# FORMATION LAW OF PHASES IN

# ULTRAFINE POWDERS OF Al-Cu ALLOY PREPARED

# BY GAS EVAPORATION PROCESS[①]

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**ABSTRACT**  Ultrafine powders of Al-Cu alloy were prepared by gas evaporation process , formation law of the phases in the as-prepared powders were examined . The results showed that the phases formed in ultrafine powders are within the scope of the phases given in Al-Cu alloy phase diagram . There are only $\theta$-CuAl$_2$ , $\gamma_2$-Al$_4$Cu$_9$ , $\beta$-AlCu$_3$ alloy phases formed in the tested powders . The kinds of the phases formed in the powders and their fractions are controlled by the pressure fraction of the components in the mixed vapor and the cooling conditions of the experimental equipment . Changing pressure of Ar gas could only change the fractions of different phases in the powders . The solid solubility of Al and Cu atoms in the lattice of phase Cu and phase Al in the powders was within the scope of that in Al-Cu alloy diagram . The structure of the phases in the as-prepared powders were in equilibrium state .

**Key words**  gas evaporation   vapor condensation   ultrafine powders   alloy powder

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## 1   INTRODUCTION

Ultrafine powders with a particle size less than 100 nm have excellent properties in contrast to coarse grain materials[1,2] and have widespread application prospects in metallurgy , materials , chemistry etc industrial fields . Ultrafine powders of pure metals have been investigated intensively in the past[3] . If a certain transition phase or alloy phases can form in ultrafine powders , the powders may show excellent structure and properties , such as unique magnetic properties , good catalytic characteristics in reactivity , selectivity and durability . It has been shown that ultrafine powders with alloy phases have special properties[4,5] . Some investigations have been done on some metal/ceramic composite ultrafine powders[6,7,8] and alloy ultrafine powders[4,9,10] in recent years , but a few are on the formation law and mechanisms of alloy phases in ultrafine powders . To clarify these problems is very important in preparation of ultrafine powders with controlled alloy phases formation for special application .

Gas evaporation method is an effective mean for preparation of pure metal ultrafine powders , it can also be used to prepare alloy ultrafine powders by evaporating a master alloy from a single evaporation source or by evaporating the constituent metals from two sources to make confluence of two metal smokes . Induction current , electron beam , risistance ( in spiral or boat shape) , laser or plasma flame can be chosen as the heating source .

This paper intends to examine the formation law of phases in ultrafine powders of Al-Cu alloy prepared by evaporating master alloys with different compositions and in various argon gas pressure using induction current as the heating source .

## 2   EXPERIMENTAL

Fig .1 gives the schematic illustration of the

experimental equipment with 800 mm in diameter and 350 mm in height. Al-Cu alloys were evaporated at 1 400 ℃ in Ar gas atmosphere with a purity about 99.995 %, using an alumina crucible of 120 mm in diameter and 100 mm in height. The purity of aluminum and copper was about 99.95 %. Argon gas was supplied from the bottom of the chamber. Amount of the master alloy in the crucible was about 4 ~ 5 kg. Temperature of the alloy melt was examined by an optic pyrometer and controlled by adjusting the input power of the equipment with a fluctuation less than 30 K. A slow oxidation treatment was applied to the as-prepared powders before being exposed to air after the evaporation procedure. Samples were collected at the height of 300 mm above the evaporation source where the temperature are lower than 373 K and there is no change in phase and particle size in as-prepared powders.
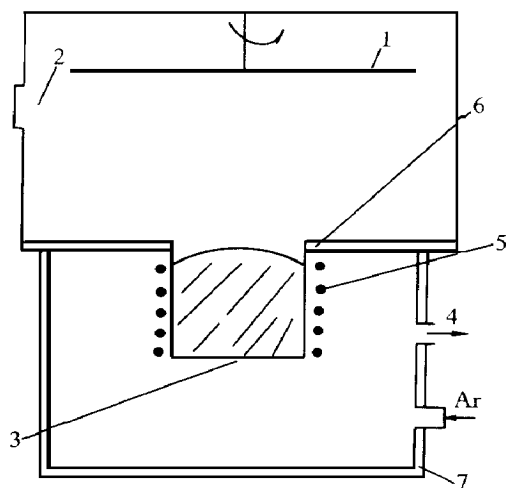


**Fig.1**   Schematic diagram of
evaporation equipment
1 —Powder collector; 2 — Window;
3 —Crucible; 4 —Vacuum pump;
5 —Coil; 6, 7 —Water cooled wall

Kinds of the phase and morphology of the particles were examined by X-ray diffraction and transmission electron microscopy. The relative amount of each phase is calculated by their relative area ratio of the diffraction peaks in the XRD patterns.

Evaporation time was kept at about 10 min

to get enough samples for XRD and TEM exam, there was no changing in Ar gas pressure during the experiments.

## 3   RESULTS

### 3.1   Effects of composition of master alloy on formation law of phases in as-prepared ultrafine powders

A series of master alloy with the composition of $Al_{100-x}Cu_x$ ( $x = 15.5$, 30, 40, 46.3, 32.3, 63, 75.7 % ( mole fraction, %)) were evaporated at 1 400 ℃ in $5.0 \times 10^3$ Pa Ar gas atmospheres. X-ray diffraction patterns of the as-prepared ultrafine powders are given in Fig.2.

As identified in Fig.2, the resulting ultrafine powders were composed of Al phase for the master alloy with Cu less than 30 %, Al + $\theta$-$CuAl_2$ for the master alloy with Cu from 30 % to 46.3 %, Al( Cu) + $\theta$-$CuAl_2$ + $\gamma_2$-$Al_4Cu_9$ for the master alloy with Cu from 46.3 % to 52.2 %, $\alpha$-Cu( Al) + $\gamma_2$-$Al_4Cu_9$ + $\beta$-$AlCu_3$ for the master alloy with Cu from 52.2 % to 63.0 %. There was no alloy phase in the powders when the amount of Cu in master alloy was above 75.5 %.

The dependence of fraction of the alloy phases upon the composition of the master alloy was given in Fig.3 and the changing tendency in lattice parameter $a_0$ of Al phase and Cu phase in the powders was given in Fig.4 which was obtained from the XRD results. Kinds of the alloy phases and their fraction in the powders were obviously affected according to Fig.3. Lattice parameters $a_0$ of Al phase in the powders decreased with increasing Cu in the master alloy, which showed a solution of Cu atoms in Al lattice. The maximum lattice distortion ($\Delta a / a_0$) for Al was 0.5 %, so the maximum solid solubility of Cu in Al was about 4.93 % according to the Vegard equation[11]. When fraction of Cu in the master alloy was above 63.0 %, the maximum lattice distortion ($\Delta a / a_0$) for Cu was 1.2 %, so the maximum solid solubility of Al in Cu was 9.9 % according to the Vegard Equation. It is obvious that the solid solubility of Al and Cu atoms in the lattice of phase Cu and phase Al in the powders was within the scope of that in Al-Cu alloy diagram.

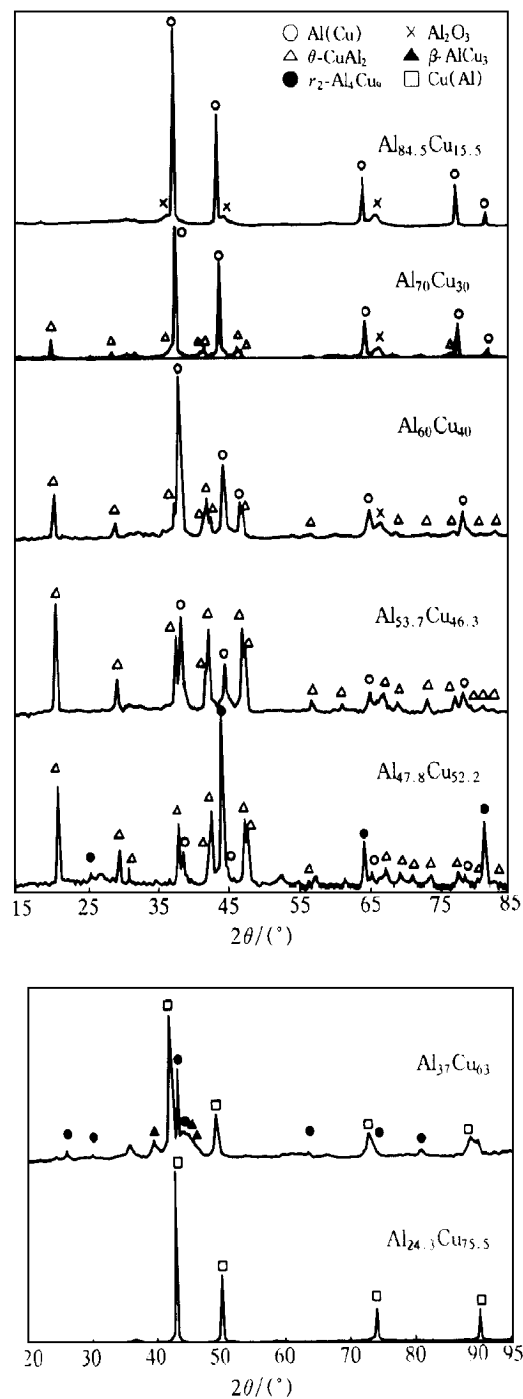## 3 .2  Effect of Ar gas pressure on phases in powders



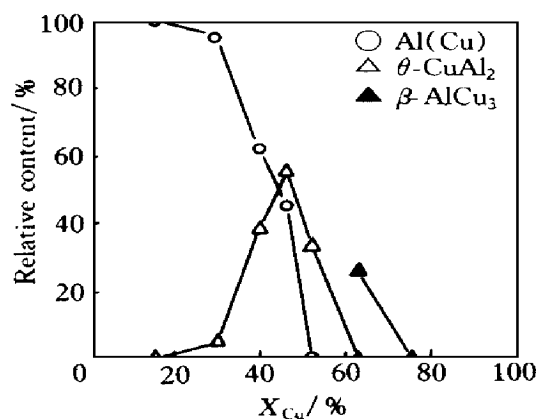Fig .2   X- ray diffraction patterns of ultrafine powders



Fig .3   Correlation between composition of master alloy and relative amount of alloy phases in as- prepared powders
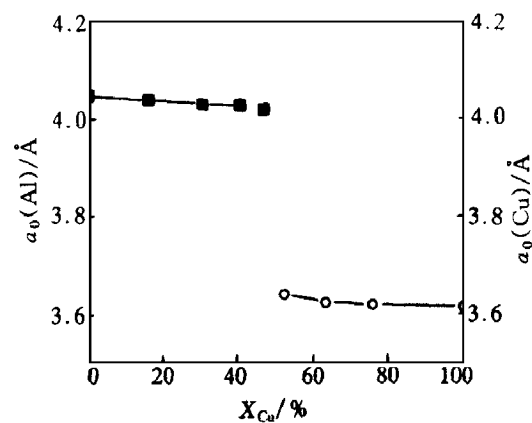


Fig .4   Effect of Cu content on lattice parameters of Al phase and Cu phase of as- prepared powders

The master alloy $Al_{37}Cu_{63}$ was chosen to investigate the formation law of phases in ultrafine powders when changing Ar gas pressure from $1 .0 \times 10^2$ Pa to $1 .0 \times 10^4$ Pa , the X- ray diffraction patterns of the powders were given in Fig . 5 . It is obvious that the kinds of phases in the powders remain constant , but the fraction of each phase changed according to the characteristics of the diffraction peak patterns as shown in Fig .6 .

X- ray diffraction measurements showed that the structure of all the phases formed in the as- prepared powders were in equilibrium state and
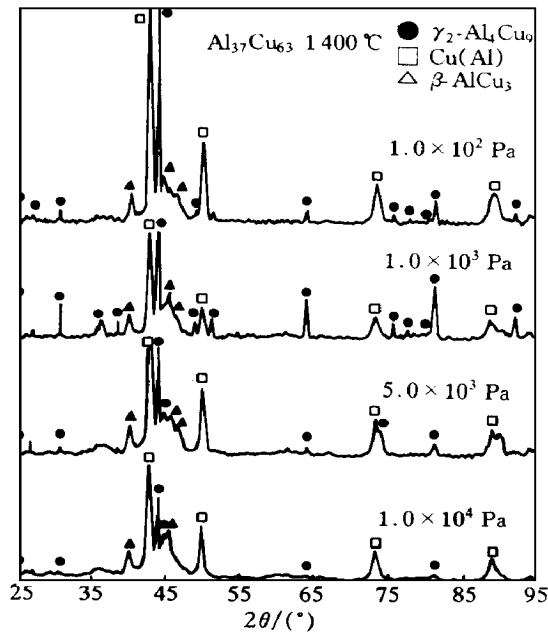
**Fig .5**   X- ray diffraction patterns
of powders obtained from
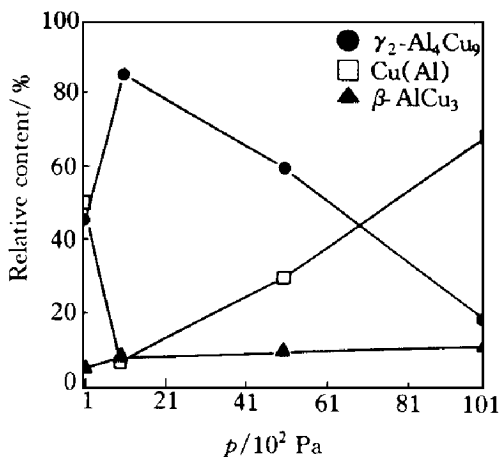master alloy of $Al_{37}Cu_{63}$



**Fig .6**   Effects of Ar gas
pressure on fractions of phases
in as- prepared powders

within the phase scope given in Al- Cu alloy dia-
gram .

### 3 .3   Particle morphology

Fig .7 shows morphology and structure of
the particles under different experiment condi-
tions .

The particle in Fig .7( a) is tadpole- like in
shape , particle size in Fig .7( b) is between 20 ~
50 n m in spherical shape , particle A shows dif-
ferent scattering contrast , particles B shows bi-
layer structure . These results are very different
from that of pure Al particles and pure Cu parti-
cles[3], which means these particles comprises
different phases .

## 4   DISCUSSION

To provide insight into the mechanisms that
controlling the formation law of alloy phases in
the as- prepared powders , it is necessary to anal-
ysis the partial pressure of the component in va-
por and nucleation , growth procedure of parti-
cles . The partial pressure can be calculated by e-
quation :

$$P_{Al} = a_{Al} P_{Al}^0 , \quad P_{Cu} = a_{Cu} P_{Cu}^0 \qquad (1)$$

where $a_{Al}$ and $a_{Cu}$ are the activity of Al
and Cu in alloy melt , $P_{Al}^0$ and $P_{Cu}^0$ are the satura-
tion vapor pressure of aluminum and copper at a
given temperature . $P_{Al}^0$ and $P_{Cu}^0$ are 22 .6 Pa and
7 .3 Pa at 1 400 ℃ calculated by equation[12] :

$$\lg P_{Al} = - 16 450/ T - 1 .23\lg T + 12 .36 \qquad (2)$$

$$\lg P_{cu} = - 17 650/ T - 1 .274\lg T + 13 .39 \qquad (3)$$

Table 1 gives the activity of Al and Cu in
master alloy melt with different composition .
Table 2 gives the partial pressure of Al and Cu in
the mixed vapors calculated by Eq .(1) .

Table 3 shows the correlation among the
composition of the master alloys , the fraction of
components in the mixed vapor calculated by
Eq . ( 4) and the phases in ultrafine powders :

$$\left. \begin{array}{l} X_{Al} = \dfrac{P_{Al}}{P_{Al} + P_{Cu}} \times 100 \% \\[4mm] X_{Cu} = \dfrac{P_{Cu}}{P_{Al} + P_{Cu}} \times 100 \% \end{array} \right\} \qquad (4)$$

It was obvious that relation between the
fraction of components in the vapor and the
phases in the as- prepared powders was very dif-
ferent from that in the phase diagram given in
Fig .8 . There only $\theta$- $CuAl_2$ , $\gamma_2$- $Al_4Cu_9$ and $\beta$-
$AlCu_3$ alloy phases formed in the as- prepared
powders when composition of the master alloy

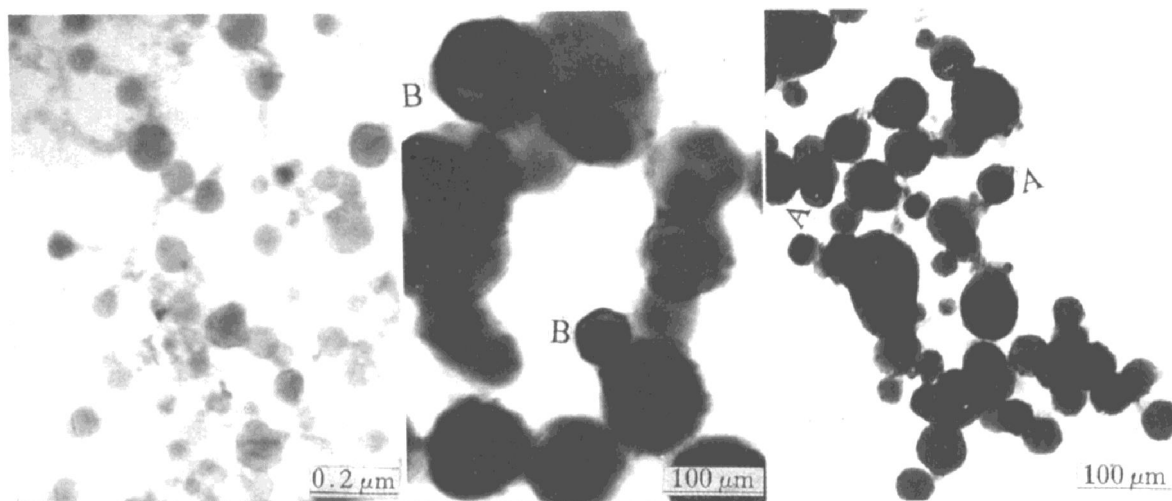**Fig .7**    Micrographs of ultrafine particles
( a) $-Al_{53.7}Cu_{46.3}$ ; ( b) $-Al_{37}Cu_{63}$

**Table 1**    Activities of Al and Cu in $Al_{100-x}Cu_x$ alloy melts at 1 400 ℃( mole fraction , %)[13]

| Composition of the master alloy | | $x = 15.5$ | $x = 30.0$ | $x = 40.0$ | $x = 46.3$ | $x = 52.2$ | $x = 63.0$ | $x = 75.7$ |
|---|---|---|---|---|---|---|---|---|
| Activities | $a_{Al}$ | 0.8239 | 0.6090 | 0.4543 | 0.3321 | 0.2549 | 0.1183 | 0.0166 |
| | $a_{Cu}$ | 0.0145 | 0.0721 | 0.0976 | 0.1134 | 0.1550 | 0.2925 | 0.5806 |

**Table 2**    Partial pressure ( Pa) of Al and Cu in mixed vapor at 1 400 ℃( mole fraction , %)

| Composition of master alloy | | $x = 15.5$ | $x = 30.0$ | $x = 40.0$ | $x = 46.3$ | $x = 52.2$ | $x = 63.0$ | $x = 75.7$ |
|---|---|---|---|---|---|---|---|---|
| Partial Pressure | $p_{Al}$ | 18.62 | 13.76 | 10.27 | 7.51 | 5.76 | 2.67 | 0.38 |
| | $p_{Cu}$ | 0.11 | 0.53 | 0.71 | 0.83 | 1.13 | 2.14 | 4.24 |

**Table 3**    Correlation between composition of master alloy, fractions of components in mixed vapor and phases in powders

| Composition of master alloy/ % | Composition of alloy vapor/ % | Phases in as-prepared powders |
|---|---|---|
| $Al_{84.5}Cu_{15.5}$ | $Al_{99.4}Cu_{0.6}$ | Al |
| $Al_{70}Cu_{30}$ | $Al_{96.3}Cu_{3.7}$ | $Al + \theta\text{-}CuAl_2$ |
| $Al_{60}Cu_{40}$ | $Al_{93.5}Cu_{6.5}$ | $Al + \theta\text{-}CuAl_2$ |
| $Al_{53.7}Cu_{46.3}$ | $Al_{90}Cu_{10}$ | $Al + \theta\text{-}CuAl_2$ |
| $Al_{47.8}Cu_{32.2}$ | $Al_{83.5}Cu_{16.5}$ | $Al + \theta\text{-}CuAl_2 + \gamma_2\text{-}Al_4Cu_9$ |
| $Al_{37}Cu_{63}$ | $Al_{55.7}Cu_{44.3}$ | $\alpha\text{-}Cu + \beta\text{-}AlCu_3$ |
| $Al_{24.3}Cu_{75.7}$ | $Al_8Cu_{92}$ | $\alpha\text{-}Cu$ |

changing from $Al_{70}Cu_{30}$ to $Al_{37}Cu_{63}$ .

The present results are some different from that of other studies . In Umemoto M' s experiment[14] , there formed $\theta$- $CuAl_2$ , $\beta$- $AlCu_3$ , $\gamma_2$- $Al_4Cu_9$ , $\eta_2$- $AlCu$ phases in ultrafine powders of Al-Cu alloy by plasma flame method , but Nosaki K only obtained $\theta$ , $\gamma_2$ phases by arc plasma method[4] . When Ohno evaporated Al-Cu master alloy by resistance heating method , there formed $\gamma_2$ , $\delta$ phases[15] , but Kaito C obtained $\delta$ , $\gamma_2$ , $\eta_2$ phases by the same method[16] .

So we can determine that the phases in ultrafine powders of the same alloy changes with the preparation process and the cooling effect of the experimental equipment . In the present experiment , metal smoke is observed to form above the evaporating source just at the height of sev-

eral millimeters where the atmosphere tempera-
ture is still very high and near to the evaporating
temperature, the primary particles in the smoke
is generally only 1 ~ 3 nm[17], so it can be said
that these particles may be in liquid state. Onho
T[9] had shown in his experiment of preparing
ultrafine powders of Cu-Zn alloy that there first-
ly formed the alloy phase with the highest melt-
ing point in the primary particles, then the phase
can change to several other phases during the fol-
lowing period of cooling. According to the above
state, the reason why there no $\chi$ and $\varepsilon_1$ phases
formed in the as-prepared powders can be ex-
plained as that even though there formed $\chi$ and
$\varepsilon_1$ phases, they will change to $\beta$ and $\gamma_2$ phases in
the following period of cooling.
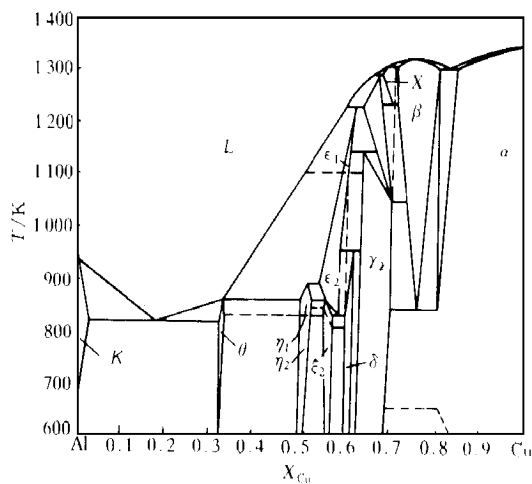


**Fig.8**   Phase diagram of Al-Cu system

## 5   CONCLUSIONS

The formation law of the phases in ultrafine
powders of Al-Cu alloy system were investigat-
ed. The results are summarized as follows.

(1) The kinds of the phases formed in the
as-prepared powders and their fractions are con-
trolled by the pressure fraction of the compo-
nents in the mixed vapor and the cooling condi-
tions of the experimental equipment. Changing

in pressure of Ar gas can only change the fraction
of different phase in the as-prepared powders in
present experiment.

(2) There only $\theta$-CuAl$_2$, $\gamma_2$-Al$_4$Cu$_9$, $\beta$ Al-
Cu$_3$ alloy phases can form in the ultrafine pow-
ders in present experiment, the phase structure
of these phases are of equilibrium state structure.

(3) The solid solubility of Al and Cu atoms
in the lattice of phase Cu and phase Al in the
powders was within the scope of that in Al-Cu
alloy diagram.

(4) The structure and morphology of the
alloy particles are different from that of the pure
Al and pure Cu particles.

### REFERENCES

1   Kubo R. J Phys Soc Jap, 1962, 17: 975.
2   Hayashi C. Physics Today, 1987, (12): 44.
3   Uyeda R. Prog in Mater Sci, 1991, 35: 1.
4   Nosaki K, Inoue A, Yamaguchi T et al. Mater Trans
    JI M, 1994, 35(3): 149.
5   Itoh H and Kikuchi E. Appl Catal, 1990, 67: 1.
6   Yamaguchi T, Inoue A et al. Mater Trans JI M,
    1994, 35(8): 538.
7   Inoue A, Yamaguchi T, Takeuchi A et al. Mater
    Trans JI M, 1994, 35(10): 663.
8   Onho T, Honma K et al. J Jap Inst Metals, 1989,
    53(9): 936.
9   Ohno T. J Crystal Growth, 1984, 70: 541.
10   Saito Y, Yanagida A et al. J Crystal Growth, 1984,
    70: 536.
11   Hume-Rothery W. The Structure of Metals and Al-
    loys. 5th ed. 1969: 349.
12   Dai Yongnian, Zhao Zhong. Vaccum Metallurgy,
    (in Chinese). Beijing: Metallurgy Industry Press,
    1998: 105 - 108.
13   Wu Kaisheng. SGET(Scientific Group Thermodata
    Europ) (Private Communication).
14   Umemoto M. Powder & Powder Metallurgy, (in
    Japanese), 1994, 4(15): 496.
15   Ohno T. J Crystal Growth, 1983, 64: 345.
16   Kaito C. Jap J Appl Phys, 1984, 23(3): 525.
17   Granqvist C G and Buhrman R A. Jap J Appl Phys,
    1976, 13: 2287.

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