Diffusion Multiple Study of Co-Ni-Ti system at 1073K

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Abstract: Co-Ni-Ti system is a key system ~~for the~~ several-industrial applications. The thermodynamic and kinetic information of this system is crucial ~~for to optimize the~~ alloy ~~design~~ and process design. ~~However, a~~ Although there are many literature works on this aspect ~~the system has been studied largely, there are~~ is still discrepancies on confusion about the stability of the ternary phase τ -Ti(Ni_{0.5}Co_{0.5})₃ ~~phase, and only~~ few data on the diffusion ~~information of in~~ the intermediate compounds as available. In this work, high throughput diffusion multiple approach was applied to investigate the isothermal section and interdiffusion ~~of in~~ this system at 1073K. The stability of the ternary phase τ -Ti(Ni_{0.5}Co_{0.5})₃ at 1073K ~~was could be verified~~ confirmed based on detailed EPMA element mapping and XRD analysis. ~~The A scheme of the isothermal section and phase relations of the~~ Ni-Co-Ti system at 1073K ~~including the new findings was determined is presented~~. The parabolic growth constant of intermediate phases of the binary Ni-Ti and Co-Ti systems at 1073K were also calculated and the corresponding integrated interdiffusion coefficients were ~~calculated determined~~ using Integrated-integrated Wagner ~~Equation equations~~. ~~The obtained information are quite important for the completion of the thermodynamic and kinetic information of this key system.~~

Key words: A. High temperature alloy; B. Diffusion, Phase stability; C. Diffusion-bonding; F. Electron microprobe

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1 Introduction

The Co-Ni-Ti system is an important system with a lot of applications in different fields, such as shape memory alloys [1], high entropy alloys [2], high temperature alloys etc. Thermodynamic and kinetic information is consequently crucial for the alloy design and process design [3,4]. Hence it is necessary to have complete, accurate thermodynamic and kinetic information of the Co-Ni-Ti system.

1.1 Thermodynamic information of the Co-Ni-Ti system

Due to the importance of the Co-Ni-Ti system for industrial application, thermodynamics and phase relations of this system have attracted a lot of investigations [5–11]. Isothermal sections of this system have been determined for 1373K [12], 1173K [5,7], 1123K [6], and 1073K [10], where one ternary phase $\tau\text{-Ti}(\text{Ni}_{0.5}\text{Co}_{0.5})_3$ was reported [5]. Riani et al. [7] critically assessed this system. Recently, Zhou et al. [12] established the liquid surface and proposed the invariant reaction scheme for the Co-Ni-Ti system. In ~~Totally-total~~ eight intermediate phases exist in the three sub-binary systems, where CoTi and NiTi ~~is-are~~ isostructural, and CoTi_2 and NiTi_2 ~~are~~ isostructural. Hence the unlimited solubility of the binary phases CoTi_2 and NiTi_2 as $(\text{Co},\text{Ni})\text{Ti}_2$, CoTi and NiTi as $(\text{Co},\text{Ni})\text{Ti}$ have been observed. A large solubility of the third member in the binary phases of Ni_3Ti and Co_3Ti ~~was~~ also reported [7]. The stable temperature range of the ternary phase $\tau\text{-Ti}(\text{Ni}_{0.5}\text{Co}_{0.5})_3$ is still ~~in~~ controversial. This ternary phase was not observed in the experimental work by Gryzunov et al. [10] (at 1073K) and Du et al. [6] (at 1123K). Riani et al [7] reported the ~~cat~~ stability of the ternary phase $\tau\text{-Ti}(\text{Co},\text{Ni})_3$ down to 773°C, ~~derived from microstructure analysis of -by the equilibrium information shown in the-annealed alloys which is-were cooled down after arc-melting. However, it can be questioned that -where the the annealed alloys had reached the equilibrium status shown in these-annealed alloys can also be questioned~~. Therefore, the stability of this ternary phase and, further, the phase relations of this ternary system still need more investigation.

1.2 Diffusion and kinetic information of the Co-Ni-Ti system and sub-systems

No intermediate phase exists in the Co-Ni system. The ~~diffusion-growth~~ of intermediate phases in Ni-Ti ~~diffusion jointssystem~~ has been investigated ~~in-many~~

literatures largely [13–18], where the growth ~~consequence~~ of the intermediated phases and ~~diffusion~~ morphology were reported. Few literatures ~~for-on~~ the investigation of the ~~diffusion~~ growth of intermediate phases in Co-Ti ~~diffusion system joints~~ have been found. Taguchi et al [19] reported the reaction diffusion ~~in-for the~~ Co-Ti system and the layer growth of Co_3Ti and CoTi_2 . Mutual diffusion in the system Co-Ni-Ti ~~wasere~~ investigated by Gryzunov et al. [10,20] and Van Loo et al. [5]. However, ~~No-no~~ diffusion parameters of ~~bianry-the binary~~ phases ~~in-corresponded system~~ were reported.

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Since the diffusion information of intermediate phases in ~~the~~ Ni-Ti system and intermediate phases in Co-Ti system are still lacking, the aim of the current work is to investigate the isothermal section of Co-Ni-Ti ~~phase-at~~ 800°C and determine diffusion information of ~~the~~ intermediate phases in ~~the~~ Ni-Ti ~~system~~ and ~~their~~ Co-Ti system using diffusion multiple approach [21].

2 Experimental method

High-throughput diffusion multiple approach [21] was applied for the current investigation. Plates with dimension of 5 mm × 1 mm × 10mm were cut from high purity Co, Ti, and Ni (99.999 mass%, NewMet) ingots, polished, and cleaned with ethanol in an ultrasonic bath to obtain flat and clean surfaces. Afterwards, the plates were inserted into a nickel can. Finally, the Ni can with diffusion multiple was sealed in a Ti can using electron beam welding method. The complete setup is shown in Fig. 1. Then the high temperature iso-static pressing treatment of the whole assembly were performed at 1073K for 4 hours with pressure 20 mPa, as shown in Fig. 2. Consequently, the whole assembly was sealed in quartz ampoule and put in the muffle furnace and annealed at 1073K for 288 hours and water quenched. The assembly was cut perpendicular in the middle, grinded, and polished and cleaned in an ultrasonic bath.

Philips XL30 FEG scanning electron microscope (SEM) was used to analyze the phase structure and morphology of the diffusion zone. The morphology of the diffusion zone was analyzed using Back Scatter Electron (BSE) mode. Phase composition of the diffusion layer was analyzed using field emission electron probe micro-analyzer (EPMA) under wavelength dispersive spectroscopy (WDS) mode.

Fig. 1 scheme of multicomponent diffusion assembly.

Fig. 2 high temperature iso-static pressing treatment of the diffusion multiple assembly

To verify the equilibrium of the phases, some alloys were synthesized using arc-melting method. The synthesized ingots were sealed in quartz tubes and annealed in muffle furnace at 1073K for 30 days. Afterward, the ingots in the quartz crucible were quenched in water. X-ray diffraction analysis were performed on the alloys for phase identification. EPMA analysis were performed on the samples for determination of phase compositions.

3 Calculation method

With annealed diffusion couples, growth rate and integrated diffusion coefficients of the intermediated phases can be calculated based on the composition profile of the diffusion region [22–24]. Growth constants of corresponding intermetallic compounds were calculated using equation (1) :

$$k^{(j)} = \frac{(\Delta x^{(j)})^2}{2t} \quad (1)$$

where superscript j denotes the investigated phase; $\Delta x^{(j)}$ is thickness of j phase layer in the diffusion zone after annealing for a time t , $k^{(j)}$ is parabolic growth constant of phase j in the diffusion couple.

If volume change and solubility in the primary phase are neglected, the integrated interdiffusion coefficient for IMC with a narrow homogeneity range, can be calculated using equation (2), as proposed by Wagner [22]

$$\begin{aligned}
 \bar{D}_{\text{int}}^{(j)} &= \int_{N_i^{(j)-}}^{N_i^{(j)+}} \bar{D} dN_i \\
 &= \frac{(N_i^{(j)} - N_i^{-\infty})(N_i^{+\infty} - N_i^{(j)})}{(N_i^{+\infty} - N_i^{-\infty})} \times \left[\frac{(\Delta x^{(j)})^2}{2t} \right] \\
 &\quad + \frac{\Delta x^{(j)}}{2t} \left[\frac{(N_i^{+\infty} - N_i^{(j)})}{(N_i^{+\infty} - N_i^{-\infty})} \times \int_{x^{-\infty}}^{x^{(j-1,j)}} \frac{V_m^{(j)}}{V_m} (N_i^{(j)} - N_i^{-\infty}) \cdot dx + \frac{(N_i^{(j)} - N_i^{-\infty})}{(N_i^{+\infty} - N_i^{-\infty})} \times \int_{x^{(j,j+1)}}^{x^{+\infty}} \frac{V_m^{(j)}}{V_m} (N_i^{+\infty} - N_i^{(j)}) \cdot dx \right] \\
 &= (N_i^{(j)+} - N_i^{(j)-}) \times \bar{D}_{\text{average}}^{(j)}
 \end{aligned}
 \tag{2}$$

where $N_i^{(j)+}$ and $N_i^{(j)-}$ are the composition boundaries of j phase, $N_i^{(j)}$ is stoichiometric composition of j phase. $\bar{D}_{\text{int}}^{(j)}$ is integrated interdiffusion coefficient of j phase in its homogeneity range.

4 Results and discussion

4.1 Diffusion morphology and isothermal section

Fig. 3 shows the morphology of binary diffusion regions where all the binary intermetallic compounds are found to be presented in the diffusion region.

Fig. 3: BSE image of diffusion region of Ti-Co joint region (a), Ti-Ni joint region (b), and Co-Ni joint region (c).

The Ti-Co system has ~~ve~~ five binary compounds [7]. As shown in Fig. 3(a), from ~~the~~ Co side to ~~the~~ Ti side, ~~a~~ layer of TiCo_3 , TiCo_2 , TiCo and Ti_2Co are presented in the diffusion region. Because the composition of TiCo_2 and $\text{Ti}_{0.9}\text{Co}_{2.1}$ are quite close to each other, no explicit phase boundary is shown in the BSE image.

The Ti-Ni system have three binary compounds [7]. As shown in Fig. 3(b), from ~~the~~ Ni side to ~~the~~ Ti side, all the compounds are presented in the diffusion region of ~~the~~ Ti-Ni joint. ~~It is seen in the TiNi layer, there are~~ Some small Ti_2Ni precipitates ~~are seen in the TiNi layer,~~ which ~~is-are~~ formed during the cooling process as the composition range of TiNi decreases ~~with-when~~ the temperature decreases.

There is no intermediate phase observed in the Co-Ni diffusion region, which is coincident with its phase diagram.

The diffusion morphology of the Co-Ni-Ti ternary joint is shown in Fig. 4. Because the three elements Co, Ni and Ti are quite clos~~ing~~ to each other in the ~~element~~-periodical table, it is possible to miss~~ing~~ presented phases in the BSE mode. To distinguish the phases, element maps of Co, Ni and Ti were performed on the diffusion ~~area~~.

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Fig. 4 BSE image and element mapping results of the ternary diffusion region.

According to the EPMA results, the phase regions were labeled and the phase boundaries were marked using white lines, as shown in Fig. 4 (a). TiNi_3 and $\tau\text{-Ti}(\text{Ni}_{0.5}\text{Co}_{0.5})_3$ are hardly distinguishable in Fig. 4(a), because Co and Ni are close to each other in the element-periodical table and show quite-low contrast in the BSE image mode. However, the phase boundary between TiNi_3 and $\tau\text{-Ti}(\text{Ni}_{0.5}\text{Co}_{0.5})_3$ is presented in both the Co mapping image and the Ni mapping image.

Du et al [6] also investigated the isothermal section of Ni-Co-Ti system at 850 °C using diffusion triple. They didn't report the existence of the τ phase in their schemed schematic isothermal section. Probably they did not distinguish TiNi_3 and τ phases from each other due to their similar color in BSE mode.

To verify the existence of the ternary phases and phase relations, several alloys were synthesized and characterized by quantitative analysis and XRD analysis. According to the

quantitative measured composition profiles of the ternary joint and the equilibrium phase information presented in the annealed alloys, combining the literature information [7], the schemed isothermal section of Ti-Ni-Co at 1073K is plotted and shown as Fig. 5. The stability of the τ -Ti(Ni_{0.5}Co_{0.5})₃ is verified. The BSE images of the selected alloys were are shown in Fig. 6.

Fig. 5 The schemed isothermal section of Ti-Ni-Co system at 1073K

○ represent compositions of annealed alloys, * represent equilibrium phase compositions determined from annealed alloys, ◇ represent compositions determined from the diffusion couple

Fig. 6 BSE images of some equilibrium alloys.

4.2 The Calculation of the diffusion properties of the binary intermetallic compounds in binary joint

Firstly, the area of each phase layer was measured from the 2D BSE image of the microstructure using a digitization method based on the grayscale values. Then, the thickness of the IMC layer was calculated using the measured area of the IMC layer divided by interface length. Because of the wavy boundaries of the IMC phase layers as shown in Fig. 3, the average thicknesses of the phase layers were used.

Integrated diffusion coefficients were calculated using equation (2). No composition range or corresponding volume change was considered during the current calculation. Calculated parabolic growth constants and integrated interdiffusion coefficients of intermetallic compounds are listed in Tab. 1 and shown in Fig. 7.

Tab.1 Calculated parabolic growth constants and integrated interdiffusion coefficients of binary intermetallic compounds in the Ti-Ni-Co system

	Phase	T(K)	k (m ² /s)	$\tilde{D}_{int}$ (m ² /s)
Ti-Ni system	TiNi ₃	1073	1.05×10^{-16}	7.38×10^{-17}
	TiNi	1073	1.59×10^{-15}	5.69×10^{-16}
	Ti ₂ Ni	1073	4.76×10^{-17}	1.30×10^{-16}
Co-Ti system	TiCo ₃	1073	6.23×10^{-16}	3.51×10^{-16}
	TiCo ₂	1073	2.56×10^{-17}	4.53×10^{-17}
	TiCo	1073	2.10×10^{-17}	4.62×10^{-17}
	Ti ₂ Co	1073	3.25×10^{-17}	1.83×10^{-16}

Fig. 7 Square thickness of intermetallic layer vs annealing time at 1073K

5 Conclusion

Isothermal section and interdiffusion of Ni-Co-Ti system at 1073K were investigated using diffusion couple approach and annealed key alloys.

(1) The ternary phase τ was observed at 1073K.

(2) ~~An update of the Isothermal-isothermal~~ section of Ni-Co-Ti system at 1073K was ~~determined-presented.~~ ~~T—Three~~ ~~the~~ three-phase regions $\text{Ni}_3\text{Ti}+\tau+(\text{Co,Ni})\text{Ti}$, $\text{Ni}_3\text{Ti}+\tau+\text{fcc}(\text{Co,Ni})$, $\text{Co}_3\text{Ti}+\tau+\text{fcc}(\text{Co,Ni})$, and $(\text{Co,Ni})\text{Ti}+\tau+\beta$, as well as ~~the~~ two-phase ~~equilibrium-region of~~ $(\text{Co,Ni})\text{Ti}+(\text{Co,Ni})\text{Ti}_2$ was determined.

(3) ~~The Parabolic-parabolic~~ growth constant of ~~the~~ binary intermediate phases within the Ni-Ti and Co-Ti, systems at 1073K were calculated. ~~and~~ ~~t~~ The integrated interdiffusion coefficients of the corresponding ~~intermediated~~ phases were ~~also~~ calculated using Wagner equation.

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