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Phase equilibria in the Cu-rich portion of the Cu–Al binary system

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Abstract

The phase equilibria in the Cu–Al binary system over the temperature range 500~1000°C and the composition range 15~60 at.% Al have been determined using diffusion couple technique, differential scanning calorimetry (DSC) and high temperature X-ray diffraction (XRD) methods. While the results from this study pertaining to the phase equilibria α/β and $\epsilon_1(\epsilon_2)$/liquid are in agreement with those reported in previous works, significant differences have been found between the earlier results and the present work in the composition range 25~40 at.% Al. They are: (a) In the composition range 32~38 at.% Al only a second order reaction, γ_1 ($D8_3$)$\rightarrow\gamma_0$ ($D8_2$), is seen to occur and not a two-phase equilibrium γ_0/γ_1 reaction as reported before (b) The β_0 phase is absent at high temperature near 1000°C and compositions near 30 at.% Al. (c) The equilibrium eutectoid $\gamma_0\rightarrow\beta+\gamma_1$ and peritectoid $\gamma_0+\epsilon_1\rightarrow\gamma_1$ reactions do not occur in this system.

Keywords: Phase equilibria; Order–disorder transformation; Diffusion couple; Cu–Al phase diagram; Crystal structure

1. Introduction

The copper–aluminum system is one of those systems that has been extensively studied, not only because the alloys of this system have a wide range of technological applications but also because the various features of this system such as the martensitic [1,2] and massive transformations [3], β phase ordering reactions [4,5], and the occurrence of the unique metastable precipitates designated Guinier–Preston (GP) zones [6,7] render it a system of considerable theoretical interest. The results from numerous investigations on the phase equilibria, phase transformations, crystal structure etc. pertaining to this system have been assessed by Murray [8,9] and the assessed phase diagram is shown in Fig. 1. Many doubtful or uncertain points on the phase equilibria, however, still remain unresolved, especially in the composition range of 25~40 at.% Al. It is also to be noted from Fig. 1 that majority of the investigations on the phase equilibria in this system were carried out during the years 1920~1940s and the experimental methods used were mainly confined to differential thermal analysis (DTA) and metallography.

The purpose of the present work was to re-investigate the phase equilibria in the Cu-rich portion of the Cu–Al system using mainly the diffusion couple technique, which has not been used previously as an investigation technique in this system, to establish the phase equilibria in a wider composition range. Differential scanning calorimetry (DSC) and high temperature X-ray diffraction (XRD) techniques were also employed to determine the temperatures of phase transformation and crystal structures, respectively.

2. Unresolved questions in the Cu-rich portion of the diagram

The assessed phase diagram shown in Fig. 1 is based on data from dilatometric investigations on the phase equilibria by Campbell [10] in 1902, followed by data from further investigations based on DTA and metallography by others [11,12,15,16,22–25]. The diagrams shown in Fig. 2 show the diagrams as published by different authors. It is seen that the data corresponding to the α/β phase boundary in all these figures is in broad agreement. However, the phase equilibria associated with the β, β_0, γ_0 and γ_1 phases differ widely.

The β_0 phase was postulated by Dowson [11] on the basis of an arrest that was observed in the heating curves in the temperature interval between 965°C and 970°C in the different alloys in the composition range 15.5~16.25wt.% Al. Based on this observation, the eutectoid reaction β_0(unknown)$\rightarrow\beta$(A2:W type)$+\gamma_0$(unknown) and the peritectic reaction Liquid$+\beta\rightarrow\beta_0$ at 963°C and

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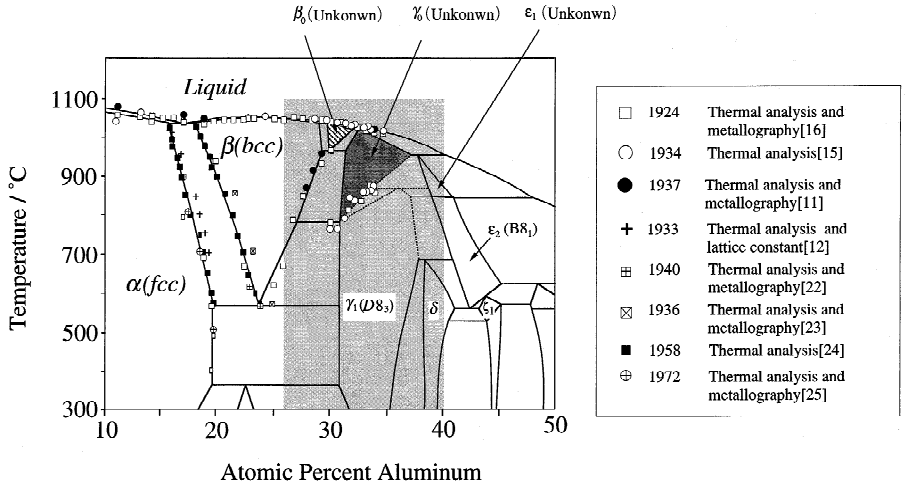

Fig. 1. The phase diagram of the Cu-rich portion of the Cu–Al binary system assessed by Murray in 1990 [9].

1073°C, respectively, were also proposed. However, no corresponding microstructural observations of the single β_0 phase were given in his original paper.

The occurrence of the $\gamma_0 \rightarrow \gamma_1(D8_3{:}Cu_9Al_4)$ transition was first detected by thermal analysis [10,12]. The presence of the eutectoid reaction $\gamma_0 \rightarrow \gamma_1 + \beta$ at 780°C and the peritectoid reaction $\gamma_0 + \epsilon_1(\text{unknown}) \rightarrow \gamma_1$ at 873°C were reported subsequently [13–15] but with no accompanying details of experimental information on these two invariant reactions. Stockdale [16] pointed out that the microstructures of the γ_0 and γ_1 phases were not distinguishable. Even though the crystal structure of the γ_1 phase was subsequently determined as $D8_3$, Cu_9Al_4 type [17,18], that of γ_0 is still unknown. The temperatures and composition

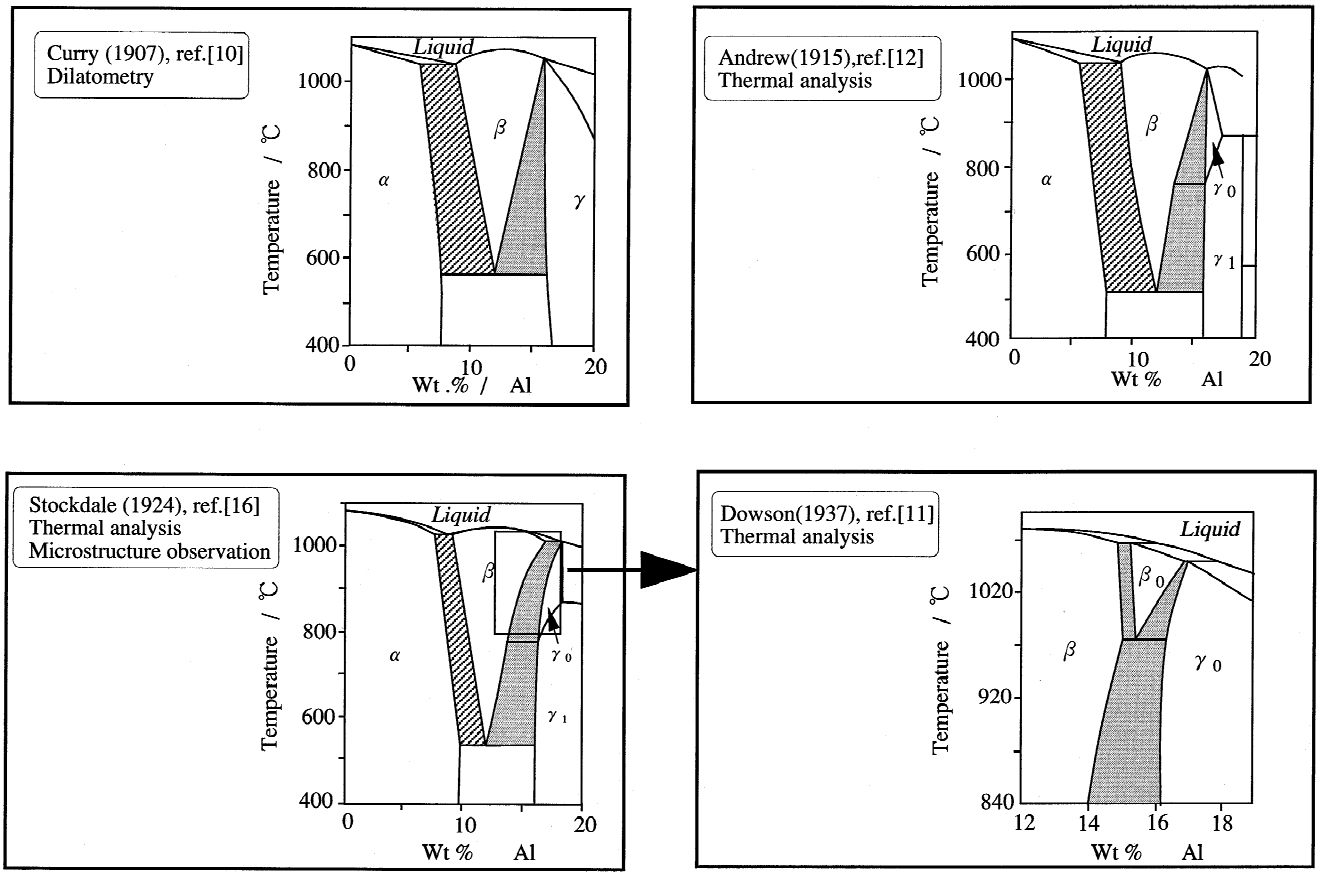

Fig. 2. Several main versions of phase diagram in the Cu-rich portion of the Cu–Al binary system reported between 1922 and 1937.

ranges of stability of the phases ϵ_1 and ϵ_2 as assessed by Murray [9], are also based only on XRD [19,20] experimental data of the phase equilibria. The eutectoid reaction $\beta \rightarrow \alpha$(A1:Cu type)$+\gamma_1$ has been studied by many investigators, but there is a large scatter in the reported values of the eutectoid temperature which is mainly due to the sluggishness of this reaction [9]. In spite of the numerous studies devoted to the determination of phase equilibria in the Cu–Al system, there still remain some questions, the most important of which are as follows:

(1) Does the β_0 phase originally proposed by Dowson [11] exist at high temperatures and if so, what is its structure?.

(2) What are the microstructural features of the phase equilibrium γ_0/γ_1 which have been detected only by DTA, and what is the crystal structure of the γ_0 phase?.

(3) Can the invariant eutectoid reaction $\gamma_0 \rightarrow \beta + \gamma_1$ and peritectoid reaction $\gamma_0 + \epsilon_1 \rightarrow \gamma_1$ be better characterised by acquiring more experimental information?.

3. Experimental procedure

Binary Cu–Al alloys were prepared by arc-melting electrolytic copper (99.9%) and aluminum (99.99%) in water-cooled copper crucibles under an argon atmosphere. The compositions of the alloys, given in Table 1 were determined by chemical analysis or energy dispersive spectroscopy (EDS). All the alloys were given an initial homogenization treatment at 800°C for 24 h.

In the present study, the diffusion couples Cu/37Al and 25Al/34Al were the main ones used to determine the solid–solid phase equilibria among the α,β and $\gamma_0(\gamma_1)$ phases. The Cu/Al solid–liquid diffusion couple was prepared to determine the phase equilibria in the whole composition range, including the $\epsilon_1(\epsilon_2)$/liquid phase equilibrium. The methods of preparation of diffusion couples and the examination of the phase equilibria were identical to the ones described in a previous work [21]. The prepared diffusion couples were sealed in transparent quartz capsules and equilibrated in the temperature range 500~1000°C for 2~168 h in the case of the solid–solid couples and at 700, 800 and 900°C for 0.5~1.5 h in the case of the solid/liquid couples and quenched in iced water. After metallographic examination by optical microscopy, the concentration–penetration curves for each element were determined along the direction of diffusion flux by EDS, and the equilibrium compositions of each phase were obtained by extrapolating the curves to the interphase boundary. A ($FeCl_3$:HCl:H_2O=10g:25ml:100ml) solution was used as the etchant for metallographic examination.

Transformation temperatures were determined by DSC using the heating curve. The specimens were tested either after sealing in transparent quartz under vacuum or kept in flowing argon atmosphere during the DSC experiment and heated and cooled at rates of 3°C/min or less using sintered Al_2O_3 as the reference specimen.

Homogenized powder specimens fixed on a platinum heating stage were analysed by high temperature XRD using Cu Kα radiation to identify the crystal structure at elevated temperatures.

Table 1
The compositions of alloys used in the present study

No.	Alloy	Composition (at.%)	
		Cu	Al
1	25Al	75.0	25.0 (E)
2	30Al	69.4	30.6 (E)
3	34Al	66.02	33.98 (C)
4	37Al	63.1	36.9 (E)
5	39Al	60.9	39.1 (E)
6	41Al	59.02	40.08 (C)

C=Chemical analysis, E=EDS analysis.

4. Results and discussion

4.1. The α/β and $\epsilon_1(\epsilon_2)$/liquid phase equilibria

The phase equilibria in the Cu-rich portion of the Cu–Al system as determined from the present study is shown in Fig. 3 and the equilibrium compositions are summarized in Table 2. The results from the two-phase alloys, solid/solid and solid/liquid diffusion couples are almost in total agreement with each other. It can be seen, from Fig. 3, that the α/β phase equilibrium is in agreement with the previous works, but the phase boundary $\gamma_1(\gamma_0)/\gamma_1(\gamma_0)+\beta$ is located at about 31.5at.% Al, which is about 1at% of Al higher than that reported before. The phase equilibria $\epsilon_1(\epsilon_2)$/liquid determined from the solid/liquid couple are basically in agreement with the assessed diagram. It was confirmed by high-temperature XRD that the ϵ_2 phase at 750°C and 780°C had the $B8_1$ structure which was the same as that determined by Boragy et al. [24] on a quenched specimen.

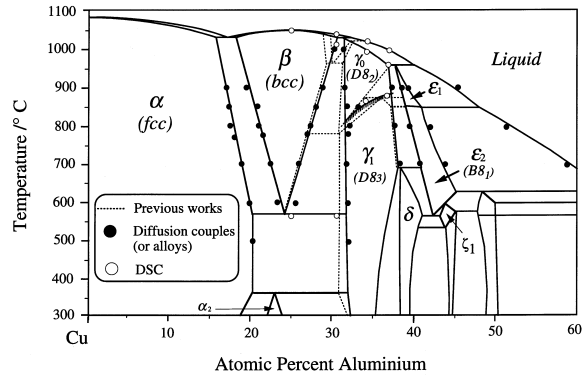

Fig. 3. Cu-rich portion of the Cu–Al phase diagram as determined in the present investigation.

Table 2
The equilibrium composition in the Cu–Al system determined by the present study

Couple or alloy	Temp. (°C)	Equilibrium composition (at.%)									
		α	β	β	γ_1 (γ_0)	γ_1 (γ_0)	ϵ_1 (ϵ_2)	ϵ_1 (ϵ_2)	Liquid	α	γ_1	Order–disorder γ_0/γ_1
25Al/34Al	1000	[a]	[a]	30.6	31.4	–	–	–	–	–	–	–
Cu/34Al	900	17.2	21.1	29.3	31.4	[a]	[a]	[a]	[a]	–	–	–
37Al	900	–	–	–	–	37.0	38.5	[a]	[a]	–	–	–
Cu/Al[b]	900	17.4	21.4	28.9	31.0	36.8	38.9	39.5	45.0	–	–	–
Cu/34Al	800	17.4	21.4	28.4	31.8	[a]	[a]	[a]	[a]	–	–	33.5
39Al	800	–	–	–	–	37.5	39.1	[a]	[a]	–	–	–
Cu/Al[b]	800	17.1	21.0	28.8	32.6	37.1	39.5	41.5	50.1	–	–	–
Cu/34Al	780	18.5	22.1	28.2	31.5	[a]	[a]	[a]	[a]	–	–	–
Cu/34Al	700	18.2	22.5	27.1	31.8	[a]	[a]	[a]	[a]	–	–	–
39Al	700	[a]	[a]	[a]	[a]	38.2	40.8	[a]	[a]	–	–	–
Cu/Al[b]	700	18.1	22.2	26.8	31.5	38.7	40.5	43.5	58.5	–	–	–
Cu/34Al	600	19.9	23.8	26.5	32.0	[a]	[a]	[a]	[a]	–	–	–
Cu/34Al	500	–	–	–	–	–	–	–	–	20.1	32.3	–

[a] Phase equilibria not determined.
[b] Solid/liquid diffusion couple.

4.2. The β_0 phase region

The diffusion couple 25Al/34Al was prepared to determine the β/β_0 and β_0/γ_0 equilibria at temperatures ranging from 980 to 1100°C because according to the phase diagram in Fig. 1, the two interphase boundaries β/β_0 and β_0/γ_0 can be expected to form in this couple. The microstructure and the concentration profile obtained from this diffusion couple heat treated at 1000°C for 2 h are shown in Fig. 4. A single interphase boundary between the β phase (with martensitic features) and the γ_0 phase is observed. It is also observed that in the alloy Cu-30Al equilibrated at 1000°C there are two-phases, rather than a single β_0 phase. DSC experiment carried out on this alloy also show a peak only at about 1019°C as given in Table 3, which is at a higher temperature than that reported by Dowson [11]. This temperature corresponds more to the solidus of the β phase, than to the eutectoid $\beta_0 \rightarrow \beta + \gamma_0$ transformation temperature. From these observations it is concluded, therefore, that no β_0 phase exists at high temperatures of about 1000°C near the composition 30at.% Al.

4.3. The $\gamma_1 \rightarrow \gamma_0$ transformation

Fig. 5 shows the microstructure made up of the α, β and $\gamma_0(\gamma_1)$ phases and the concentration profile observed in the Cu/34Al diffusion couple heat treated at 850°C for 24 h. It can be seen that two interphase boundaries α/β and β/γ_0 had formed, with the β phase (transformed to martensite) growing between the α and γ_0 phases. However, the phase boundary γ_0/γ_1 which would be expected to form according to Fig. 1, was not observed explicitly in this as well as the other diffusion couples. Considering the concentration profile in the γ phase region (including γ_0 and γ_1 phases), it can be seen, however, that there is a singular point at about 33at.% Al, which corresponds to the phase equilib-

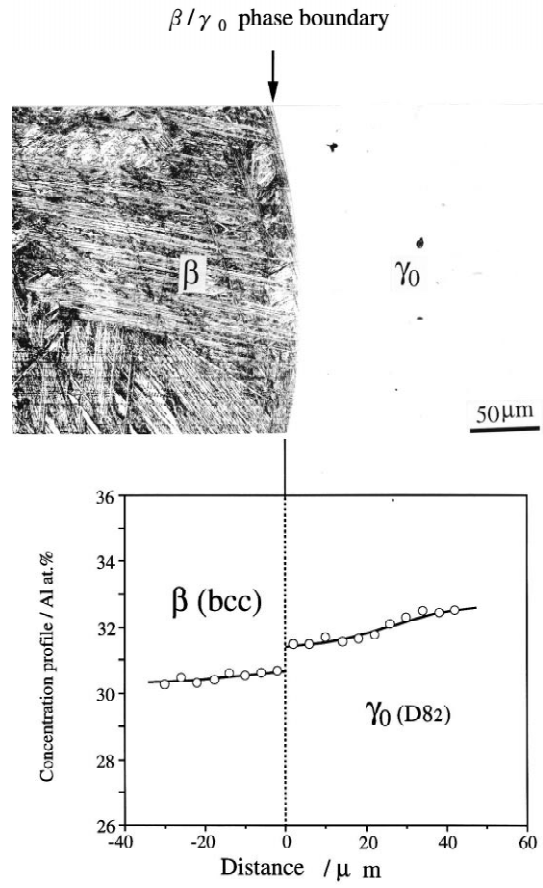

Fig. 4. The microstructure and concentration profile obtained on the diffusion couple 25Al/34Al heat treated at 1000°C for 2 h.

Table 3
Transformation temperatures determined by DSC

Alloy	Temperature of phase transformation (°C)			
	Eutectoid reaction	Solidus	Liquidus	Order–disorder reaction
25Al	559	–	1049	–
30Al	560	1019	1041	–
34Al	–	991	1025	871
37Al	–	962.4[a]	980	885

[a] Temperature of peritectoid reaction liquid$\leftrightarrow\gamma_0+\epsilon_1$.

rium γ_1/γ_0 reported previously [15,16]. DSC experiments carried out on the alloys 34Al and 37Al also showed transformation peaks at about 871°C and 885°C respectively for the two alloys. These observations suggested that there existed a second order ordering reaction in the composition range 32~38at.% Al in the temperature range 850°C~890°C, rather than a first order reaction as reported before. In order to confirm this point, high temperature XRD examinations were carried out on the alloy 34Al at temperatures of 700°C and 900°C. From the XRD patterns shown in Fig. 6 it is confirmed that the γ_1 phase has the $D8_3$ structure at 700°C which is in agreement with that reported by Bradlay et al. [18,19]. As illustrated in Fig. 7 the $D8_3$ (Cu_9Al_4 type) structure can be assigned the space group P43m with 52 atoms per unit cell and can be described as an ordered bcc structure made up of two different kinds of clusters (which are designated as clusters A and B in Fig. 7) with the same fundamental configuration consisting of 26 atoms. Every cluster consists of four sets of structurally equivalent positions designated as CO (cubo-octahedral), OH (octahedral), OT (outer-tetrahedral) and IT (inner tetrahedral) respectively. It is to be noted that the distributions of Al atoms in CO and IT positions

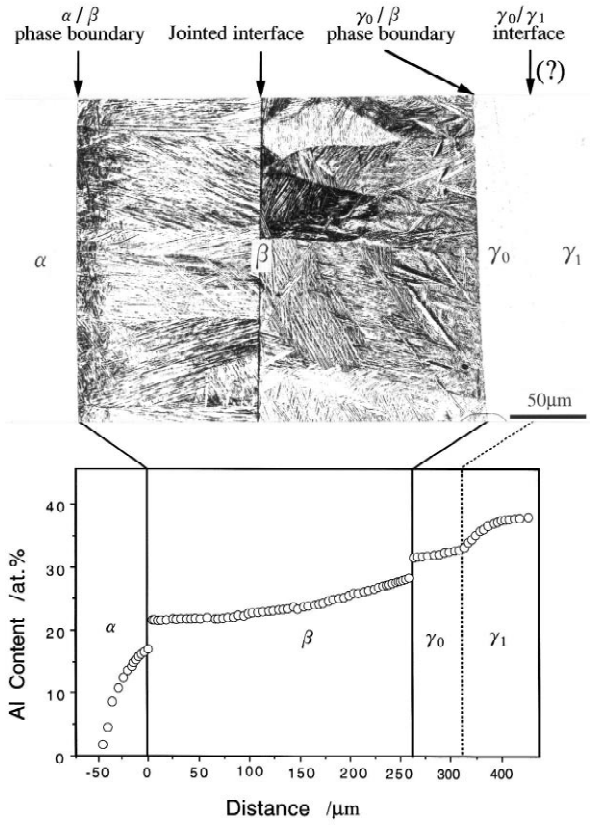

Fig. 5. The microstructure and concentration profile obtained on the diffusion couple Cu/37Al heat treated at 850°C for 2 days.

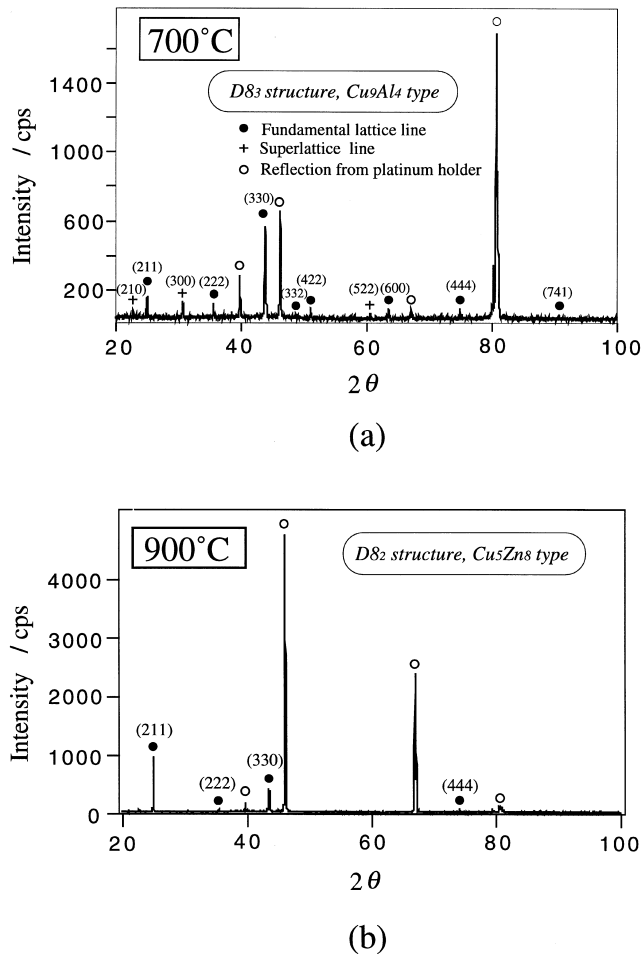

Fig. 6. High-temperature XRD patterns of the alloy 34Al at 700°C and 900°C. Open circles represent the diffraction lines from the pure Pt specimen holder.

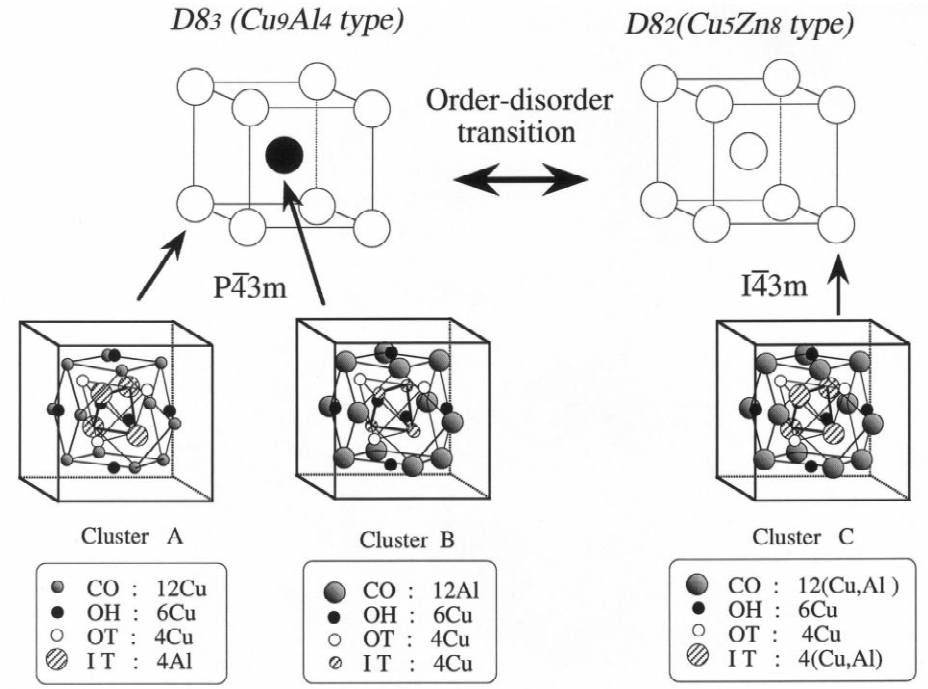

Fig. 7. Schematic illustrations of the crystal structures $D8_3$ and $D8_2$ and the order–disorder transformation between the two. CO: cubo-octahedral, OH: octahedral, OT: outer tetrahedral and IT: inner tetrahedral.

are different in clusters A and B. It is also important to note that the Al content of cluster A (4/26) is different from that of cluster B (12/26).

The diffraction patterns taken from powders of alloy Cu-34Al at 700°C and 900°C are shown in Fig. 6. It can be seen that, of all the reflections present at 700°C, only the ones whose indices satisfy the relation $h^2+k^2+l^2$=even are present at 900°C, while the ones such as the reflections (210), (300) and (522) that satisfy the relation $h^2+k^2+l^2$=odd are absent. This is a direct result of the disappearance of the difference in atomic configuration between clusters A and B due to the transformation from γ_1 to γ_0 phase which is accompanied by a change in the space group from P43m to I43m. This is comparable to the disordering transition from B2 to A2 structure in the bcc lattice. It was difficult to determine precisely the crystal structure of the γ_0 phase from the results of the present XRD examination because of low peak intensities associated with the lines. However, it is with some confidence concluded that the γ_0 phase has the $D8_2(Cu_5Zn_8$ type) structure in which the degree of order in the IT and CO sites of a cluster is lower than that in the $D8_3$ structure, as illustrated in Fig. 7. Both the $D8_2$ and $D8_3$ phases are a typical electron compounds with the same electron concentration (21/13), and the $D8_2$ structure is a kind of disordered version of the $D8_3$ structure.

On the basis of the above arguments it suggested that the $\gamma_1 \rightarrow \gamma_0$ transition detected by DSC and diffusion couple technique in the temperature range 800 to 900°C is a kind of order–disorder transition between the structures $D8_3 \rightarrow D8_2$.

4.4. Phase equilibria related with the $\gamma_0(\gamma_1)$ phases

The transformation temperatures relating to the invariant reaction measured by DSC are shown in Table 3. In the present work the eutectoid transformation temperature of the reaction $\beta \rightarrow \alpha+\gamma_1$ was measured at different heating and cooling rates, 1, 3, 5 and 10°C/min. All the results show that the eutectoid temperature is 559±1°C, which is sightly lower than Murray's assessed value (567±2°C) [9]. A typical DSC curve for the alloy 30Al is shown in Fig. 8. It can be seen that a peak characteristic of an invariant reaction is observed for this alloy.

Although the assessed diagram [9] suggests that the eutectoid reaction of $\gamma_0 \rightarrow \beta+\gamma_1$ and peritectoid reaction $\gamma_0+\epsilon_1 \rightarrow \gamma_1$ occur at 780°C and 873°C respectively, very little data on these reactions have been reported. In the present study, the DSC traces obtained on the alloy 30Al do not exhibit any peak at about 780°C, while those obtained on a 37Al alloy show one peak at about 885°C and another at 962°C. Although the first transformation temperature 885°C is close to that of the peritectoid reaction $\gamma_0+\epsilon_1 \rightarrow \gamma_1$ in the assessed diagram [9], the peak does not exhibit the characteristic feature associated with an invariant reaction. Thus, this transformation temperature is considered to be associated with the $\gamma_0 \rightarrow \gamma_1$ order–

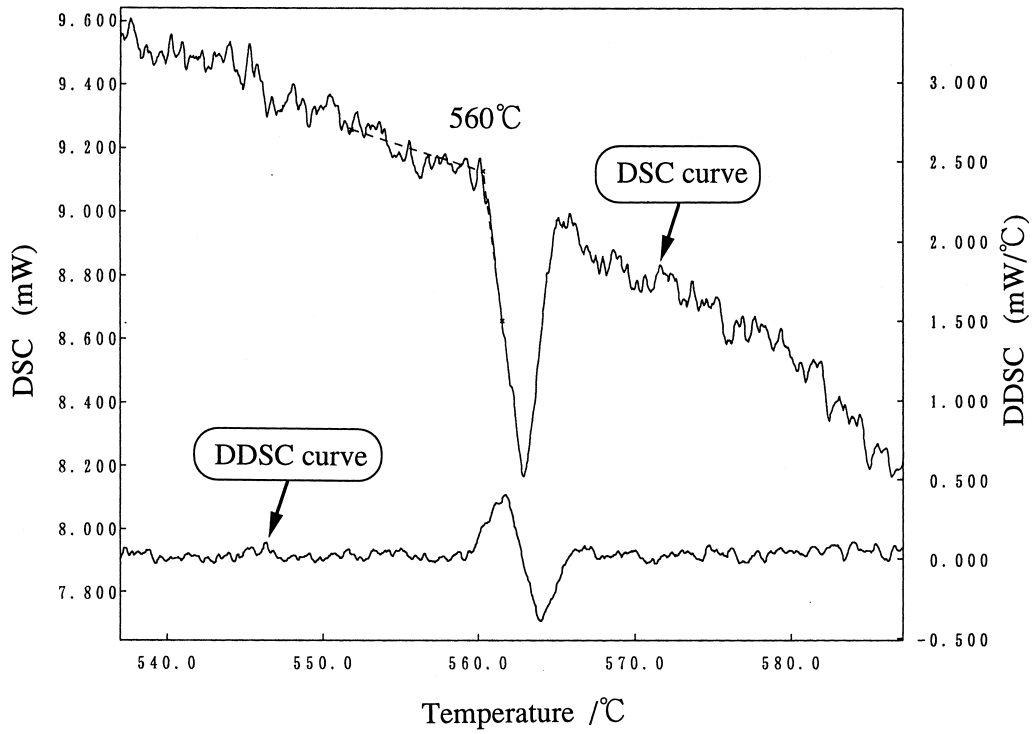

Fig. 8. DSC trace obtained on a specimen of 30Al at a heating rate of 3°C/min.

disorder transition as discussed in the foregoing section, than with the peritectoid reaction $\gamma_0+\epsilon_1\rightarrow\gamma_1$. It is also to be noted that the phase field γ_0/ϵ_1 determined in this work is narrower than that previously reported. The second transformation temperature in the 37Al alloy is associated with the peritectic reaction liquid$+\gamma_0\rightarrow\epsilon_1$.

5. Conclusions

(1) The phase equilibria in the Cu–Al system in the composition range between 15 and 60 at.% Al were determined. The earlier results on the α/β and $\epsilon_1(\epsilon_2)$/liquid phase equilibria are in agreement with the results from this study.

(2) The β_0 phase does not exist at about 1000°C in the composition range near 30at.% Al.

(3) The crystal structure of the γ_0 phase is likely to be of the $D8_2$, Cu_5Zn_8 type. The transformation observed in the temperature range 800~900°C in the composition range 32~38at.% Al is not a first order reaction but a kind of second order ordering reaction between $\gamma_1(D8_3)$ and the $\gamma_0(D8_2)$ structures.

(4) The temperature of eutectoid reaction $\beta\rightarrow\alpha+\gamma_1$ is 559±1°C. The invariant eutectoid reaction $\gamma_0\rightarrow\beta+\gamma_1$ and the peritectoid reaction $\gamma_0+\epsilon_1\rightarrow\gamma_1$ are not present in this system.

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