Phase Equilibria of the Ternary Al-Cu-Ni System and Interfacial Reactions of Related Systems at 800 °C

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A series of Al-Cu-Ni alloys of various compositions were made and annealed at 800 °C. The equilibrium phases were studied by metallography, X-ray diffraction (XRD) analysis, and electron probe microanalysis. The isothermal section of the ternary Al-Cu-Ni system at 800 °C was then determined based on these experimental results and the available phase relationship knowledge of the three constituent binary systems. No ternary compound was found. All three phases, $AlNi_3$, AlNi, and Al_3Ni_2, have very high ternary solubility, especially the AlNi phase, which almost reaches the binary Al-Cu side. However, no continuous solid solution was formed between the AlNi phase and any of the binary Al-Cu phases. Interfacial reactions of Al/Ni, Al/Cu, Al-Cu/Ni, and Al-Ni/Cu at 800 °C were investigated by using reaction couple techniques. The results showed that Al_3Ni and Al_3Ni_2 phases were formed in the Al/Ni couples; β-$AlCu_4$, γ_1-Al_4Cu_9, and ε_2-Al_2Cu_3 phases were formed in the Al/Cu couples. As for the results in the Al-2 at. pct Ni/Cu, Al-5 at. pct Ni/Cu, and Al-2 at. pct Cu/Ni, Al-4.5 at. pct Cu/Ni, and Al-6 at. pct Cu/Ni were similar to those in the binary Al/Cu and Al/Ni couples, respectively. A different reaction path was found in the Al-7.5 at. pct Cu/Ni couples, and an AlNi solid solution layer was formed instead of the Al_3Ni and Al_3Ni_2 phases.

I. INTRODUCTION

INFORMATION on phase equilibria and interfacial reactions can provide a fundamental understanding of various industrial processes. For example, knowledge of phase equilibria in the Al-Cu-Ni system and interfacial reactions of related systems appeared to be valuable in our recent interest to develop the spray coating technology of Cu-Ni alloys on an Al substrate.[1,2] However, only limited results from previous studies are available.[3–19] This study determined the isothermal section of the Al-Cu-Ni ternary system and interfacial reactions of Al/Ni, Al/Cu, Al-Cu/Ni, and Al-Ni/Cu systems at 800 °C. These fundamental data are beneficial to the development of coating technology and other applications.

Austin and Murphy[3] were the first to determine the phase relationship of the Al-Cu-Ni system, and they proposed the formation of a continuous solid solution between the β-$AlCu_3$ and the AlNi phases. It should be mentioned that Llewelyn Leach[20] studied the β phase in the Al-Cu binary system and found that the β phase should be $AlCu_4$ not $AlCu_3$, as commonly used in the literature. Bingham and Haughton[4] studied only at the Al-rich corner, and found a ternary T compound with an unknown composition. Alexander[5] studied this ternary system on the (Cu,Ni) side containing aluminum from 1 to 35 pct. They reported the formation of a solid solution between β-$AlCu_4$ and AlNi phases, but no ternary compound. Rudolph determined the phase boundaries of the α-(Cu,Ni) solid solution from the Al-5 wt pct Ni-80 wt pct Cu/Ni diffusion couples,[19] and he found a higher Al solubility in the α phase than that reported by Alexander.[5] Bradley and Lipson[6] examined the slowly cooled ternary alloys by X-ray diffraction (XRD), and reported the formation of a ternary Cu_3NiAl_6 phase.

Literature on interfacial reactions is available for the binary couples Al/Ni and Al/Cu,[7–16] although none of it is carried out at 800 °C. Furthermore, barely any previous studies of interfacial reactions can be found of the ternary Al-Cu/Ni and Al-Ni/Cu systems.[17,18,19] In the binary Al-Ni system, there are five stable compounds, Al_3Ni, Al_3Ni_2, AlNi, Al_3Ni_5, and $AlNi_3$, when temperatures are lower than 700 °C;[21] however, only the Al_3Ni phase is found in all of the Al/Ni reaction couples.[7–11] Unlike the Al/Ni system, Funamizu and Watanabe[12] found formation of all five stable compounds,[22] θ-Al_2Cu, η_2-AlCu, ζ_2-Al_3Cu_4, δ-Al_2Cu_3, and γ_1-Al_4Cu_9, in the Al/Cu bulk diffusion couples reacted at temperatures from 400 °C to 535 °C. However, in the thin-film Al/Cu couples, some of the stable phases are missing.[13–16]

II. EXPERIMENTAL PROCEDURES

Alloys were prepared with elements of high purities, Al (99.98 wt pct), Cu (99.99 wt pct), and Ni (99.98 wt pct). Proper amounts of elements were weighed and arc-melted together. The arc-melted alloy button was placed in a boron nitride crucible and was encapsulated in a quartz tube under a vacuum of 10^{-3} torr. The sample capsule was then annealed at 800 °C. After 30 days, the quartz capsule was removed from the furnace and quenched into ice water. One part of the alloy was metallographically examined, and the other part of the alloy was prepared for powder XRD analysis. The phases formed were determined based on the electron probe microanalysis (EPMA) compositional measurement, XRD analysis, and metallographical results. A standard ZAF calibration procedure without any self-prepared standard was used for the EPMA. The relative error associated with the reported compositions was about 3 pct.

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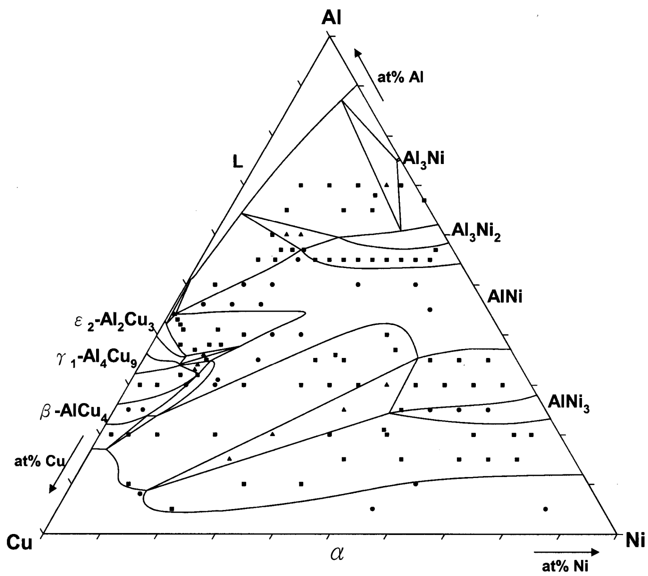

Fig. 1—The isothermal section of the Al-Cu-Ni ternary system superimposed with the compositions of the alloys examined in this study.

Sandwich-type reaction couples were prepared in this study. The high-melting-point substrates, Ni foil and Cu foil, were 500-μm thick and placed in the center of a boron nitride mold. The low-melting-point materials, Al, Al-Ni alloy, and Al-Cu alloys, were melted and poured into the boron nitride mold, which was then quenched immediately. The reaction couple was sealed in a quartz tube similar to that used in the phase equilibria study, and then placed in a furnace at 800 °C. After a predetermined length of time, the sample was removed from the furnace and examined metallographically. The length of reaction time should be long enough to have a noticeable reaction layer, but it should not be too long to avoid excessive reaction, so that the diffusion couple could still be treated as an infinite couple. Compositions of the formation layers were determined by EPMA, and the layer thickness was measured by using an image analysis system equipped with an optical microscope.

III. RESULTS AND DISCUSSION

There are a total of 112 alloys prepared for the phase equilibria study. Their compositions are shown in Figure 1 and Table I. Figure 2 is the backscattered electron image (BEI) micrograph of alloy 106 (Al-50 at. pct Cu-40 at. pct Ni). Composition of the dark phase determined by using EPMA is Al-16.5 at. pct Cu-60.9 at. pct Ni, and that of the bright phase is Al-60.9 at. pct Cu-33.6 at. pct Ni. As is shown in Figure 2, although the sample has been annealed, the dendritic structure of the bright phase can still be noticed, which indicates that the bright phase is the primary solidification phase. Based on the EPMA analysis and XRD results, it is concluded that these two phases are $AlNi_3$ and α-(Cu,Ni), respectively. A similar procedure has been used for phase identification of all the other alloys examined in this study. Similar results are found in alloys 95 through 108, and are all in the $AlNi_3$ and α-(Cu,Ni) two-phase region.

Figure 3 is the BEI micrograph of alloy 84 (Al-10 at. pct Cu-60 at. pct Ni). Compositional analysis by using EPMA indicates the needle-shape phase is the $AlNi_3$ phase, and the continuous dark phase is the AlNi phase. As is shown in Table I, similar results are found for alloys 80 through 87. Figure 4 is the BEI of alloy 77 (Al-70 at. pct Cu-10 at. pct Ni). Analysis indicates the bright and continuous phase is the α-(Cu,Ni) phase, while the dark phase is the AlNi phase. Figure 5 is the BEI micrograph of alloy 91 (Al-25 at. pct Cu-45 at. pct Ni) in which three phases are found: the dark matrix phase is the AlNi phase, the gray phase is the $AlNi_3$ phase, and the bright phase is the α-(Cu,Ni) phase. It has also been found that alloys 88 through 90 are all in the $AlNi_3$ single-phase region. The EPMA results and the phase identifications of all alloys are summarized in Table I. These aforementioned results delineate the phase relationship around the Ni-rich corner. The compositional homogeniety range of the AlNi phase is very large and is in parallel with the (Cu,Ni) side. These results are in agreement with those by Alexander.[5] Most of the Al-Ni binary phases have a solubility range parallel to the (Cu,Ni) side, which suggests that the Cu atoms reside most often in the Ni site of the Al-Ni phases.

Figure 6 is the BEI of alloy 18 (Al-20 at. pct Cu-25 at. pct Ni). The dark phase is the Al_3Ni_2 phase, and the bright phase is the AlNi phase. The needlelike dark phase appeared in the bright AlNi phase is also Al_3Ni_2 phase. Because of its dispersion in the AlNi phase matrix, the Al_3Ni_2 phase is likely formed during solid-state annealing. Figure 7 is the BEI of alloy 1 (Al-2.5 at. pct Cu-27.5 at. pct Ni). A significant portion of voids has been found beside the dark Al_3Ni phase and the bright Al_3Ni_2 phase. Figure 8 is the BEI of alloy 5 (Al-15 at. pct Cu-15 at. pct Ni). A very large bright phase is adjacent to a dark area with a fine structure. The bright phase is the Al_3Ni_2 phase. The dark region has various phases, and it is likely that the dark region is liquid phase prior to quenching. Generally, the primary solidification phase, *i.e.*, the Al_3Ni_2 phase in this example, tends to grow larger in comparison with other phases, which are grown as secondary phases or are precipitated in the solid state.[23]

Figure 9 is the BEI of alloy 3 (Al-5 at. pct Cu-25 at. pct Ni). Two large phases and a region with a fine structure have been found. The large gray phase is the Al_3Ni phase, the bright phase is the Al_3Ni_2 phase, and the dark and fine structure region is the liquid phase prior to solidification. Alloy 3 is located in the three-phase region. The compositions of the Al_3Ni_2 and Al_3Ni phases are determined to be Al-7.1 at. pct Cu-32 at. pct Ni and Al-0.4 at. pct Cu-24.3 at. pct Ni by EPMA, respectively. While that of the liquid phase has been calculated by using the lever rule. The aforementioned results of phase equilibria study are used to construct the equilibrium phase relationships around the Al-rich corner. At 800 °C, aluminum is in the molten state. Austin and Murphy[3] determined the liquidus surface of the Al-Cu-Ni system. Phase boundary points of the liquid phase at 800 °C determined from their Figures 7 and 8[3] are Al-7.4 at. pct Cu-8 at. pct Ni, Al-10.4 at. pct Cu-6.2 at. pct Ni, Al-23 at. pct Cu-3.2 at. pct Ni, and Al-39.8 at. pct Cu-1.4 at. pct Ni, which are consistent with the results of this study.

Although Austin and Murphy[3] and Alexander[5] reported the formation of a continuous solid solution between the β-$AlCu_4$ and AlNi phase, it has been found that the structures of the AlNi phase and the β-$AlCu_4$ phase are B2 and A2, respectively.[21,22] Since these two phases have different

Table I. Phase Identification of Alloys Examined in This Study

Number	Alloy Composition, At. Pct	Phases in Equilibrium	Composition, At. Pct		
			Al	Cu	Ni
1	70 at. pct Al-2.5 at. pct Cu-27.5 at. pct Ni	Al_3Ni_2	60.8	5.5	33.7
		Al_3Ni	75.1	0.3	24.6
2	67 at. pct Al-0 at. pct Cu-33 at. pct Ni	Al_3Ni_2	61.9	0	38.1
		Al_3Ni	75.3	24.7	0
3	70 at. pct Al-5 at. pct Cu-25 at. pct Ni	Al_3Ni_2	60.9	7.1	32.0
		Al_3Ni	75.3	0.4	24.3
		L	—	—	—
4	70 at. pct Al-10 at. pct Cu-20 at. pct Ni	Al_3Ni_2	60.3	11.1	28.6
		L	—	—	—
5	70 at. pct Al-15 at. pct Cu-15 at. pct Ni	Al_3Ni_2	60	14.7	25.3
		L	—	—	—
6	70 at. pct Al-20 at. pct Cu-10 at. pct Ni	Al_3Ni_2	59.3	16.4	24.3
		L	—	—	—
7	68 at. pct Al-8 at. pct Cu-24 at. pct Ni	Al_3Ni_2	60.5	9.1	30.4
		L	—	—	—
8	65 at. pct Al-10 at. pct Cu-25 at. pct Ni	Al_3Ni_2	60.2	10.4	29.4
		L	—	—	—
9	65 at. pct Al-15 at. pct Cu-20 at. pct Ni	Al_3Ni_2	59.6	14.9	25.5
		L	—	—	—
10	65 at. pct Al-25 at. pct Cu-10 at. pct Ni	Al_3Ni_2	59.3	17.9	22.8
		L	—	—	—
11	57 at. pct Al-3 at. pct Cu-40 at. pct Ni	AlNi	53.9	3	43.1
		Al_3Ni_2	57.8	2.8	39.4
12	55 at. pct Al-5 at. pct Cu-40 at. pct Ni	AlNi	53.6	5.5	40.9
		Al_3Ni_2	57.3	4.7	38
13	55 at. pct Al-7.5 at. pct Cu-37.5 at. pct Ni	AlNi	53.6	7.8	38.6
		Al_3Ni_2	57.2	6.4	36.4
14	55 at. pct Al-10 at. pct Cu-35 at. pct Ni	AlNi	53.4	11.2	35.4
		Al_3Ni_2	57	8	35
15	55 at. pct Al-12.5 at. pct Cu-32.5 at. pct Ni	AlNi	53.6	13.9	32.5
		Al_3Ni_2	57.2	10.5	32.3
16	55 at. pct Al-15 at. pct Cu-30 at. pct Ni	AlNi	53.4	16.3	30.3
		Al_3Ni_2	57.5	11.8	30.7
17	55 at. pct Al-17.5 at. pct Cu-27.5 at. pct Ni	AlNi	53.6	19.1	27.3
		Al_3Ni_2	57.7	14.1	28.2
18	55 at. pct Al-20 at. pct Cu-25 at. pct Ni	AlNi	54.0	22.5	23.5
		Al_3Ni_2	58.0	15.4	26.6
19	55 at. pct Al-22.5 at. pct Cu-22.5 at. pct Ni	AlNi	54.4	23.5	22.1
		Al_3Ni_2	58.2	16.1	25.7
20	55 at. pct Al-25 at. pct Cu-20 at. pct Ni	AlNi	54.8	25.7	19.5
		Al_3Ni_2	—	—	—
21	57 at. pct Al-26 at. pct Cu-17 at. pct Ni	AlNi	56.6	26.3	17.1
		Al_3Ni_2	59.2	18.8	22
22	60 at. pct Al-25 at. pct Cu-15 at. pct Ni	AlNi	57.1	26.4	16.5
		Al_3Ni_2	59.5	19	21.5
		L	—	—	—
23	60 at. pct Al-27.5 at. pct Cu-12.5 at. pct Ni	AlNi	56.9	26.4	16.7
		Al_3Ni_2	59.2	18.7	22.1
		L	—	—	—
24	60 at. pct Al-30 at. pct Cu-10 at. pct Ni	AlNi	56.5	26.7	16.8
		L	—	—	—
25	57 at. pct Al-28 at. pct Cu-15 at. pct Ni	AlNi	56.4	26.8	16.8
		L	—	—	—
26	57 at. pct Al-30 at. pct Cu-13 at. pct Ni	AlNi	55.7	28.8	15.5
		L	—	—	—
27	55 at. pct Al-32 at. pct Cu-13 at. pct Ni	AlNi	53.8	31.8	14.4
		L	—	—	—
28	55 at. pct Al-35 at. pct Cu-10 at. pct Ni	AlNi	52.3	34.6	13.1
		L	—	—	—
29	50 at. pct Al-45 at. pct Cu-5 at. pct Ni	AlNi	48.1	46	5.9
		L	—	—	—
30	55 at. pct Al-28 at. pct Cu-17 at. pct Ni	AlNi	—	—	—
31	50 at. pct Al-10 at. pct Cu-40 at. pct Ni	AlNi	—	—	—
32	50 at. pct Al-20 at. pct Cu-30 at. pct Ni	AlNi	—	—	—

Table I. (Continued) Phase Identification of Alloys Examined in This Study

Number	Alloy Composition, At. Pct	Phases in Equilibrium	Composition, At. Pct		
			Al	Cu	Ni
33	50 at. pct Al-35 at. pct Cu-15 at. pct Ni	AlNi	—	—	—
34	50 at. pct Al-40 at. pct Cu-10 at. pct Ni	AlNi	—	—	—
35	45 at. pct Al-10 at. pct Cu-45 at. pct Ni	AlNi	—	—	—
36	40 at. pct Al-35 at. pct Cu-25 at. pct Ni	AlNi	—	—	—
37	46 at. pct Al-39 at. pct Cu-15 at. pct Ni	AlNi	—	—	—
38	46 at. pct Al-44 at. pct Cu-10 at. pct Ni	AlNi	—	—	—
39	46 at. pct Al-49 at. pct Cu-5 at. pct Ni	AlNi	—	—	—
40	35 at. pct Al-54 at. pct Cu-11 at. pct Ni	AlNi	—	—	—
41	40 at. pct Al-40 at. pct Cu-20 at. pct Ni	AlNi	—	—	—
42	35 at. pct Al-45 at. pct Cu-20 at. pct Ni	AlNi	—	—	—
43	31 at. pct Al-54 at. pct Cu-15 at. pct Ni	AlNi	—	—	—
44	30 at. pct Al-55 at. pct Cu-15 at. pct Ni	AlNi	—	—	—
45	44 at. pct Al-55 at. pct Cu-1 at. pct Ni	ε_2-Al_2Cu_3	42	57	1.0
		AlNi	44.1	54.8	1.1
		L	—	—	—
46	43 at. pct Al-55 at. pct Cu-2 at. pct Ni	ε_2-Al_2Cu_3	41.5	57.3	1.2
		AlNi	43.7	53.9	2.4
47	42 at. pct Al-55 at. pct Cu-3 at. pct Ni	ε_2-Al_2Cu_3	40.1	57.6	2.3
		AlNi	42.7	53.4	3.9
48	40 at. pct Al-45 at. pct Cu-15 at. pct Ni	ε_2-Al_2Cu_3	35.71	56.92	7.4
		AlNi	44.4	32.4	23.2
49	41 at. pct Al-49 at. pct Cu-10 at. pct Ni	ε_2-Al_2Cu_3	36.9	57.7	5.4
		AlNi	44.6	41.9	13.5
50	41 at. pct Al-55 at. pct Cu-4 at. pct Ni	ε_2-Al_2Cu_3	39.7	57.7	2.6
		AlNi	44.3	49.5	6.2
51	38 at. pct Al-50 at. pct Cu-12 at. pct Ni	ε_2-Al_2Cu_3	35.5	57.3	7.2
		AlNi	42.2	37.3	20.5
52	38 at. pct Al-52 at. pct Cu-10 at. pct Ni	ε_2-Al_2Cu_3	36.2	57.2	6.6
		AlNi	44.2	36.0	19.8
53	37 at. pct Al-55 at. pct Cu-8 at. pct Ni	ε_2-Al_2Cu_3	36.1	57.3	6.6
		AlNi	44.6	36.4	19.0
54	38 at. pct Al-57 at. pct Cu-5 at. pct Ni	ε_2-Al_2Cu_3	37.8	57.8	4.4
		AlNi	45.6	43.4	11
55	36 pct Al-54 at. pct Cu-10 at. pct Ni	ε_2-Al_2Cu_3	35.7	56.9	7.4
56	35 at. pct Al-54 at. pct Cu-11 at. pct Ni	γ_1-Al_4Cu_9	34	58.7	7.3
		AlNi	36.4	49	14.6
57	34 at. pct Al-56 at. pct Cu-10 at. pct Ni	γ_1-Al_4Cu_9	33.8	59.4	6.8
		AlNi	35.2	53.1	11.7
		β-$AlCu_4$	32.4	56.2	11.4
58	33 at. pct Al-57 at. pct Cu-10 at. pct Ni	γ_1-Al_4Cu_9	33.7	59.4	6.9
		AlNi	35	53	12.0
		β-$AlCu_4$	32.3	56.4	11.3
59	32 at. pct Al-60 at. pct Cu-8 at. pct Ni	γ_1-Al_4Cu_9	34.1	58.7	7.2
		β-$AlCu_4$	29.1	62.3	8.6
60	30 at. pct Al-65 at. pct Cu-5 at. pct Ni	γ_1-Al_4Cu_9	27.5	67.1	5.4
		β-$AlCu_4$	33.2	61.4	5.4
61	30 at. pct Al-68 at. pct Cu-2 at. pct Ni	γ_1-Al_4Cu_9	32.4	65	2.6
		β-$AlCu_4$	26.5	72.1	1.4
62	32 at. pct Al-57 at. pct Cu-11 at. pct Ni	AlNi	35	53.2	11.8
		β-$AlCu_4$	32.3	56.6	11.1
63	30 at. pct Al-60 at. pct Cu-10 at. pct Ni	β-$AlCu_4$	—	—	—
64	25 at. pct Al-70 at. pct Cu-5 at. pct Ni	β-$AlCu_4$	—	—	—
65	25 at. pct Al-72.5 at. pct Cu-2.5 at. pct Ni	β-$AlCu_4$	—	—	—
66	20 at. pct Al-78 at. pct Cu-2 at. pct Ni	α	18	80.4	1.6
		β-$AlCu_4$	22.1	75	2.9
67	40 at. pct Al-20 at. pct Cu-40 at. pct Ni	α	13.3	80.1	6.6
		AlNi	41.2	16.2	42.6
68	37 at. pct Al-20 at. pct Cu-43 at. pct Ni	α	10.3	79.2	10.5
		AlNi	38.3	15.5	46.2
69	36 at. pct Al-31 at. pct Cu-33 at. pct Ni	α	16.2	78.3	5.5
		AlNi	42.7	19.6	37.7
70	35 at. pct Al-30 at. pct Cu-35 at. pct Ni	α	12.7	79.8	7.5
		AlNi	40.6	16.6	42.8
71	35 at. pct Al-35 at. pct Cu-30 at. pct Ni	α	15.07	79.59	5.34

Table I. (Continued) Phase Identification of Alloys Examined in This Study

Number	Alloy Composition, At. Pct	Phases in Equilibrium	Composition, At. Pct		
			Al	Cu	Ni
		AlNi	42.02	18.85	39.13
72	30 at. pct Al-30 at. pct Cu-40 at. pct Ni	α	9	77.8	13.2
		AlNi	35.6	17.2	47.2
73	30 at. pct Al-35 at. pct Cu-35 at. pct Ni	α	10.5	79.4	10.1
		AlNi	37.5	16.1	46.4
74	30 at. pct Al-40 at. pct Cu-30 at. pct Ni	α	11.8	80.8	7.4
		AlNi	40.3	15.8	43.9
75	30 at. pct Al-50 at. pct Cu-20 at. pct Ni	α	17.3	78.8	3.9
		AlNi	39.2	29.1	31.7
76	20 at. pct Al-60 at. pct Cu-20 at. pct Ni	α	10.8	81.2	8
		AlNi	38.9	16.1	45
77	20 at. pct Al-70 at. pct Cu-10 at. pct Ni	α	15.5	80.1	4.4
		AlNi	42.1	20.4	37.5
78	20 at. pct Al-75 at. pct Cu-5 at. pct Ni	α	17.0	80.1	2.9
		AlNi	28.6	57.8	13.6
79	10 at. pct Al-80 at. pct Cu-10 at. pct Ni	α	9.5	80.9	9.6
		AlNi	37.8	16.3	45.9
80	35 at. pct Al-5 at. pct Cu-60 at. pct Ni	$AlNi_3$	26.5	6.5	67.0
		AlNi	37.4	3.9	58.7
81	35 at. pct Al-10 at. pct Cu-55 at. pct Ni	$AlNi_3$	25.9	14.8	59.3
		AlNi	36.9	8.6	54.5
82	35 at. pct Al-15 at. pct Cu-50 at. pct Ni	$AlNi_3$	24.9	23.5	51.6
		AlNi	35.8	14.1	50.1
83	30 at. pct Al-5 at. pct Cu-65 at. pct Ni	$AlNi_3$	26.5	5.4	68.1
		AlNi	36.9	3.5	59.6
84	30 at. pct Al-10 at. pct Cu-60 at. pct Ni	$AlNi_3$	25.6	11.8	62.6
		AlNi	36	7.6	56.4
85	30 at. pct Al-15 at. pct Cu-55 at. pct Ni	$AlNi_3$	25.7	18.5	55.8
		AlNi	36.7	10.4	52.9
86	30 at. pct Al-20 at. pct Cu-50 at. pct Ni	$AlNi_3$	24.4	24.8	50.8
		AlNi	35.5	15.1	49.4
87	25 at. pct Al-25 at. pct Cu-50 at. pct Ni	$AlNi_3$	24.4	25.0	50.6
		AlNi	35.4	15.1	49.5
88	25 at. pct Al-10 at. pct Cu-65 at. pct Ni	$AlNi_3$	—	—	—
89	25 at. pct Al-15 at. pct Cu-60 at. pct Ni	$AlNi_3$	—	—	—
90	25 at. pct Al-20 at. pct Cu-55 at. pct Ni	$AlNi_3$	—	—	—
91	30 at. pct Al-25 at. pct Cu-45 at. pct Ni	α	14.7	77.5	7.8
		AlNi	35.1	16.1	48.8
		$AlNi_3$	24	26.1	49.9
92	25 at. pct Al-35 at. pct Cu-40 at. pct Ni	α	9.6	76.3	14.1
		AlNi	35.5	16.6	47.9
		$AlNi_3$	23.5	30.5	46.0
93	20 at. pct Al-50 at. pct Cu-30 at. pct Ni	α	8.8	77.3	13.9
		AlNi	35.5	16.7	47.8
		$AlNi_3$	24.4	27.6	48
94	15 at. pct Al-60 at. pct Cu-25 at. pct Ni	α	9.7	76.1	14.2
		AlNi	35.2	16.8	48.1
		$AlNi_3$	23.7	30.1	46.3
95	20 at. pct Al-5 at. pct Cu-75 at. pct Ni	α	11.8	7.6	80.6
		$AlNi_3$	22.6	4.3	73.1
96	20 at. pct Al-8 at. pct Cu-72 at. pct Ni	α	10.8	13.1	76.1
		$AlNi_3$	22.3	6.5	71.2
97	20 at. pct Al-15 at. pct Cu-65 at. pct Ni	α	10.7	28.9	60.4
		$AlNi_3$	22.9	11.3	65.8
98	21 at. pct Al-30 at. pct Cu-49 at. pct Ni	α	4.6	77.9	17.5
		$AlNi_3$	23.5	22.9	53.6
99	20 at. pct Al-30 at. pct Cu-50 at. pct Ni	α	4.5	73.7	21.8
		$AlNi_3$	23.3	21	55.7
100	20 at. pct Al-40 at. pct Cu-40 at. pct Ni	α	8.5	76.9	14.6
		$AlNi_3$	24.3	26.4	49.3
101	15 at. pct Al-10 at. pct Cu-75 at. pct Ni	α	11.3	11.9	76.8
		$AlNi_3$	22.1	5.8	72.1
102	15 at. pct Al-15 at. pct Cu-70 at. pct Ni	α	11.3	18.0	70.7
		$AlNi_3$	22.2	7.9	69.9

Table I. (Continued) Phase Identification of Alloys Examined in This Study

Number	Alloy Composition, At. Pct	Phases in Equilibrium	Composition, At. Pct		
			Al	Cu	Ni
103	15 at. pct Al-20 at. pct Cu-65 at. pct Ni	α	11.3	25.7	63
		$AlNi_3$	21.9	11.2	66.9
104	15 at. pct Al-30 at. pct Cu-55 at. pct Ni	α	7.8	44	48.2
		$AlNi_3$	21.5	17.8	60.7
105	15 at. pct Al-40 at. pct Cu-45 at. pct Ni	α	4.8	66.0	29.2
		$AlNi_3$	22.6	18.5	58.9
106	10 at. pct Al-50 at. pct Cu-40 at. pct Ni	α	5.5	60.9	33.6
		$AlNi_3$	22.6	16.5	60.9
107	10 at. pct Al-60 at. pct Cu-30 at. pct Ni	α	4.4	75.3	20.3
		$AlNi_3$	23.3	19.5	57.2
108	5 at. pct Al-75 at. pct Cu-20 at. pct Ni	α	4.4	76.2	19.4
		$AlNi_3$	22.9	21.8	55.3
109	10 at. pct Al-30 at. pct Cu-60 at. pct Ni	α	—	—	—
110	5 at. pct Al-10 at. pct Cu-85 at. pct Ni	α	—	—	—
111	5 at. pct Al-40 at. pct Cu-55 at. pct Ni	α	—	—	—
112	8 at. pct Al-79 at. pct Cu-13 at. pct Ni	α	—	—	—

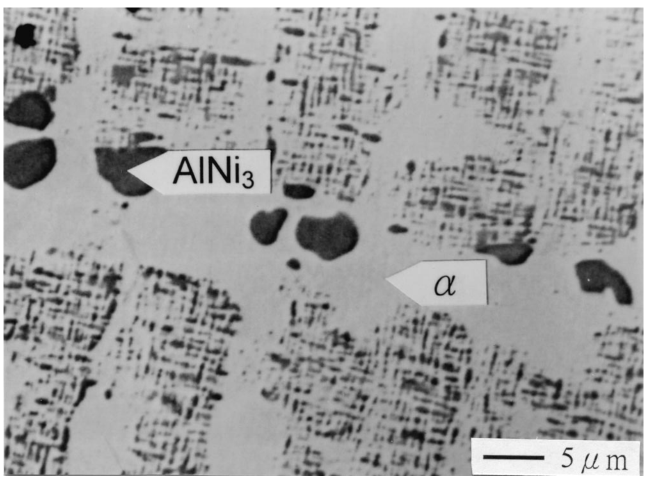

Fig. 2—BEI micrograph of alloy 106 (Al-50 at. pct Cu-40 at. pct Ni) annealed at 800 °C.

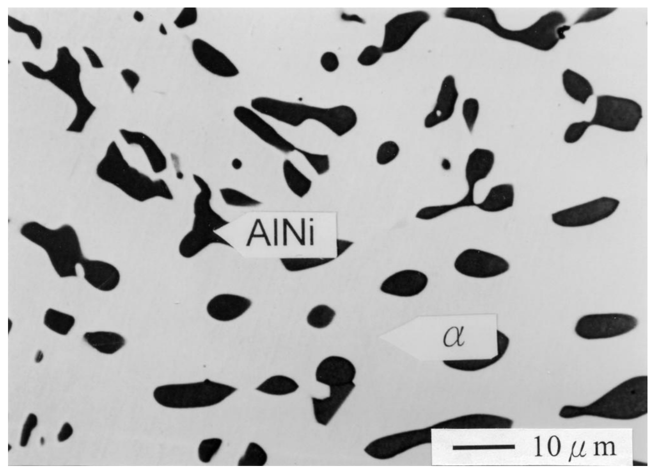

Fig. 4—BEI micrograph of alloy 77 (Al-70 at. pct Cu-10 at. pct Ni) annealed at 800 °C.

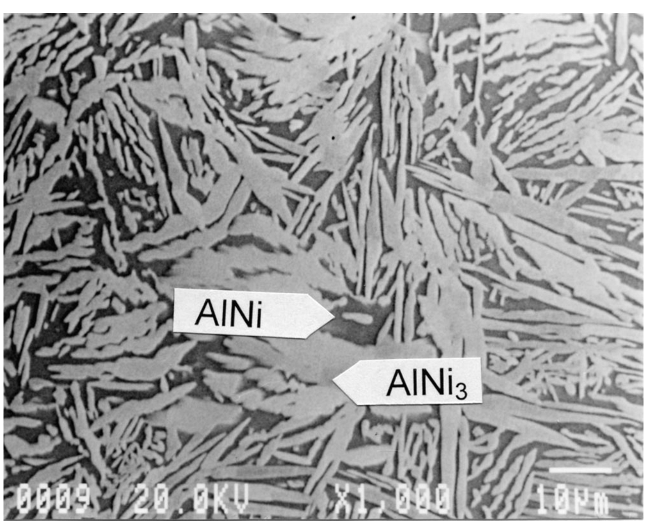

Fig. 3—BEI micrograph of alloy 84 (Al-10 at. pct Cu-60 at. pct Ni) annealed at 800 °C.

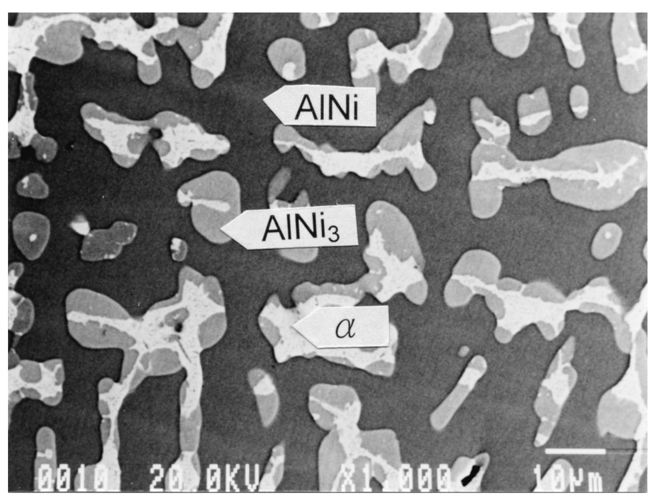

Fig. 5—BEI micrograph of alloy 91 (Al-25 at. pct Cu-45 at. pct Ni) annealed at 800 °C.

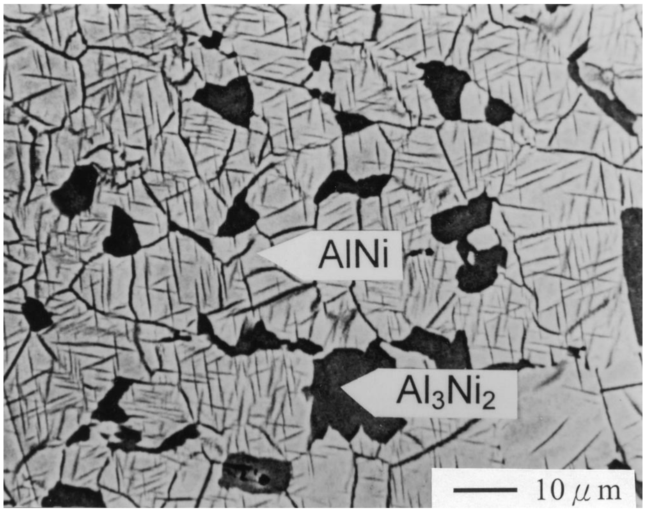

Fig. 6—BEI micrograph of alloy 18 (Al-20 at. pct Cu-25 at. pct Ni) annealed at 800 °C.

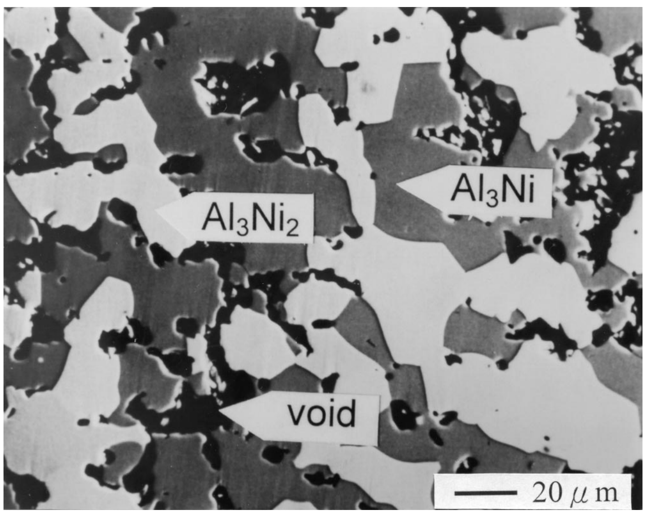

Fig. 7—BEI micrograph of alloy 1 (Al-2.5 at. pct Cu-27.5 at. pct Ni) annealed at 800 °C.

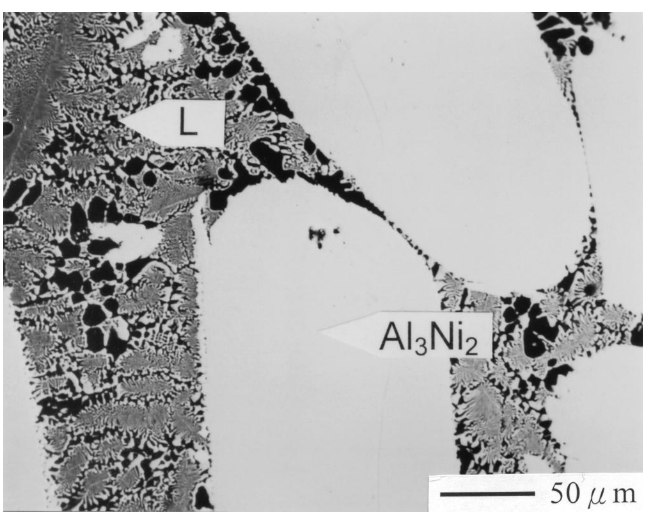

Fig. 8—BEI micrograph of alloy 5 (Al-15 at. pct Cu-15 at. pct Ni) annealed at 800 °C.

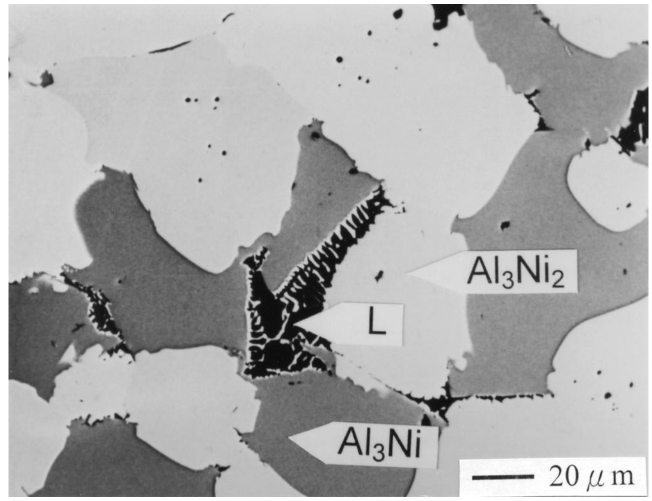

Fig. 9—BEI micrograph of alloy 3 (Al-5 at. pct Cu-25 at. pct Ni) annealed at 800 °C.

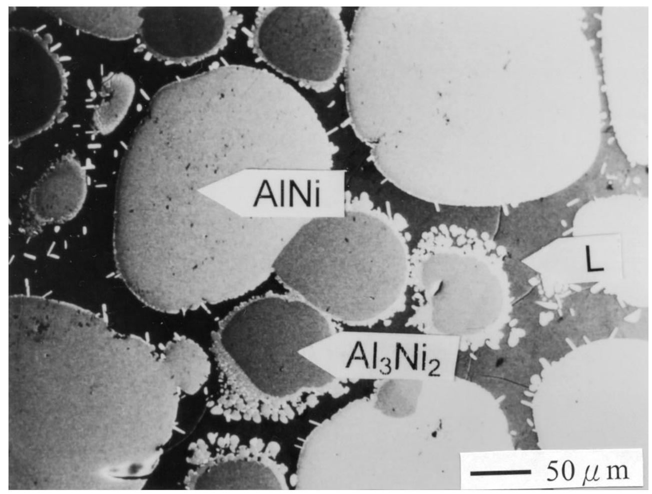

Fig. 10—BEI micrograph of alloy 23 (Al-27.5 at. pct Cu-12.5 at. pct Ni) annealed at 800 °C.

structures, naturally, there cannot be a continuous solid solution between them. Figures 10 through 15 are the BEI of alloys 23 (Al-27.5 at. pct Cu-12.5 at. pct Ni), 24 (Al-30 at. pct Cu-10 at. pct Ni), 54 (Al-57 at. pct Cu-5 at. pct Ni), 56 (Al-54 at. pct Cu-11 at. pct Ni), 55 (Al-54 at. pct Cu-10 at. pct Ni), and 62 (Al-57 at. pct Cu-11 at. pct Ni), respectively. The two-phase structure of alloy 62 shown in Figure 15 clearly indicates the immiscibility between the AlNi and the β-$AlCu_4$ phases. The star-shaped phase is the AlNi phase with 53.2 at. pct Cu solubility, whereas the matrix is the β-$AlCu_4$ phase. The vertical section prepared by Dunne and Kennon[25] at 3 wt pct Ni has a different phase region between the β-$AlCu_4$ and AlNi phases. Their results are in agreement with this study, which also indicates these two phases do not form a continuous solid solution. Owing to the similarities of compositions of these two phases, they are barely distinguishable without etching. Figure 15 is the SEI of an etched sample (50 pct HNO_3 + 50 pct H_2O, 15 seconds), and the voids surrounding the AlNi phase are caused by etching effect. It is worthy noting that a martensite structure was

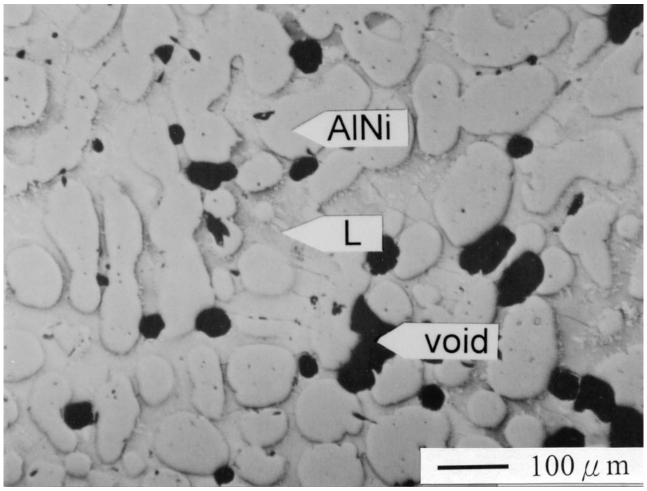

Fig. 11—Optical micrograph of alloy 24 (Al-30 at. pct Cu-10 at. pct Ni) annealed at 800 °C.

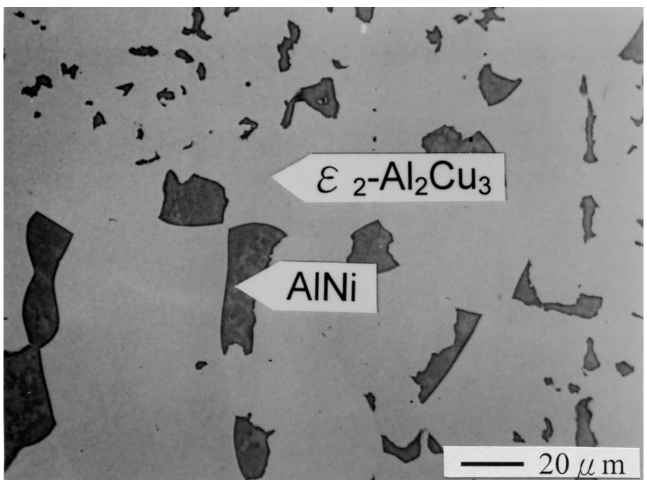

Fig. 12—BEI micrograph of alloy 54 (Al-57 at. pct Cu-5 at. pct Ni) annealed at 800 °C.

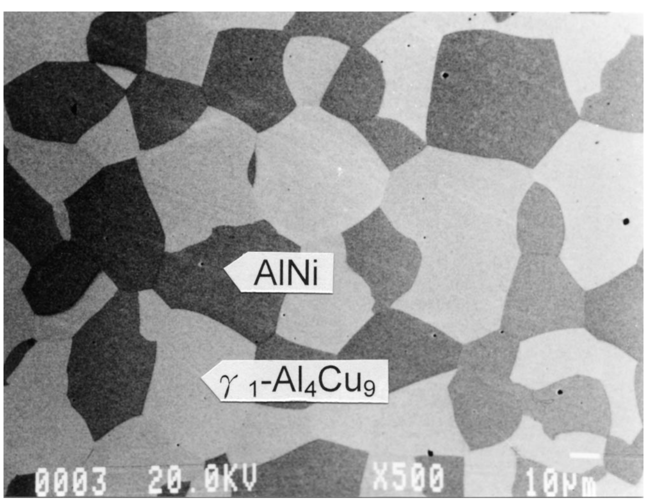

Fig. 13—BEI micrograph of alloy 56 (Al-54 at. pct Cu-11 at. pct Ni) annealed at 800 °C.

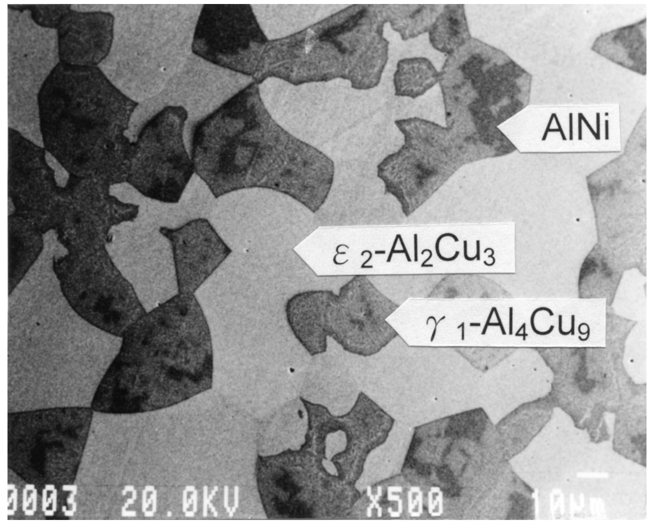

Fig. 14—BEI micrograph of alloy 55 (Al-54 at. pct Cu-10 at. pct Ni) annealed at 800 °C.

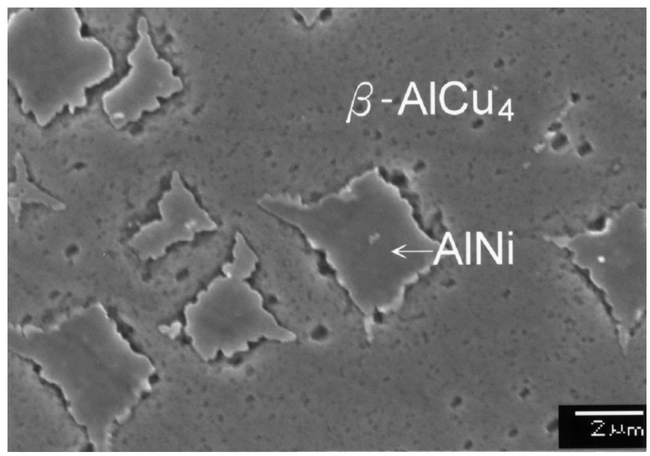

Fig. 15—SEI micrograph of alloy 62 (Al-57 at. pct Cu-11 at. pct Ni) annealed at 800 °C.

found in the quenched alloy 64 even though it does not affect the determination of the 800 °C isothermal section.

Based on the experimental results of phase identifications and phase diagrams of the three constituent binary systems,[21,22,24] the isothermal section of Al-Cu-Ni ternary system at 800 °C is proposed as is shown in Figure 1. The most distinct feature of this study is the investigation of the phase relationship along the region between the AlNi phase and the Al-Cu binary system. The phase relationship is complicated and it has never been studied. However, the solubility region of the AlNi phase found in this study looks very peculiar. Efforts have been made to check the consistency with the Schreinmaker's rule,[26] *i.e.*, the metastable extensions of the two equilibrium curves in the neighborhood of the point of the intersection lie either inside or outside the corresponding three-phase triangle. Various alloys have been prepared and re-examined, such as alloys 36 through 44, and the results indicate that they are all in the AlNi single-phase region. The cause of the peculiar shape of the AlNi phase region could probably only be realized if a thorough thermodynamic assessment of the ternary Al-Cu-Ni system

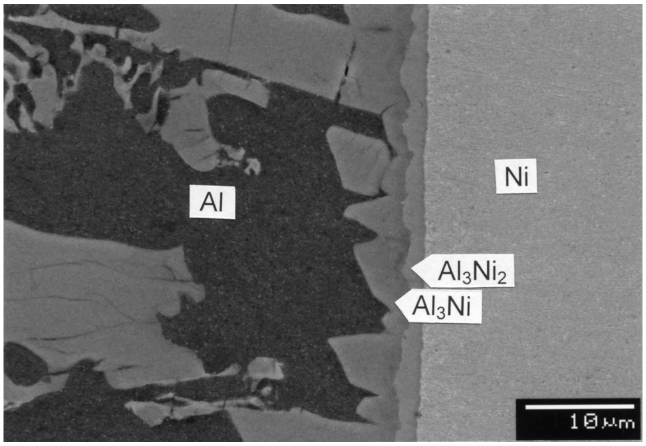

Fig. 16—SEI micrograph of the Al/Ni couple reacted at 800 °C for 12 min.

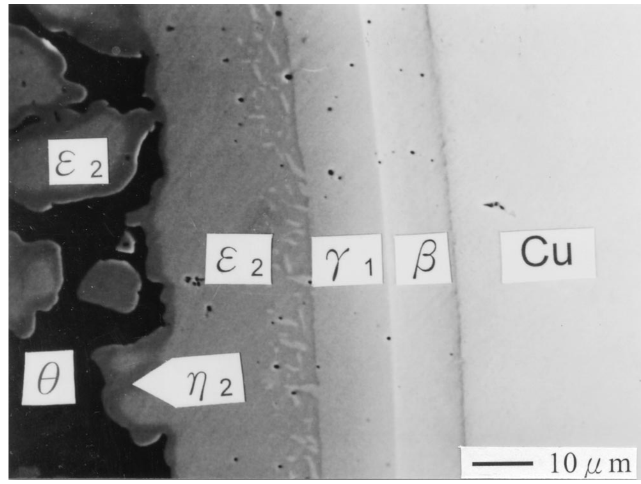

Fig. 17—BEI micrograph of the Al/Cu couple reacted at 800 °C for 6 min.

were conducted. However, it could be challenging owing to the complicated phase relationships in both the Al-Cu and Al-Ni binary systems,[21,22] even though no ternary compounds are found at 800 °C.

Figure 16 is the SEI micrograph Al/Ni couple reacted at 800 °C for 12 minutes. Two reaction layers can be found at the interface. Composition of the layer adjacent to the Ni phase determined by using EPMA is Al-40.76 at. pct Ni. Based on the 800 °C isothermal section, the layer is presumed to be the Al_3Ni_2 phase. The composition of the other layer with an irregular morphology is Al-25.19 at. pct Ni and is most likely to be the Al_3Ni phase. It should be pointed out that this study does not carry out structural determination of the phases formed in the couples, and phase identification has been conducted based on the results of compositional analysis only. In addition to the two reaction layers, the Al_3Ni phase is also found in the Al matrix. A significant amount of Ni was dissolved into the molten Al at 800 °C, and presumably the observed Al_3Ni phase in the Al matrix was precipitation from the molten Al-Ni alloy during solidification. This presumption is supported by the fact that the thickness of the Ni foil decreased significantly when in contact with the molten aluminum.

Although there are no previous results of reactions at 800 °C, the literature of Al/Ni interfacial reactions can be found at some other temperatures varied from 400 °C to 750 °C. Similar to the results found in this study at 800 °C, Al_3Ni_2 and Al_3Ni phases are formed at other temperatures from 400 °C to 750 °C.[7,8] At 800 °C and other lower temperature, there are at least two other stable intermetallic phases, AlNi and $AlNi_3$, but they are not found in most of the Al/Ni reaction studies.[7,8] It is not uncommon that some stable phases are missing in the reaction couples,[7,11,27] and it might be due to the high nucleation barriers of the missing phases or due to their very slow growth rates. Castleman and Seigle[7] carefully examined Al/Ni reaction couples with longer reaction time at higher magnification rates. They proposed that the two phases, AlNi and $AlNi_3$, were formed by interfacial reactions but were just too thin to be detected in most of the Al/Ni couples.

Figure 17 is the BEI micrograph of the Al/Cu couple reacted at 800 °C for 6 minutes. Compositions of the three phase layers from the Cu substrate side are Al-76.6 at. pct Cu, Al-62.0 at. pct Cu, and Al-56.1 at. pct Cu, and they are

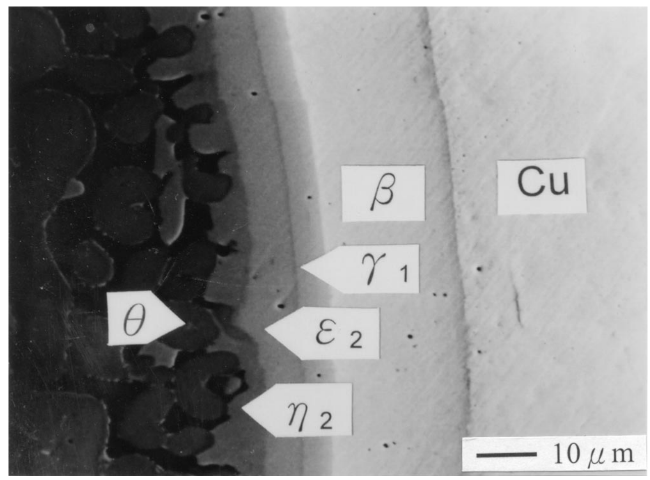

Fig. 18—BEI micrograph of the Al-2 at. pct Ni/Cu couple reacted at 800 °C for 5 min.

β-$AlCu_4$, γ_1-Al_4Cu_9 and ε_2-Al_2Cu_3, respectively. The growth rate of the β-$AlCu_4$ phase is very fast at 800 °C. In just six minutes, a 20 μm-thick layer of β-$AlCu_4$ phase is formed. Some γ_1-Al_4Cu_9 precipitates in the ε_2-Al_2Cu_3 phase can be found in some of the Al/Cu couples. Efforts are not carried out to determine whether these precipitates are formed at 800 °C or are transformed from the ε_2-Al_2Cu_3 phase during quenching. η_2-AlCu phase and θ-Al_2Cu phase are found as well in the couples. Since η_2-AlCu and θ-Al_2Cu phases are not stable at 800 °C, similar to that in the Al/Ni system, it is presumed that both the η_2-AlCu and θ-Al_2Cu phases are formed during solidification.

Similar results are found in the Al-2 at. pct Ni/Cu and Al-5 at. pct Ni/Cu reaction couples. Figure 18 is the Al-2 at. pct Ni/Cu couple reacted at 800 °C for 5 minutes. Three phases, β-$AlCu_4$, γ_1-Al_4Cu_9 and ε_2-Al_2Cu_3, are formed by interfacial reaction, while η_2-AlCu and θ-Al_2Cu phases are formed during solidification. No previous work is located for either Al/Cu or Al-Ni/Cu reacted at 800 °C. Funamizu and Watababe[12] investigated the interdiffusion in the Al/Cu system in the temperature range of 400 °C to 535 °C, and they found formation of all the stable intermetallic compounds. As is shown in the binary phase diagram,[21] the

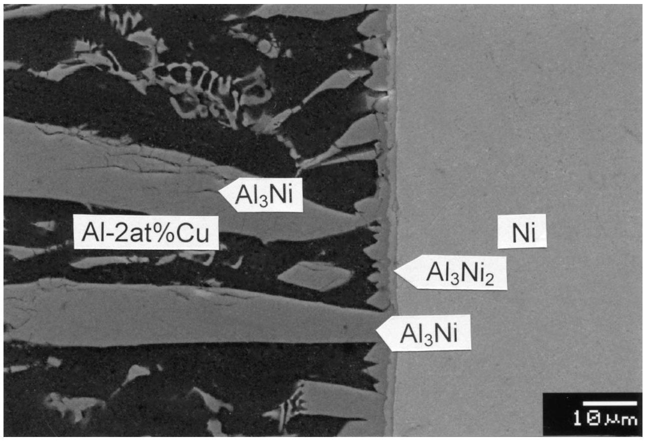

Fig. 19—SEI micrograph of the Al-2 at. pct Cu/Ni couple reacted at 800 °C for 6 min.

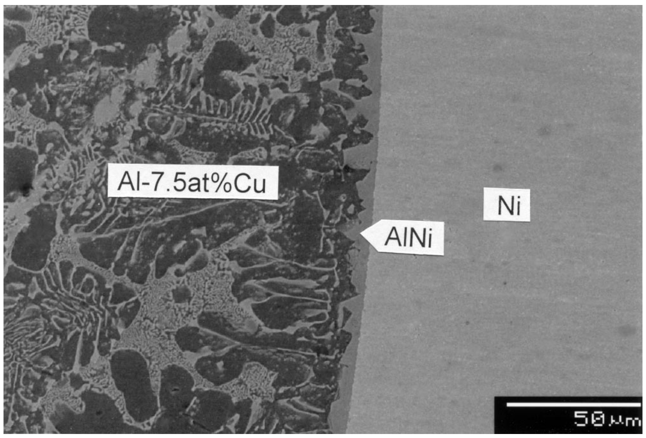

Fig. 20—SEI micrograph of Al-7.5 at. pct Cu/Ni couple reacted at 800 °C for 6 min.

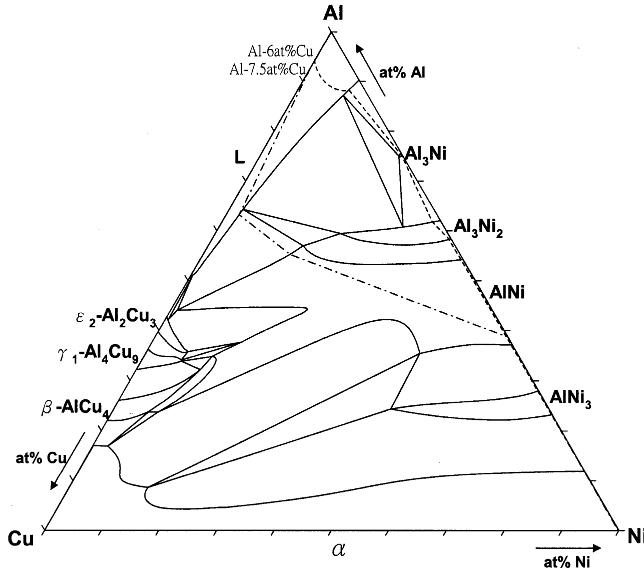

Fig. 21—Reaction paths of the Al-Cu/Ni diffusion couples.

phase transformation between γ_0 and γ_1 has not yet been confirmed. If the unconfirmed difference between these two phases, γ_0 and γ_1, is ignored, this study also finds that all the stable phases at 800 °C are formed by interfacial reactions

Two reaction layers are observed in Figure 19, which is the Al-2 at. pct Cu/Ni couple reacted at 800 °C for 6 minutes. These two layers are determined to be Al_3Ni_2 and Al_3Ni phases, and the alloying of the 2 pct copper does not have a significant change of the phase formation in the couple. A significant amount of Al_3Ni phase is detected in the aluminum matrix as well. It is presumed to be the precipitation of dissolved Ni during solidification. Similar results were found in the Al-4.5 at. pct Cu/Ni and Al-6 at. pct Cu/Ni couples. Figure 20 is the SEI micrograph of the Al-7.5 at. pct Cu/Ni couple reacted at 800 °C for 6 minutes. Similar results were found in the Al-10 at. pct Cu/Ni couples as well. Composition of the dark layer formed at the interface was Al-27 at. pct Ni-17 at. pct Cu, and this phase is the AlNi phase with significant copper solubility. In the region that is liquid phase prior to quenching, both θ-Al_2Cu and Al_3Ni phases are perceived; however, the amount of ε-Al_3Ni phase is much less compared to those in the Al-Cu/Ni couples mentioned previously.

As can be seen in Figure 21, the reaction paths in the Al-7.5 at. pct Cu/Ni and the Al-6 at. pct Cu/Ni couples are different. It appears that there is an abrupt change of reaction paths with only a 1.5 at. pct difference of copper amount. It is interesting to note that the reaction path in the Al-7.5 at. pct Cu/Ni couple is liquid/AlNi/Ni. Instead of taking a shorter route in the liquid region to form a contact with the Al_3Ni_2 phase as in the Al-6 at. pct Cu/Ni couple, the reaction path in the Al-7.5 at. pct Cu/Ni couple travels a long way in the liquid phase to form a contact with the AlNi phase. A similar phenomenon in the reaction path showing a wide compositional range in the single-phase region has also been observed in the Ag-Cu/Ni system.[28] It should be pointed out that although the reaction paths have been marked on Figure 21, there are no complete compositional analysis data across the couples. The reaction paths are determined based on the phase identification results, *i.e.*, compositions were analyzed only on limited points on the couples. Thus, the paths along the single-phase regions are not necessarily as straight as they have been marked. In fact, they are likely to have a serpentine shape, as has been demonstrated by previous studies.[19,29,30] The reaction path is a complicated combinational result of both the chemical potential gradient and the diffusivity of each species. With the help of a complete ternary phase diagram, knowledge of mass transfer, and previous efforts of theoretical diffusion couple studies,[29,30] it might be possible to explain why there is an abrupt change in the path. However, it should be acknowledged that it could still be a very difficult task.

IV. CONCLUSIONS

The isothermal section of the Al-Cu-Ni system at 800 °C has been determined experimentally. There is no ternary compound. Most of the binary compounds have very extensive ternary solubility. However, unlike the results reported in some previous literature, this study has found that no continuous solid solution is formed between the AlNi phase with any of the binary Al-Cu phases. Al_3Ni and Al_3Ni_2 phases are formed in the Al/Ni, Al-2 at. pct Cu/Ni, Al-4.5 at. pct Cu/Ni, and Al-6 at. pct Cu/Ni couples. β-$AlCu_4$, γ_1-Al_4Cu_9, and ε_2-Al_2Cu_3 phases are formed in the Al/Cu, Al-2 at. pct Ni/Cu, and Al-5 at. pct Ni/Cu couples. A different reaction path is found and an AlNi solid solution layer is formed in the Al-7.5 at. pct Cu/Ni and Al-10 at. pct Cu/Ni couples.

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