Diffusion multiple study of the Co-Fe-Ni system at 800 °C

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Abstract: The Co-Fe-Ni system is a key system in a wide range of industrial applications. Knowledge of the thermodynamic and kinetic properties of the system is crucial for the alloy and process design. Although the system has been studied extensively, there remain several unexplained discrepancies between different literature data and, for mediate low temperatures, the information is scarce. In this work, a high throughput diffusion multiple approach was applied. The isothermal phase diagram section at 800 ^{o}C was determined using the Co-Fe-Ni multiple. The interdiffusion coefficients of the binary Co-Fe, Co-Ni, Fe-Ni systems and their composition dependence were calculated using the Sauer-Freise method based on the compositional profiles obtained from the diffusion multiple. Different from previous experimental results for mediate low temperature, our results coincide with the extrapolated Arrhenius temperature dependence from diffusion coefficient data at high temperature range. These observations are important for a better understanding and modelling of the interdiffusion behaviour in this key alloy system.

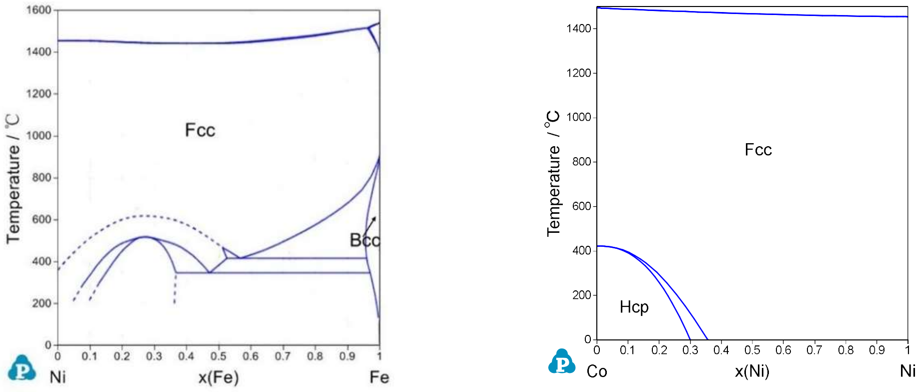
Key words: Co-Fe-Ni system; isothermal section; diffusion multiple; interdiffusion coefficients

1 Introduction

Co-Fe-Ni, as well as, its sub-binary systems are essential for many industrial fields, such as steel [1], high entropy alloy [2] and high temperature alloy. Correspondingly, phase diagrams, thermodynamic and kinetic information are crucial for the alloy and processing design. No ternary intermediate phase exists in this system. The three elements are mutual soluble in a large composition range. Fig. 1 shows the phase diagrams of the three sub-binary systems. The ternary Co-Fe-Ni system was assessed by Guillermet [3], where the two phase fcc+bcc region is an important feature in this ternary system. Raghavan [4] point out the discrepancy of the boundary of the region of fcc+bcc between experimental results [5,6] and assessed results [3] and the necessities of further experimental work. Recently, Xing et al [7] determined isothermal sections at 500 °C, 600 °C, 700 °C using the combinatorial materials chip approach, where the discrepancies with previously assessed data [3] were also present.

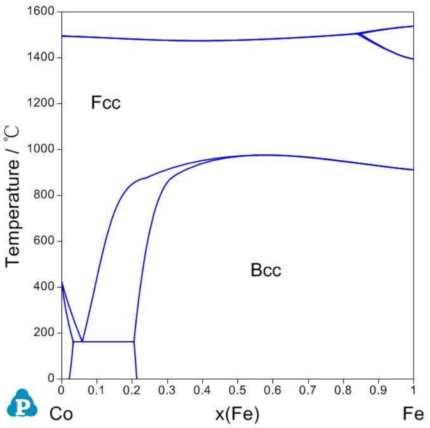
Many groups have studied the diffusion in Co-Fe-Ni system and its sub-systems [8–23], in which most studies focused on the fcc phase in the high temperature range. Heumann and Kottmann [17] studied interdiffusion of the fcc phase in the Fe-Ni system at 1310 °C and in the Co-Ni system at 1155 °C, 1305 °C and 1400 °C using diffusion couple technique and calculated the corresponding interdiffusion coefficients using Bolztmann-Matano method. Similarly, Ustad and Sorum [14] determined the interdiffusion coefficients and corresponding activation energies of the Fe-Ni, and Co-Fe systems in the temperature range of 705-1400 °C and of the Co-Ni system in the temperature range of 1000-1400 °C. In their results, consistent data in the temperature range of 1000 to 1400 °C were observed. There was, however, a discrepancy for the data at mediate low temperatures of 705 °C and 805 °C, as these data did not follow the Arrhenius relation. They attribute the discrepancy to a change in diffusion mechanism with temperature, which is, at high temperatures, lattice diffusion and, at lower temperatures, grain boundary diffusion. Ugaste et al studied the interdiffusion and Kirkendall effect in the binary Co-Ni, Fe-Ni and Co-Fe systems at 1000 -1300 °C [8,12], and in the ternary Co-Fe-Ni system [11,13,24] covering a large composition range.

Based on all these experimental results, Cui et al [9,25] assessed the experimental data and obtained the corresponding kinetic parameters based on the kinetic model developed by Agren [26]. However, the assessment doesn't go to the low temperature range because of the discrepancy in the experimental data [14,18].



(a) Ni-Fe system

(b) Co-Ni System



(c) Co-Fe system

Fig. 1 Phase diagrams of the corresponding systems calculated using PanFe database: (a) Fe-Ni system, (b) Co-Ni system, (c) Co-Fe system.

Therefore, the aim of the current work is to investigate the isothermal section of the Co-Fe-Ni phase diagram and the interdiffusion in the three binary systems at 800 °C using diffusion multiple approach. A diffusion multiple of Co-Fe-Ni-Ti were constructed in this work. The work results of Ti-Ni-Co system on this diffusion multiple were published as another work [27].

2 Experimental Processes

High-throughput diffusion multiple approach [28], which have been widely applied for studying interdiffusion behavior [29–32], was applied in the current work. Plates with dimension of 5 mm × 1 mm × 10mm were cut from high purity Fe, Co, Ti and Ag (99.999 mass%, NewMet) ingots. After polishing and cleaning with ethanol in an ultrasonic bath to obtain flat and clean surfaces, the plates were inserted into a high purity Ni (99.999 mass%, NewMet) cartridge to avoid the contamination from any other materials. Hence, a diffusion multiple including Ni, Ti, Fe and Co is assembled. This diffusion multiple was then inserted into a can made from commercial Ni and lastly, inserted in a Ti can specified for the HIP (high temperature iso-static pressing) processing. Then the Ti can was sealed using electron beam welding. The complete setup is shown in Fig. 2, where a scale to indicate the dimension of the whole assembly were provided.

High temperature iso-static pressing treatment of the whole assembly was performed at 800 °C for 4 hours with pressure 20 MPa. The process is illustrated in Fig. 3. Afterwards, the whole assembly was sealed in quartz ampoule, annealed at 800 °C for 284 hours (in total 288 hours of diffusion including the HIP time 4 hours) in a muffle furnace and water quenched. Finally, the assembly was cut perpendicular in the middle, grinded, polished, and ultrasonically cleaned using standard metallographic techniques.

Philips XL30 FEG scanning electron microscope 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. Quantitative line-scanning module with step size of 0.5 or 1 μm was utilized to obtain the concentration profiles in the Fe-Ni, Fe-Co, Ni-Co diffusion layers. For each binary diffusion layer, three or four lines perpendicular to the interface were selected for the quantitative line scanning.

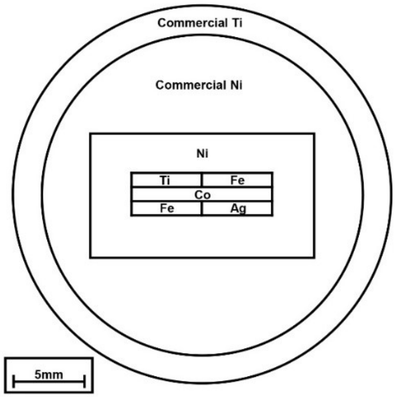


Fig. 2 The scheme of the multicomponent diffusion assembly.

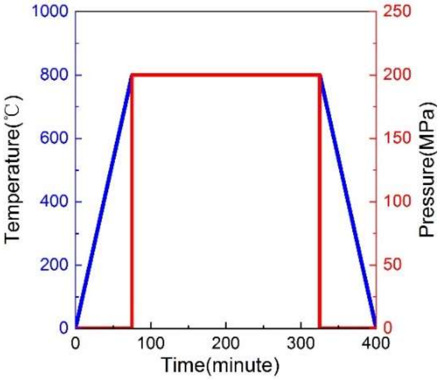


Fig. 3 The high temperature iso-static pressing treatment of the diffusion multiple assembly

3 Diffusion calculation method

The interdiffusion coefficient describing the intermixing effect due to diffusion, $\widetilde{D}$, can be determined from the composition profile measured in the diffusion couples [33]. The most widely applied method to determine the interdiffusion coefficient is the Boltzmann-Matano method [34]. Sauer and Freise [35] imported an auxiliary variable $Y(x)$ into the Boltzmann-Matano method to avoid the need of the evaluation of the position of the Matano plane. $Y(x)$ is defined by equation (1):

$$Y(x) = \frac{N_i(x) - N_i^{+\infty}}{N_i^{+\infty} - N_i^{-\infty}} \qquad (1)$$

where $N_i(x)$ is the mole fraction of specie i at the position x; superscripts $+\infty$ and $-\infty$ denote the corresponding values in the left and right end-boundaries of the diffusion couple, respectively.

The interdiffusion coefficient $\widetilde{D}$ at a certain point x^* in the diffusion zone can then be evaluated from

$$\widetilde{D}(Y^*) = \frac{V_m}{2t\left(\frac{dY}{dx}\right)_{x^*}}\left[(1-Y^*)\int_{x^{-\infty}}^{x^*}\frac{Y}{V_m}dx + Y^*\int_{x^*}^{x^{+\infty}}\frac{1-Y}{V_m}dx\right] \quad (2)$$

where the superscript * denotes the corresponding value at the investigated point x^*; and V_m is the volume of one mole atoms, which is assumed be same for the investigated system in this work.

The temperature dependence of interdiffusion coefficients is expected to follow a Arrhenius equation (3) over extended temperature ranges [33]:

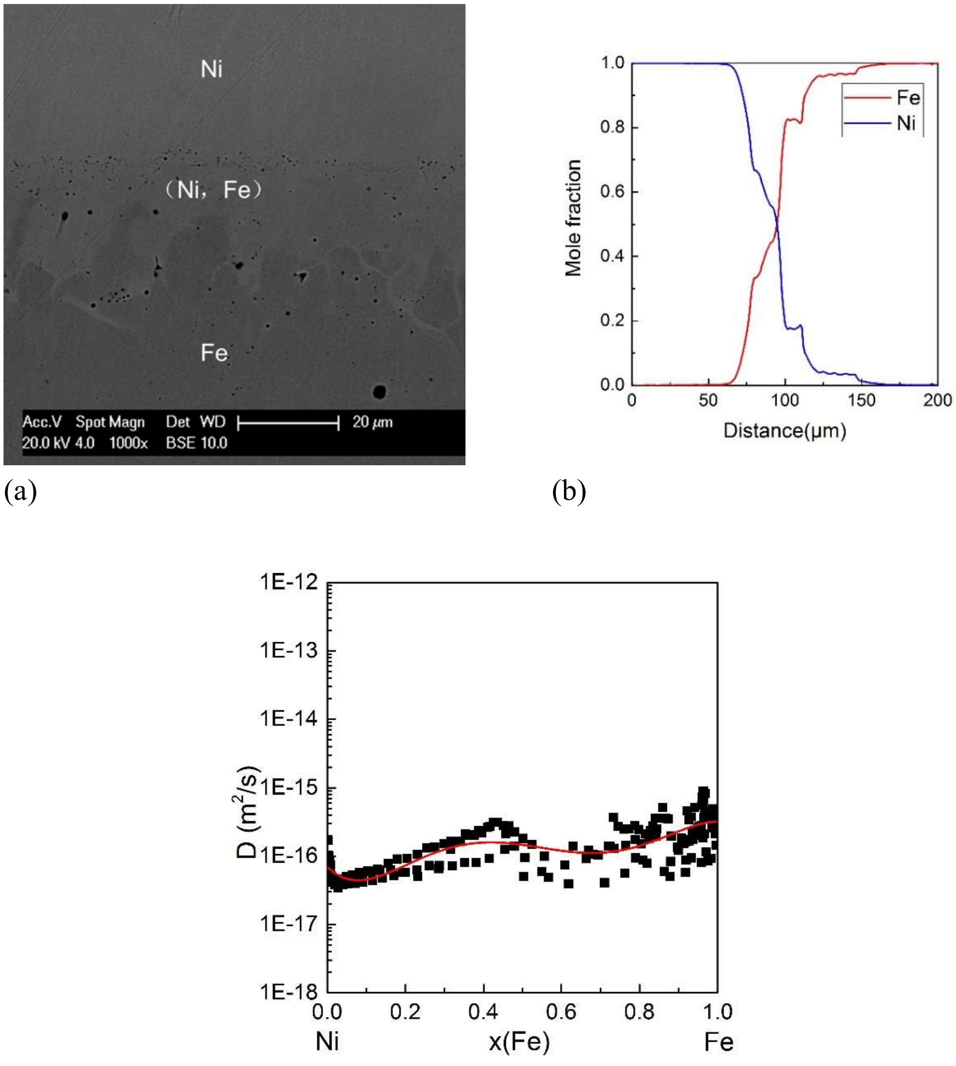
$$\widetilde{D} = D_0 \exp\ (-\mathrm{Q/RT}) \quad (3)$$

where Q is activation energy; D_0 is a frequency factor; R is gas constant; and $\boldsymbol{T}$ is absolute temperature. Using equation (3), the obtained interdiffusion coefficients can be extrapolated to other temperatures.

4 Results and discussion

4.1 Diffusion coefficients of the Fe-Ni system

Fig. 4 shows a BSE image of the binary Fe-Ni joint (a), the Composition profile of the Fe-Ni diffusion layer (b) and the calculated interdiffusion coefficients at 800 °C (c). Note that the obtained interdiffusion coefficients for compositions near the pure elements are with large uncertainty. This is because of the relative slow change and hence scattered data of composition at the boundaries can result in a large error when calculating the composition gradient.



(a) (b)

(c)

Fig. 4 (a) BSE image of the Fe-Ni binary joint at 800 °C;

(b) Measured composition profile of the Fe-Ni diffusion layer of one typical line perpendicular to the interface;

(c) interdiffusion coefficients calculated based on the measured composition profile (b) at 800 °C. In (c) black points represent the data calculated from several lines perpendicular to the interface and the red line is the fitting curve using the least squares fitting method.

The interdiffusion coefficients at different compositions are compared to literature data [14,15] in Fig. 5. Interestingly, the experimental results from Ustad et al. [14] follow an Arrhenius equation in the high-temperature region (above 1300 °C), but show a deviation from this relation for the lower temperature range. However, our $\widetilde{D}$ results show a general agreement to the Arrhenius line determined by the high temperature results from Ustad et al. [14]. According to Fig. 1(a), the phase region is changed to α+γ two phase region as Fe-Ni alloys at around 90 at% Fe at 800 °C, which could contribute to the larger spread on the experimental data in this region. Here the multi-grain material blocks were employed for the studies. The calculated interdiffusion data at 800 °C shown perfect consistent with the extrapolated data from high temperature range, hence the lattice diffusion mechanism is still believed to be the main diffusion type at this temperature

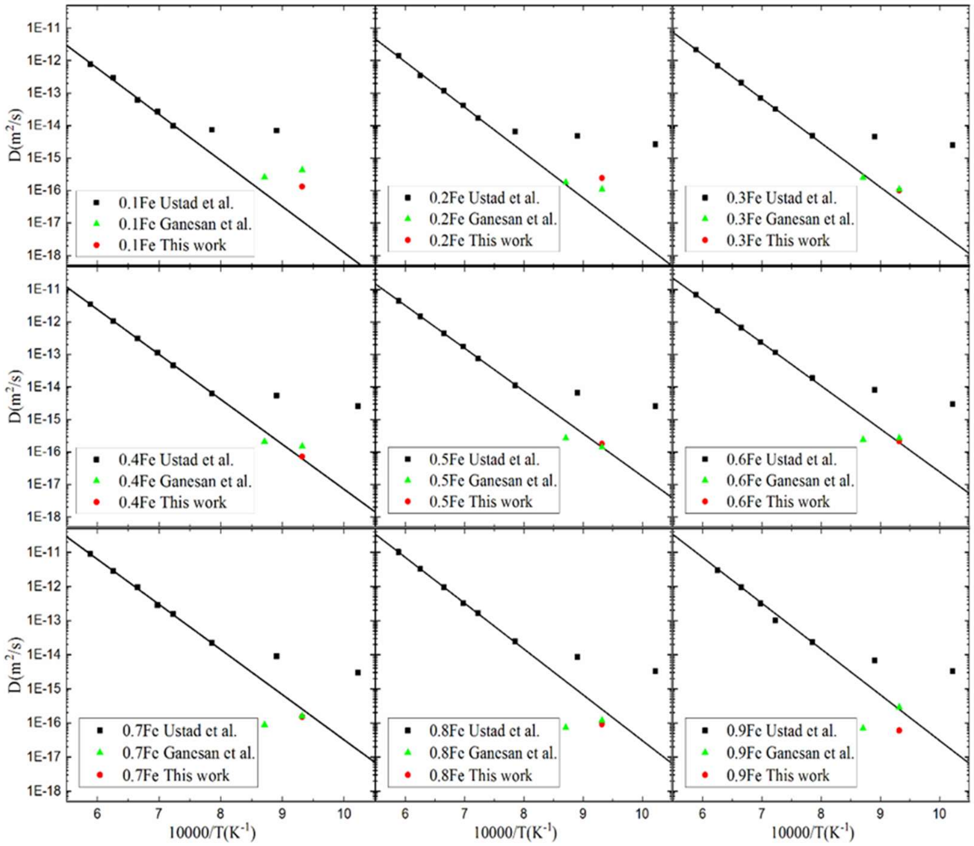
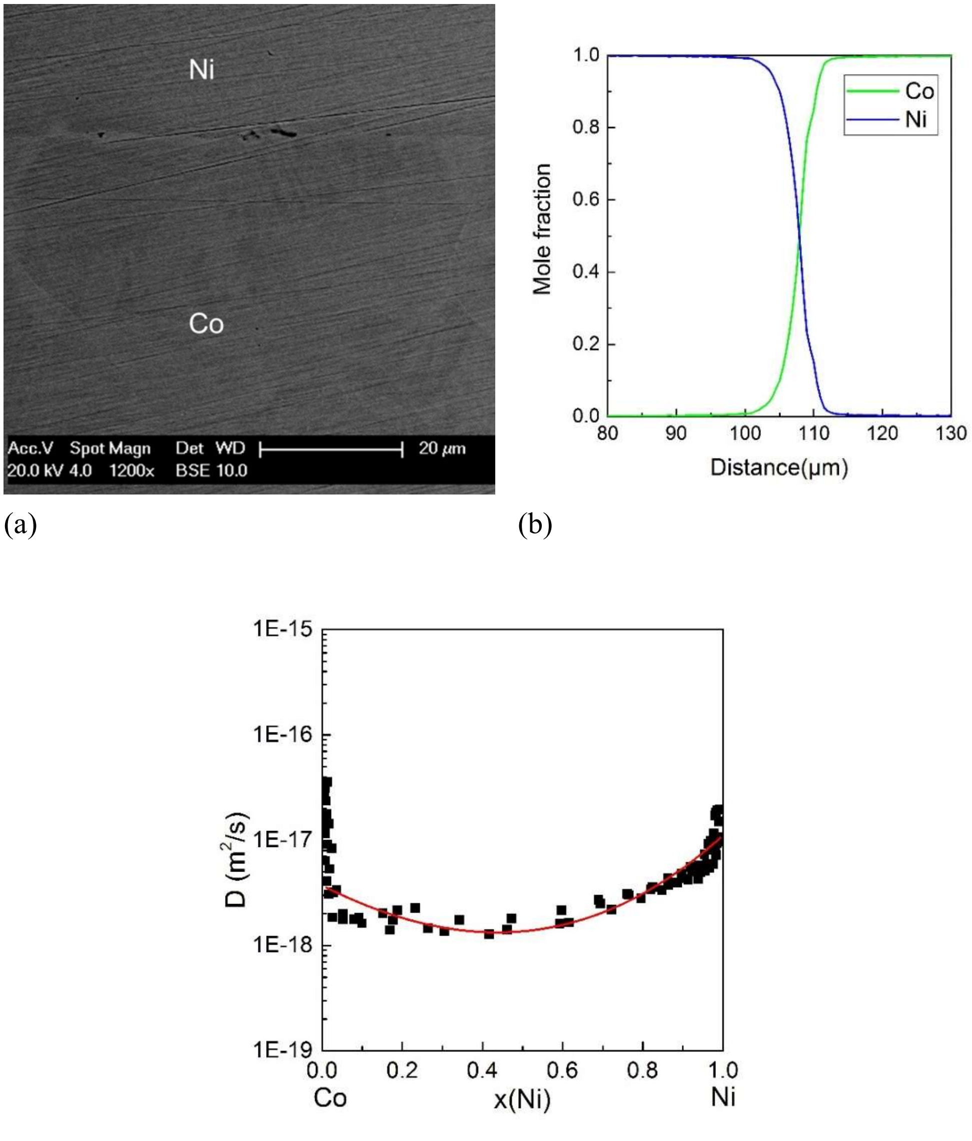


Fig. 5 Interdiffusion coefficients versus reciprocal temperature of the Fe-Ni system and compared with the data from Ustad et al [14] **and Ganesan et al** [15].

4.2 Diffusion of the Co-Ni system



(a) (b)

(c)

Fig. 6 (a) BSE image of the Co-Ni binary joint at 800 °C;
(b) Measured composition profile of the Co-Ni diffusion layer of one typical line perpendicular to the interface;
(c) Interdiffusion coefficients calculated based on the measured composition profile (b) at 800 °C. In (c) black points represent the data calculated from several lines perpendicular to the interface and the red line is the fitting curve using the least squares fitting method.

Fig. 6 shows a BSE image of the Co-Ni binary joint (a), the measured composition profile in the Co-Ni diffusion zone (b), and calculated diffusion coefficients for the Co-Ni system at 800°C (c), respectively.

Heumann ang Kottmano [17], Iijina and Hirano [36], Kucera et al. [20] and Ustad and Sorum [14] measured interdiffusion coefficients of the Co-Ni system. Similarly to the Fe-Ni system, the results from Ustad and Sorum [14] show a deviation from the Arrhenius relation extrapolated from higher temperature data for temperatures below 1300 °C. However, our values are perfectly in line with the Arrhenius relation extrapolated from higher temperature data in literature, as shown in Fig. 7. Furthermore, the change of the interdiffusion coefficients with the composition dependence is found to be quite small. This is physically reasonable since the two elements are completely mutual soluble, as shown in Fig. 1 (b), and the atomic radiuses of two elements are similar.

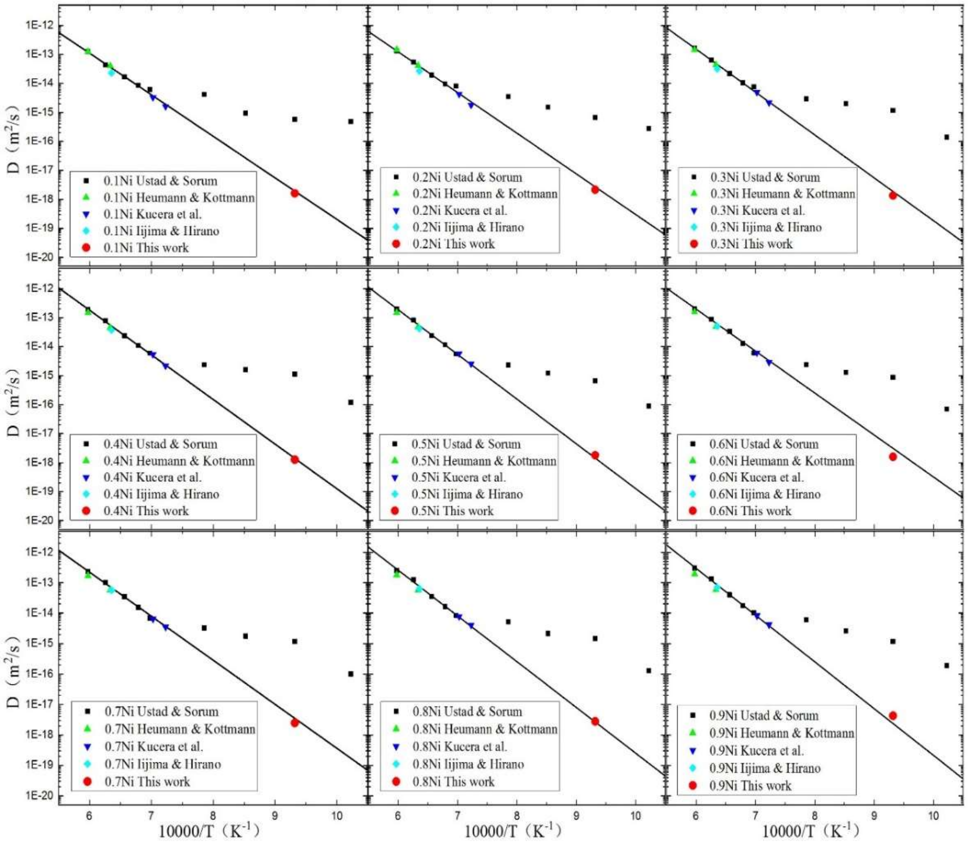
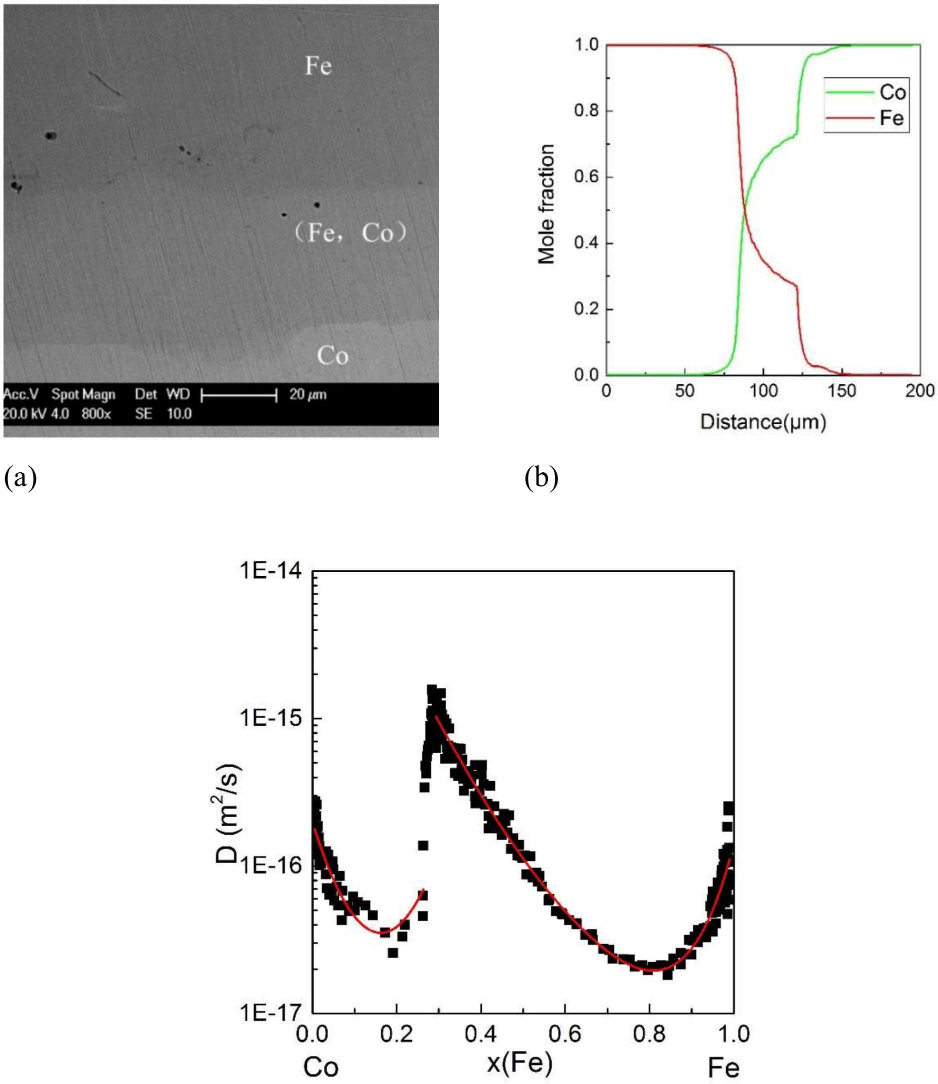


Fig. 7: The Interdiffusion coefficient versus reciprocal temperature of the Co-Ni system and compared with literature data from Heumann ang Kottmano [15], Iijina and Hirano [34], Kucera et al. [18] and Ustad and Sorum [12].

4.3 Diffusion of the Co-Fe system



(a) (b)

(c)

Fig. 8 (a) BSE image of the Co-Fe binary joint at 800 °C;

(b) Measured composition profile of the Co-Fe diffusion layer of one typical line perpendicular to the interface;

(c) Interdiffusion coefficients calculated based on the measured composition profile (b) at 800 °C. In (c) black points represent the data calculated from several lines perpendicular to the interface and the red line is the fitting curve using the least squares fitting method.

Fig. 8 shows BSE image of Fe-Co binary joint (a), the composition profile in the Fe-Co diffusion zone (b) and calculated diffusion coefficient of Fe-Co system at 800℃ (c).

At 800 °C, both bcc and fcc phases presented with the change of composition. Accordingly, the diffusion curve can be divided into two parts. Ustad et al. [14] and Badia et al. [37] investigated the diffusion in fcc Fe-Co above 1000 °C, which is above the temperatures of the fcc-bcc phase transition. Fig. 9 shows the interdiffusion coefficients versus reciprocal temperature of the Fe-Co system. It is seen that the values of $\widetilde{D}$ at temperature of 800 °C obtained in this work coincide with the Arrhenius line extrapolated from the literature data [14,37] for both fcc and bcc phase, excluding the points at 30 at% Fe and 40 at% Fe. These two composition points, as shown in Fig. 1(c), are in or near the two-phase region and the values obtained at this region was considered to be less reliable. The sharp change of the composition at the phase interface, as shown in Fig. 8(b), may results a sharp change of the gradient, as well as, a sharp change of the diffusion constants. A strong composition dependence of the interdiffusion curve for both phases was observed.

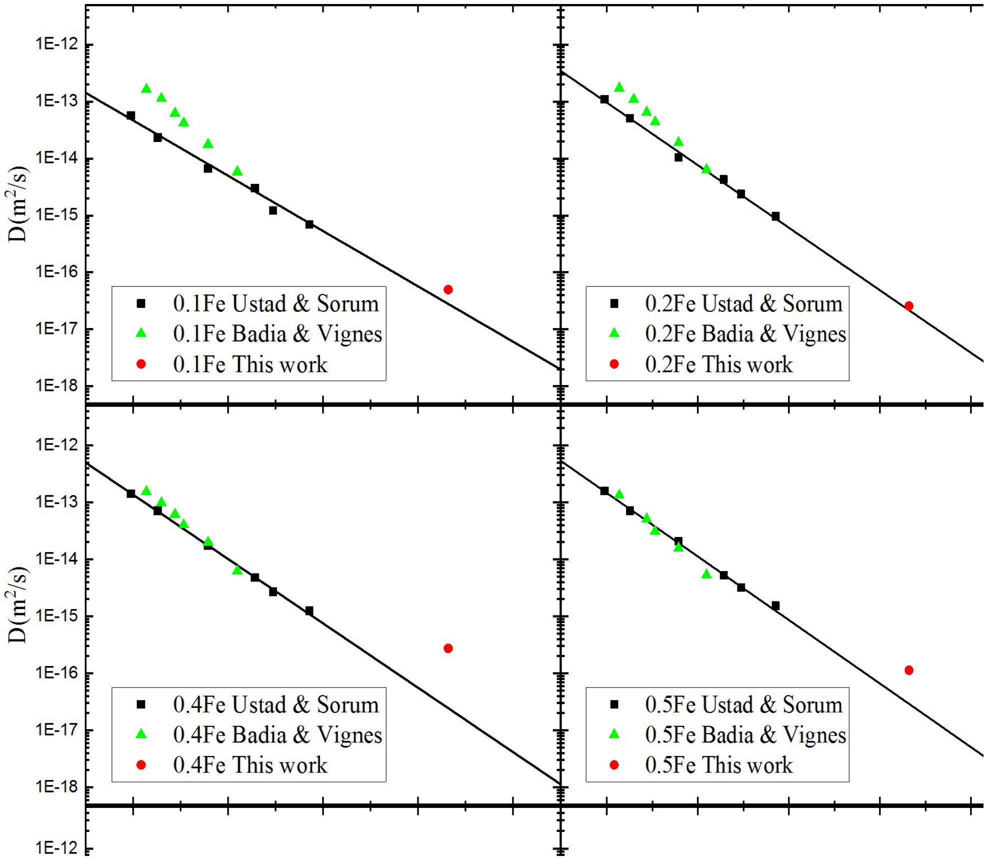
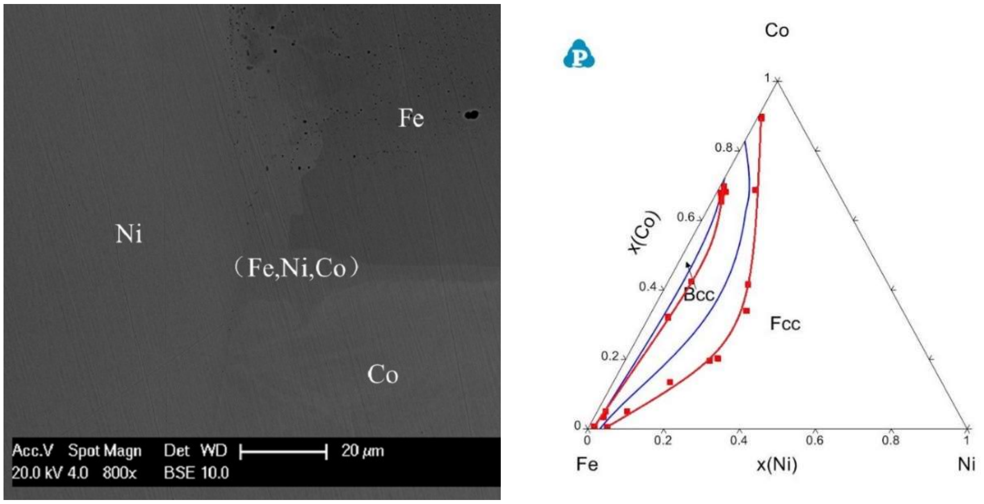


Fig. 9 Interdiffusion coefficients versus reciprocal temperature of the Co-Fe system and compared with the data from Ustad et al.[14] and Badia et al. [37].

4.4 The isothermal section of the Fe-Co-Ni system at 800 °C



(a) (b)

Fig. 10 (a) The obtained BSE image of the Co-Fe-Ni ternary joint at 800 °C
(b) The isothermal section of the Co-Fe-Ni system at 800 °C

Microscopy image of the ternary joint and the schemed isothermal-section is given in Fig. 10. No intermediate phases show up in the Co-Fe-Ni system. Mutual diffusion among the three elements has been observed in the diffusion region. According to the EPMA analysis, the schemed phase regions at the section of 800 °C is shown in Fig. 10 (b), in which the blue lines are the phase boundaries calculated using assessment database [3]. For the boundary of the two-phase fcc+bcc region, a clear discrepancy between the calculation and this experimental work can be observed. Re-assessment of the system is therefore suggested since this system is so important and broadly used.

5 Conclusion

Co-Fe-Ni system is a key system in many fields of industrial applications. The phase equilibria and binary diffusion coefficients of the Co-Fe-Ni system at 800°C were investigated using the diffusion multiple approach.

The isothermal section at 800°C was obtained based on a ternary diffusion joint, where the two-phase region of fcc+bcc is determined and a discrepancy with the assessed data is observed.

Reliable interdiffusion coefficient of Co-Fe, Fe-Ni and Co-Ni systems at 800°C is obtained. The interdiffusion coefficients are perfectly in coincident with the literature data in high temperature range extrapolated to the low temperature following the Arrhenius equation.

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Data availability

The datasets generated during and/or analyzed during the current study are available on request.

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