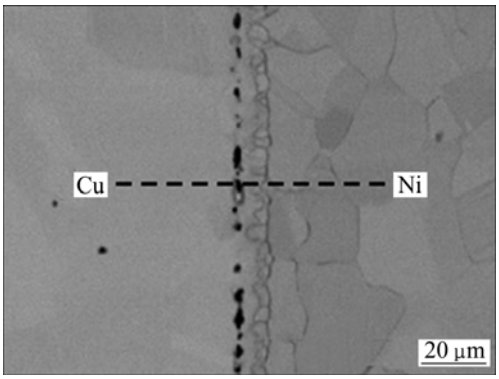

Fig. 3 BSE micrograph of diffusion couple specimen annealed at 600 °C for 32 h with 10 T magnetic frield

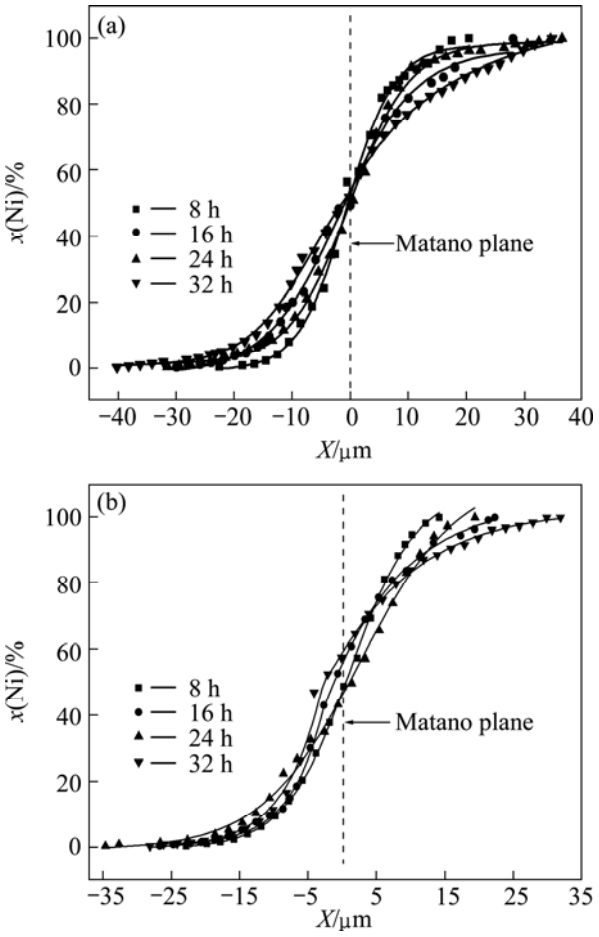

Fig. 4 Distance — concentration profiles of Ni atoms in diffusion couples annealed at temperature 750 °C with and without magnetic field and site of Matano plane: (a), 0 T; (b) 10 T

Based on the distance — concentration profiles obtained from various experimental conditions, interdiffusion coefficients $\widetilde{D}$ were measured as a function of the molar fraction of Ni, x(Ni). A typical relationship between $\widetilde{D}$ and x(Ni) is plotted in Fig. 5. For such measurements, the Boltzmann−Matano method was used, which did not take volume change into account. As can be seen from Fig. 5, $\widetilde{D}$ increases with an increase of x(Ni) in the interdiffusion zone. Especially, when the x(Ni) is larger than 60%, the change of $\widetilde{D}$ is more obvious. On the other hand, it can also be seen that when x(Ni) is the same, the interdiffusion coefficients with the field are usually smaller than those without the field.

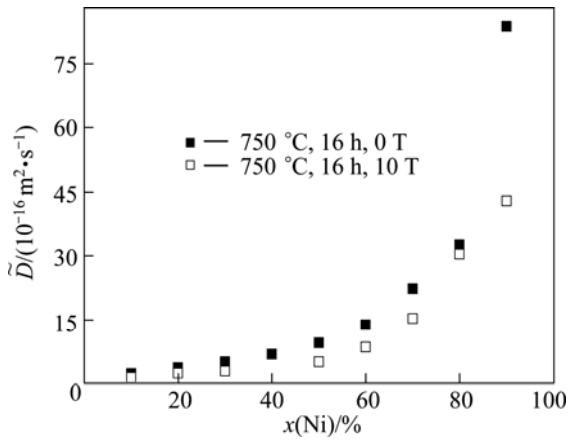

Fig. 5 Concentration dependence of interdiffusion coefficient in Ni−Cu interdiffusion zones at 750 °C with and without magnetic field

The interdiffusion coefficients at x(Ni)=10%, 20%, 70% and 80% are plotted in Fig. 6 against the reciprocal temperature. Good linearity holds in the temperature range covered in this study for each of x(Ni)=10%, 20%, 70% and 80%. Observation of the linearity in Fig. 6 suggests that the interdiffusion coefficients can be expressed by the following relationship:

$$\widetilde{D} = \widetilde{D}_0 \exp\left(-\frac{Q}{RT}\right) \quad (1)$$

where $\widetilde{D}_0$ is the frequency factor, Q the activation energy for interdiffusion, R the gas constant and T the thermodynamic temperature. The values of $\widetilde{D}_0$ and Q

for interdiffusion are listed in Table 2.

Comparing the values of $\widetilde{D}_0$ and Q listed in Table 2, it can be seen that Q for the interdiffusion is nearly the same with and without 10 T magnetic field. However, $\widetilde{D}_0$ with 10 T magnetic field greatly decreases compared with that without magnetic field. Therefore, it could be expected that high magnetic field diminishes the interdiffusion by reducing the frequency factors but not through the change in the activation energies.

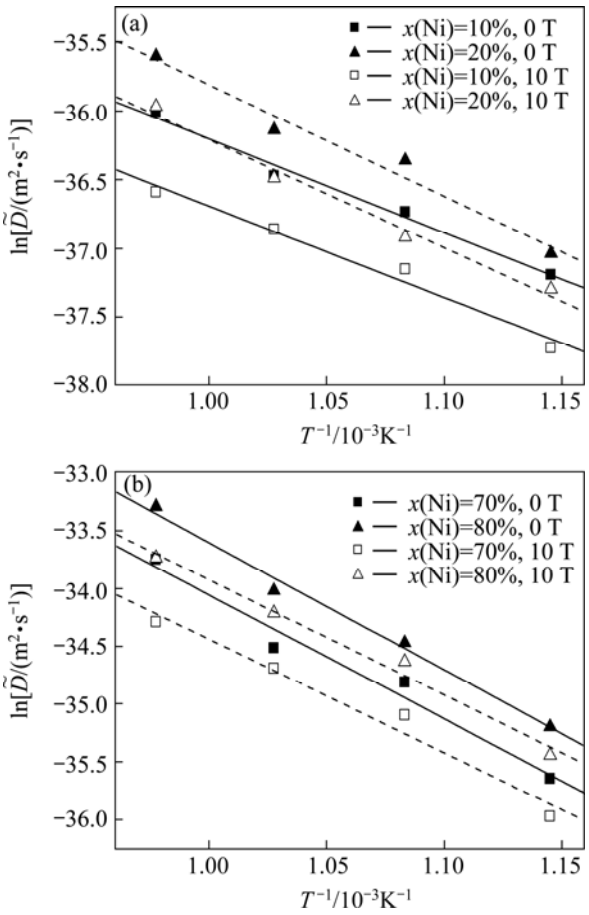

Fig. 6 Temperature dependence of interdiffusion coefficients for interdiffusion zones: (a) x(Ni)=10% and 20%; (b) x(Ni)=70% and 80%

Table 2 Frequency factors and interdiffusion activity energies for interdiffusion

B/T	x(Ni)/%	$\widetilde{D}_0$/(m^2·s^{-1})	Q/(kJ·mol^{-1})
0	10	1.704×10^{-13}	56.53
	20	9.177×10^{-13}	67.26
	70	7.021×10^{-11}	88.70
	80	1.484×10^{-10}	91.19
10	10	9.165×10^{-14}	55.43
	20	4.893×10^{-13}	65.34
	70	1.949×10^{-11}	81.26
	80	3.833×10^{-11}	86.21

4 Discussion

Under such experimental conditions, the interdiffusion in Ni−Cu diffusion couple could take place by two methods: volume diffusion and grain boundary diffusion. With the increase of temperature, the contribution of grain boundary diffusion would decrease and the volume diffusion would control the diffusion process. Usually, such atomic diffusion process is via atom−vacancy jump mechanism, in which $\widetilde{D}$ can be expressed as [12]

$$\widetilde{D}=\alpha^2 P\upsilon_0 Z\exp\left(\frac{\Delta S_{\mathrm{v}}+\Delta S_{\mathrm{m}}}{K}\right)\exp\left(-\frac{\Delta H_{\mathrm{v}}+\Delta H_{\mathrm{m}}}{KT}\right) \quad (2)$$

where α is the jump distance of atoms, P the probability of jump in the direction, υ_0 the vibration frequency of atoms, Z the coordination number of one atom, ΔS_{v} and ΔS_{m} the changes in the vibrational entropy of the crystal associated with the formation and displacement of the vacancy, respectively, ΔH_v and ΔH_m the corresponding changes in the enthalpy and K the Boltzmann constant. Comparing Eq. (1) with (2), it is suggested that high magnetic field may affect the value of atom vibration frequency and/or the entropy but not the enthalpy needed for the diffusion process during the diffusion process.

The above results are well consistent with the results published by YOUDELIS et al [10], LI et al [11] and REN et al [12]. However, YOUDELIS et al [10] have not determined whether the magnetic field affects the frequency factor or the activation energy, or even both of them. According to LI et al [11] and REN et al [12], the data analysis has strongly demonstrated that the high magnetic field retarded the diffusion process by reducing the frequency factor but not the activation energy.

Focusing on the effect of high magnetic field on the atomic diffusion behavior in non-magnetic materials, a theory based on plasma-magnetohydrodynamic has been developed by YOUDELIS et al [10]. It is suggested that mass transport in an alloy by chemical diffusion could be treated as an ambipolar diffusion process. The diffusivity is expected to decrease by a factor of $1/[(1+\omega_{\mathrm{ce}}^2)/\upsilon_{\mathrm{e}}^2]$ according to this theory, where ω_{ce} and υ_{e} are the cyclotron and collision frequencies, respectively, of the diffusion transported electrons [11,12].

The present results on the interdiffusion in Ni−Cu diffusion couples are in agreement with the above mentioned theory in terms of retardation of the atomic diffusion. It was confirmed that a decreasing frequency factor was responsible for the atomic diffusion retardation.

5 Conclusions

1) When the Ni−Cu diffusion couples were annealed with or without the magnetic field, the interdiffusion coefficients increased with the increasing molar fraction of Ni atoms in the interdiffusion zones.

2) All corresponding interdiffusion coefficients with the magnetic field are smaller than those without the magnetic field when the molar fraction of Ni atoms in the interdiffusion zones is equal. It demonstrates the retardation of the high magnetic field on the atomic interdiffusion in Ni−Cu system.

3) This retardation is achieved through reducing the frequency factors but not changing the interdiffusion activation energies.

References

[1] OHTSUKA H. Effects of strong magnetic fields on bainitic transformation [J]. Current Opinion in Solid State and Materials Science, 2004, 8(3−4): 279−284.

[2] LUDTKA G M, JARAMILLO R A, KISNER R A, NICHOLSON D M, WILGEN J B, MACKIEWICZ-LUDTKA G, KALU P N. In situ evidence of enhanced transformation kinetics in a medium carbon steel due to a high magnetic field [J]. Scripta Materialia, 2004, 51(2): 171−174.

[3] KOCH C C. Experimental evidence for magnetic or electric field effects on phase transformations [J]. Materials Science and Engineering A, 2000, 287(2): 213−218.

[4] MASAHASHI N, MATSUO M, WATANABE K. Development of preferred orientation in annealing of Fe–3.25%Si in a high magnetic field [J]. Journal of Materials Research, 1998, 13: 457−461.

[5] ZHEN L, SUN X Y, XU C Y, GAO R S, XU R G, QIN L C. Magnetic anisotropy in Fe−25Cr−12Co−1Si alloyinduced by external magnetic field [J]. Transactions of Nonferrous Metals Society of China, 2007, 17(2): 346−350.

[6] CHIO J K, OHTSUKA H, XU Y, CHOO W R. Effects of a strong magnetic field on the phase stability of plain carbon steels [J]. Scripta Materialia, 2000, 43: 221−226.

[7] CHENG C Q, HUANG M L, ZHAO J, XUE D F. Effect of uniform magnetic field on crystallization of intermetallic compound layers between Cu and liquid Sn−Zn alloys [J]. Transactions of Nonferrous Metals Society of China, 2012, 22(9): 2312−2319.

[8] SMOLUCHOWSKI R, TURNER R W. Influence of magnetic field on recrystallization [J]. Journal of Applied Physics, 1949, 20: 745−748.

[9] SAUTHOFF G, PITSCH W. Orienting of $Fe_{16}N_2$ particles in α-iron by an external magnetic field [J]. Philosophical Magazine, Part B, 1987, 56(4): 471−483.

[10] YOUDELIS W V, COLTON D R, CAHOON J. On the theory of diffusion in a magnetic field [J]. Canadian Journal of Physics, 1964, 42(11): 2217−2237.

[11] LI Z F, DONG J, ZENG X Q, LU C, DING W J, REN Z M. Influence of strong static magnetic field on intermediate phase growth in Mg−Al diffusion couple [J]. Journal of Alloys and Compounds, 2007, 440(1−2): 132−136.

[12] REN X, CHEN G Q, ZHOU W L, WU C W, ZHANG J S. Effect of high magnetic field on intermetallic phase growth in Ni−Al diffusion couples [J]. Journal of Alloys and Compounds, 2009, 472(1−2): 525−529.

[13] ZUO L, LIU C Z, XU B, ZHANG H, HE J C, TONG W P. Effect of high magnetic field on growth behavior of compound layers during reactive diffusion between solid Cu and liquid Al [J]. Journal of Materials Science & Technology, 2011, 27(9): 856−860.

[14] NAKAJIMA H, MAEKAWA S, AOKI Y, KOIWA M. Diffusion of nickel in titanium in a magnetic field [J]. Transactions of the Japan Institute of Metals, 1985, 26: 1−6.

[15] REN X, CHEN G Q, ZHOU W L, WU C W, CHAO C, ZHANG J S. Effect of a high magnetic field on the shape of the γ' precipitates in cast nickel-based superalloy K52 [J]. Journal of Materials Science & Technology, 2009, 25(3): 379−382.

[16] SPRENGEL W, NAKAJIMA H, OIKAWA H. Single-phase interdiffusion in TiAl and Ti_3Al intermetallic compounds [J]. Materials Science and Engineering A, 1996, 213(1−2): 45−50.

强磁场下 Ni−Cu 系原子的扩散行为

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摘 要：采用 Cu/Ni/Cu 扩散偶研究强磁场对 Ni−Cu 系原子扩散行为的影响。发现该扩散偶在有、无强磁场条件下退火处理时，Ni−Cu 系原子互扩散过程中的互扩散系数随着互扩散区内 Ni 原子摩尔分数的增加而增加，并且在强磁场条件下退火处理后，所有的互扩散系数均小于相应条件下无磁场处理时的互扩散系数。表明强磁场的施加延迟了 Ni−Cu 系原子的互扩散行为。分析指出，上述强磁场对原子扩散的延迟行为是通过降低互扩散过程中的频率因子而不是互扩散激活能来实现的。

关键词：Ni−Cu；强磁场；原子扩散；扩散偶

(Edited by Sai-qian YUAN)