

Phase Equilibria in Ni-Rich Portion of Ni-Si System

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The phase equilibria of the Ni-rich portion in the Ni-Si system were investigated. The phase boundaries between liquid and fcc phases were established by the diffusion couple method and those of fcc and β_1 or β_2 were determined by the SEM-EDX measurement of two-phase alloys. The liquidus of the present work well agrees with the previous experimental data determined by a thermal analysis. The solidus data are rather different from the previous experimental data, but agree with the thermodynamic calculated phase diagram. This result suggests that the present solidus and liquidus data are consistent with thermodynamic data. The solubility of Si in the fcc phase agrees with some previous experimental data, but disagrees with the thermodynamic calculated phase diagram. This fact suggests that the thermodynamic reassessment for this system is necessary by the CALPHAD approach. [doi:10.2320/matertrans.MB200702]

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1. Introduction

Ni-based brazing filler metals are widely used in various engineering fields. Knowledge of the phase diagrams and thermodynamic properties of such alloys is basic information for an understanding their solidification process and phase stability.

The Ni-Si system is an important sub-system of the Ni-based filler alloys. The experimental phase diagram of this system has been studied several times¹⁻⁷⁾ since Guertler and Tammann¹⁾ reported the entire composition, which they determined by differential thermal analysis (DTA). Experimental information on the phase diagram in this system have been previously reviewed by Nash and Nash.⁸⁾

The calculated phase diagram of this system obtained by the CALPHAD approach has also been reported by several research groups.⁹⁻¹³⁾ The CALPHAD approach can be used to check for internal consistency between thermodynamic and phase diagram data and to provide optimized thermodynamic parameters. A typical calculated phase diagram with experimental data taken into account in the thermodynamic assessment of this system by Lindholm and Sundman¹¹⁾ is redrawn in Fig. 1. The calculated results almost entirely agree with the experimental data. As shown in Fig. 1, however, the agreement of the solidus and solubility of Si in fcc phase of the Ni-rich region is insufficient. Uncertainty of experimental data as well as an incomplete optimization of the thermodynamic function are considered to be the cause of this disagreement. Nash and Nash also suggested the necessity of redetermining of the solubility of Si in the fcc phase.⁸⁾

In this study, the phase equilibria of the fcc/liquid were reexamined by diffusion couple method because the distribution coefficient is important to understand the segregation behavior during the solidification. In addition, the fcc/ β were also reexamined to establish the phase boundaries of Ni-rich side in the Ni-Si system.

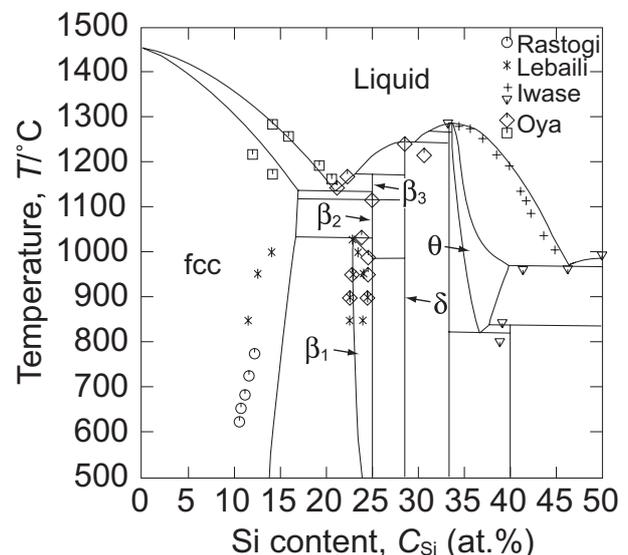


Fig. 1 Ni-Si phase diagram calculated by Lindholm and Sundman¹¹⁾ and experimental data.^{3,5-7)}

2. Experiment

The phase equilibria between the liquid and fcc phases were experimentally measured by the solid-liquid diffusion couple method. A schematic illustration of solid-liquid diffusion couple is shown in Fig. 2. Cylindrical pure Ni ingots weighing about 100 g each were prepared by induction melting of electrolytic Ni (99.9%) under an argon atmosphere. The ingots were cut section 12 mm in diameter and 10 mm in length. A small hole 2 mm in diameter and 5 mm in length was drilled into each ingot as shown in Fig. 2. Small chips of Ni-10 mass% Si alloy cut from a button prepared by arc melting of electrolytic Ni and high purity Si (99.999%) were inserted in the hole. Diffusion couples sealed in evacuated quartz capsules were heated for 30 min at temperatures ranging from 1200 to 1400 °C for equilibrium treatment. After quenching in ice water, the diffusion couples were cut parallel to the top of the cylinder and the

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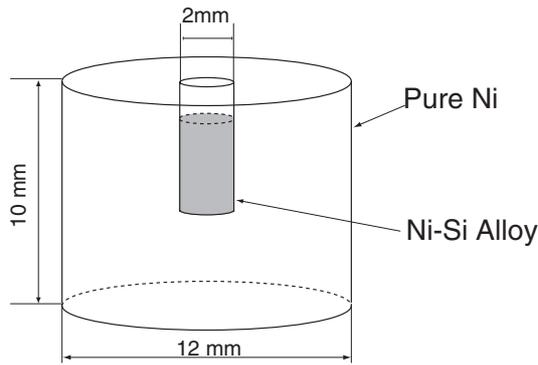


Fig. 2 Schematic illustration of diffusion couple.

concentration of each constituent near the solid/liquid interface was analyzed.

The phase equilibria between fcc and β_1 or β_2 phases were also examined by using fcc+ β two-phase alloy. Small specimens were taken from the Ni-10 mass% alloy button and sealed in evacuated quartz capsules. The specimens were heated at temperatures ranging from 800 to 1100 °C to establish equilibrium fcc and β_1 or β_2 phases and then the specimens were quenched in ice water.

The microstructure of samples, etched in 25% nitric acid and 75% hydrochloric acid solution, was examined by optical microscopy. The local chemical composition of the samples was determined by scanning electron microscopy equipped with energy dispersion x-ray spectroscopy (SEM-EDX). The chemical composition was calibrated by the standard alloys.

3. Results and Discussion

3.1 Solid-liquid diffusion couple

Typical optical photographs of solid-liquid diffusion couple are shown in Fig. 3. Figure 3(a) shows a macrograph of the hole. The chips of the Ni-10 mass%Si alloy were completely melted and the hole was permeated with the alloy. A micrograph in the vicinity of the interphase boundary between the liquid and fcc phase is shown in Fig. 3(b). In the region on the left, a dendritic structure can be observed. This fact suggests that this area melted at the annealing temperature. Small protrusions are appeared at the solid/liquid interface as shown in Fig. 3(b). These protrusions would be developed during the quenching of the sample. It can be considered that the flat part of the interface is close to the original solid/liquid interphase boundary at the annealing temperature. Therefore, the concentration profile of Si in the solid phase was measured along the direction vertical to the flat part of the interphase boundaries to determine the phase equilibria. A typical composition profile near the interphase boundary annealed at 1362 °C is shown in Fig. 4. The Si content in the fcc phase can be seen to decrease monotonously with increased distance from the interphase boundary. This result suggests that the effect of the interphase boundary movement during the quenching on the composition profile is small, because the slope of the composition profile developed during the solidification would be changed at the original interface, if the interphase boundary movement during the quenching is large. The equilibrium composition of the fcc

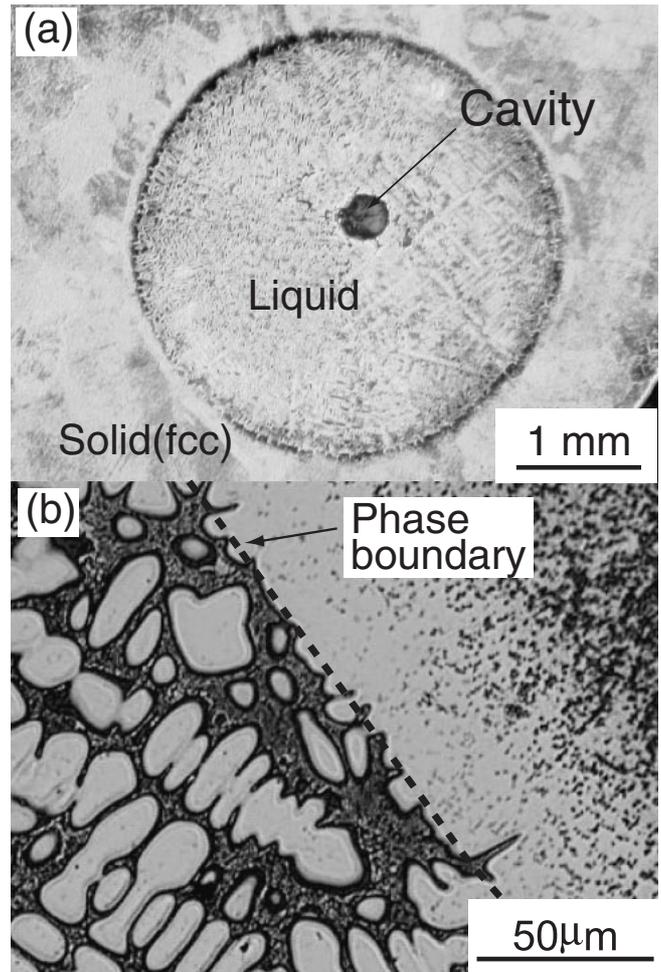


Fig. 3 Optical photographs of the diffusion couple annealed at 1300 °C for 30 min. (a) appearance of the hole and (b) microstructure near the interphase boundary between liquid and solid.

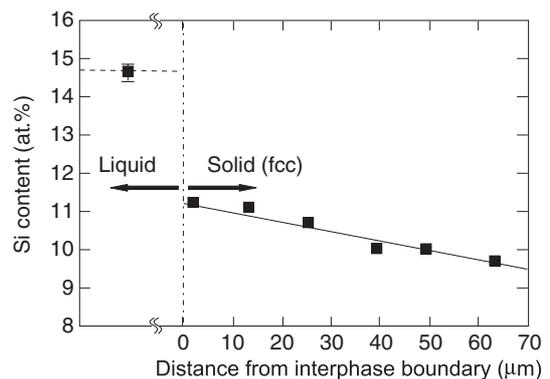


Fig. 4 Composition-penetration curve of the diffusion couple annealed at 1362 °C for 30 min.

phase was determined by extrapolating the composition-penetration profile to the interphase boundary linearly by the method of least squares. On the other hand, the compositions of the liquid phase were not always uniform due to the dendritic structure. Thus, scanning image analysis of the specimens was carried out and the average value was adopted as the equilibrium composition of the liquid phase.

Table 1 Composition of liquid, fcc, β_1 and β_2 phases in equilibrium at different temperatures.

Temp. (°C)	Annealing time	Si (at%)	
		fcc	liquid
1400	30 min.	5.6	8.3
1362	30 min.	8.2	11.1
1300	30 min.	10.9	14.7
1210	30 min.	13.8	18.1
		fcc	β_2
1100	3 days	18.8	25.1
		fcc	β_1
1000	14 days	17.3	21.2
900	14 days	13.5	21.5
800	21 days	12.4	22.1

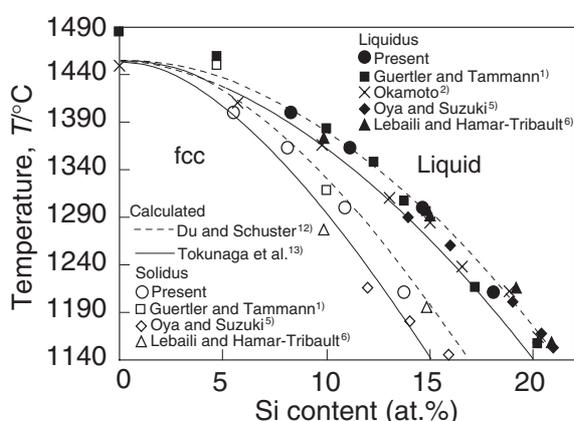


Fig. 5 Phase equilibria between the liquid and fcc phases at different temperatures.

The phase equilibria data obtained by the diffusion couple technique are listed in Table 1 and are plotted in Fig. 5 compared with previous experimental data^{1,2,5,6} and recent calculated results.^{12,13} The liquidus of the present work well agrees with the previous experimental data determined by DTA. While the solidus data is rather different from the previous experimental data. The diffusion couple method would be obtained more reliable data for the solidus than DTA method, because the solidus data determined by DTA are generally influenced by microsegregation of sample. The present experimental data are consistent with the calculated results by Du and Schuster.¹² This result suggests that the present experimental data are also consistent with the thermodynamic data. The present experimental data are useful for prediction of the segregation behavior of Si during the solidification of the Ni-base brazing filler metals.

3.2 Phase equilibria of solid phases

The micrographs of the Ni-10 mass%Si alloy annealed at 1100 and 1000 °C are shown in Fig. 6. The two-phase structure was obtained at both annealing temperatures. The chemical composition of each phase was examined by SEM-EDX. The crystal structure of the two-phase alloys can be presumed as fcc+ β_1 at 1000 °C and fcc+ β_2 at 1100 °C from the configuration of the previous phase diagram information

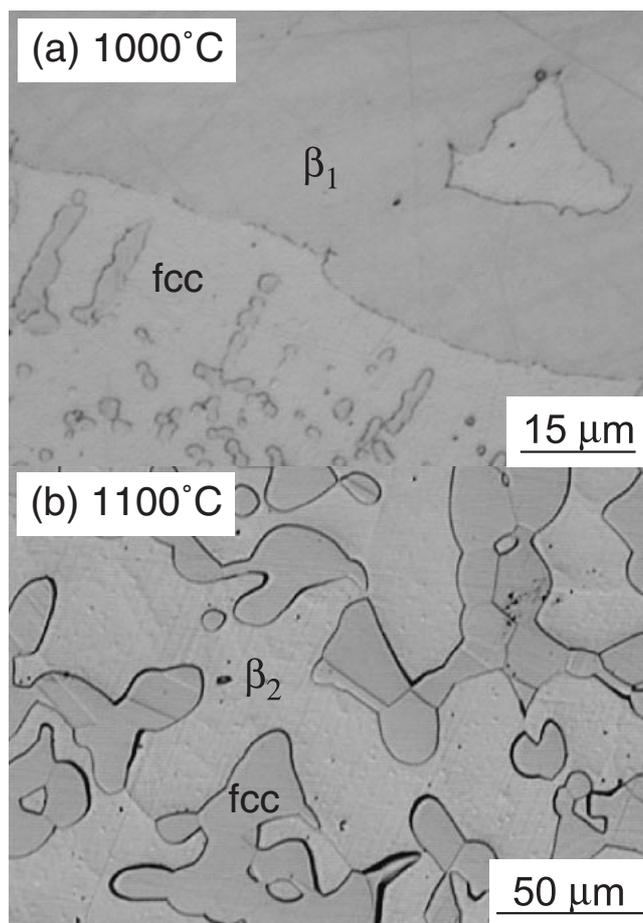


Fig. 6 Optical micrograph of two-phase alloys. (a) 1000 °C and (b) 1100 °C.

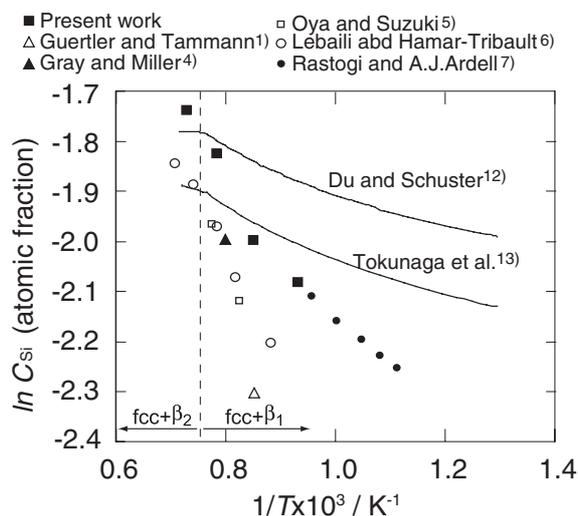


Fig. 7 Arrhenius plot of the equilibrium solubility of Si in the fcc phase.

determined by the XRD analysis.⁸ The obtained phase equilibria data are also listed in Table 1 and the solubility of Si in the fcc phase is plotted in Fig. 7 compared with the previous experimental data^{1,4-7} and the recent calculated results.^{12,13} The slope of the present results obey an Arrhenius relationship and are almost the same as that based on the results by Rastogi and Ardell.⁷ The difference

between the experimental data and the calculated data becomes large with decreasing temperature. The phase equilibria between fcc and β_1 or β_2 should be reassessed by the CALPHAD approach based on the present experimental data and thermodynamic data.⁸⁾

4. Conclusion

The phase equilibria of the Ni-rich portion in the Ni-Si system were investigated and compared with previous experimental data and calculated phase diagrams. The phase boundaries between the liquid and fcc phases were established by the diffusion couple method.

The liquidus of the present work well agrees with the previous experimental data determined by a thermal analysis. The solidus data are rather different from the previous experimental data, but agree with the thermodynamic calculated phase diagram.

The phase equilibria between fcc and β_1 or β_2 were determined by SEM-EDX measurement of two-phase alloys. The solubility of Si in the fcc phase obey an Arrhenius relationship and agrees with some previous experimental data. But the present data disagrees with the thermodynamic calculated phase diagram. The present experimental data are useful for thermodynamic reassessment of this system.

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