# Pore Nucleation in Solidifying High-Purity Copper

EIICHI KATO

High-purity copper (6 or 7 N) was melted and solidified unidirectionally in the atmosphere of a $H_2$-Ar gas mixture for the purpose of studying the mechanism of pore nucleation in solidifying metal. Hydrogen content in the melt was controlled by changing the partial pressure in the atmosphere. Pores were formed when the hydrogen partial pressure in the atmosphere was 0.3 atm or more. Oxides of aluminum and silicon were observed at the bottom of the pores and the pores were nucleated heterogeneously. Water vapor with a very low partial pressure existed in the furnace atmosphere, and the melt must have contained a small amount of oxygen in equilibrium with this water vapor. The solid/liquid (S/L) interface was planar and convection was eliminated. The redistribution of the solute during solidification can, therefore, be estimated. The concentration of oxygen in the liquid at the S/L interface is estimated to be much larger than its initial concentration, due to the very small equilibrium distribution coefficient of oxygen in copper, and aluminum and silicon were oxidized even though their concentrations were very low. The probability of homogeneous nucleation by $\alpha$ particles was very small in these experiments.

## I. INTRODUCTION

INVESTIGATIONS [1,2,8] of homogeneous nucleation of pores in liquid metals have shown that the initiation pressure that is required for nucleation is extremely high, and therefore, homogeneous nucleation is unlikely to occur in practice. In contrast, it is generally agreed[1-5] that the difficulty of nucleation is reduced if nonwetted solid surfaces exist in the liquid. Furthermore, the work of formation of an embryonic bubble is much reduced on a concave substrate.[1,4,5]

Pores in castings are more the norm than the exception. The question is whether these pores are nucleated heterogeneously or homogeneously. If pores are nucleated heterogeneously, how can solid inclusions be formed when high-purity metal is melted and solidified in an atmosphere of low oxygen potential? If pores are nucleated homogeneously, how is the high initiation pressure produced?

Liquid copper dissolves oxygen,[6] and conversely nitrogen[7] and carbon[8] are insoluble in liquid copper. Therefore, oxides can be formed in liquid copper and nitrides and carbides can not. Furthermore, oxides are nonwetted in liquid copper.[9] The nucleation of a pore in liquid copper, therefore, is considered to occur against the surface of an oxide inclusion.

In this study, high-purity copper that contained very small amounts of oxide-forming elements was melted and solidified in the atmosphere of a $H_2$ + Ar gas mixture. This condition is extremely unfavorable for the formation of oxide inclusions in the melt. The results obtained in this study could offer useful information on the mechanism of pore nucleation in metals.

Nucleation mechanisms that are outside of the normal classical approach have been proposed by Campbell.[3] Among these mechanisms, the homogeneous nucleation by $\alpha$ particles was investigated in this study.

EIICHI KATO, Professor Emeritus, is with the Department of Materials Science and Engineering, Waseda University, Tokyo 169-0072, Japan.
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## II. EXPERIMENTAL DETAIL

High-purity 6 N (from Mitsubishi Material Corp., Tokyo, Japan) and 7 N (from Dowa Corp., Tokyo, Japan) copper were used for the experiments. The impurities in these metals are given in Table I. The concentrations of Na, Mg, K, Cr, Fe, Ni, Sb, and Pb were less than 0.01 ppm.

The equipment for the unidirectional solidification experiments is shown in Figure 1. Gas mixtures of $H_2$ and Ar were used for the melting atmosphere and the hydrogen content of the melt was controlled by changing the $H_2$ partial pressure in the atmosphere. The flow rate of the gas mixture was $8.3 \times 10^{-6}$ $m^3/s$. The purities of the gases used for these experiments were 99.999 pct. High-purity graphite crucibles (24-mm external diameter, 18-mm internal diameter, and 110-mm length) were used, and the crucible containing a specimen was placed on a water-cooled copper plug. The specimen was solidified unidirectionally by withdrawing the water-cooled copper plug downward. The solidification velocity was controlled by changing the rotational speed of the motor that drove the withdrawal mechanism, and the velocity was determined by decanting the solidifying specimen and by measuring the depth of the liquid phase with a silica rod. A solidification velocity of 0.18 mm/s was used throughout this study.

The decanting method was used to observe the solidification morphology. The inclusions on the surface of the pores were observed by scanning electron microscopy (SEM). The $\alpha$ particles radiated from the surface of a specimen were determined.

## III. RESULTS

No pores were formed when the hydrogen partial pressure was 0.2 atm, and pores were formed when the hydrogen partial pressure was 0.3 atm or more. The threshold pressure must lie between these pressures. Examples of longitudinal sections of the ingots are shown in Figure 2. The solid/liquid (S/L) interface, which exhibits planar growth, is shown in Figure 3. Figures 4 and 5 indicate oxides that were formed at the bottom of pores. These oxides are very thin.

**Table I. Impurities in the Samples (Obtained from Glow Discharge Mass Spectrometric Analysis)**

| Sample | Parts per Million | | | | | | |
|---|---|---|---|---|---|---|---|
| | Al | Si | S | Ag | As | U | Th |
| 6 N | 0.02 | 0.008 | <0.01 | 0.25 | 0.05 | <0.0001 | <0.0001 |
| 7 N | 0.01 | 0.03 | 0.01 | 0.03 | <0.01 | <0.0001 | <0.0001 |
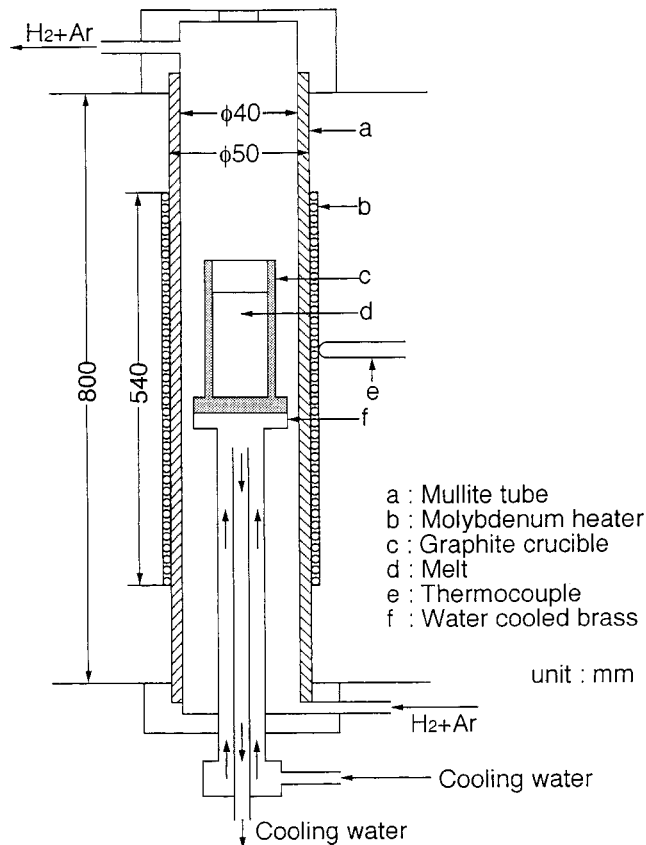


Fig. 1—Cross section of the experimental equipment.

a : Mullite tube
b : Molybdenum heater
c : Graphite crucible
d : Melt
e : Thermocouple
f : Water cooled brass

unit : mm



Fig. 2—Longitudinal cross sections of solidified specimens: (*a*) 7 N copper ($P_{H2}$ = 0.4 atm), (*b*) 7 N copper ($P_{H2}$ = 0.3 atm), (*c*) 6 N copper ($P_{H2}$ = 0.3 atm), and (*d*) 7 N copper ($P_{H2}$ = 0.2 atm).



Fig. 3—Decanted S/L interface o f 6 N copper exhibiting planar growth.

## IV. DISCUSSION

In the experiments conducted in this study, convection in the liquid was eliminated, and the S/L interface was planar. Therefore, the solute concentration profile in the liquid can be calculated approximately by the use of the solute redistribution model proposed by Tiller *et al.*[10] Because the equilibrium distribution coefficient of hydrogen in copper is 1/3,[11] the hydrogen concentration in the liquid at the S/L interface at steady state is three times as much as the initial hydrogen content. Hydrogen in metals obeys Sievert's law, and therefore the equilibrium hydrogen partial pressure corresponding to the hydrogen content in the liquid at the S/L interface is nine times as much as that in the melting atmosphere. Therefore, in the liquid at the S/L interface, the equilibrium hydrogen partial pressure is calculated to be 2.7 atm or more when pores were formed, and 1.8 atm or less when no pores were formed.

### A. *Heterogeneous Nucleation*

The wall of the crucible did not contribute to the nucleation of the blowholes because the pores were formed at the
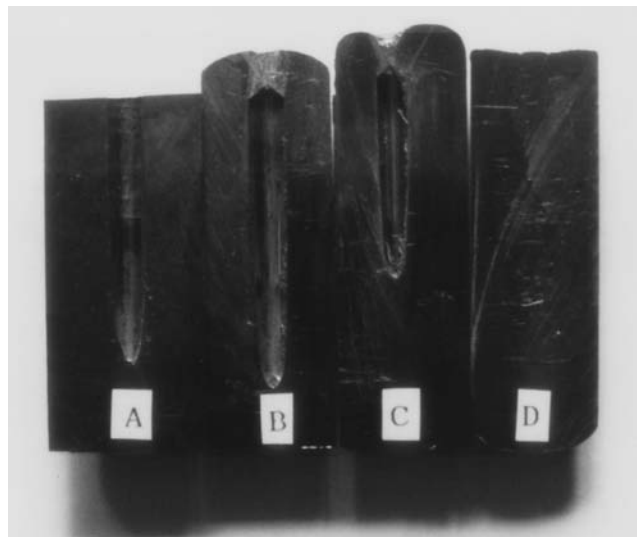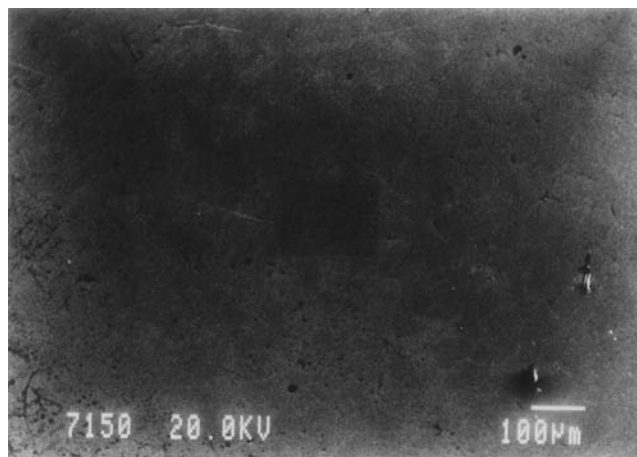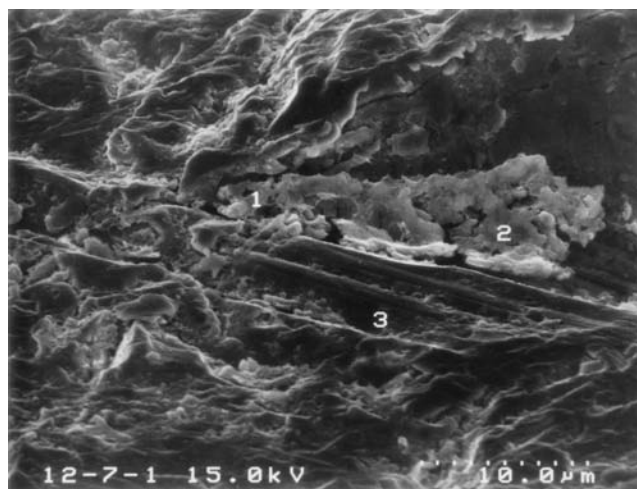


Fig. 4—SEM photomicrograph showing oxide inclusions at the bottom of the pore in 6 N copper: (1) $SiO_2$ + $Al_2O_3$, (2) $SiO_2$, and (3) Cu.
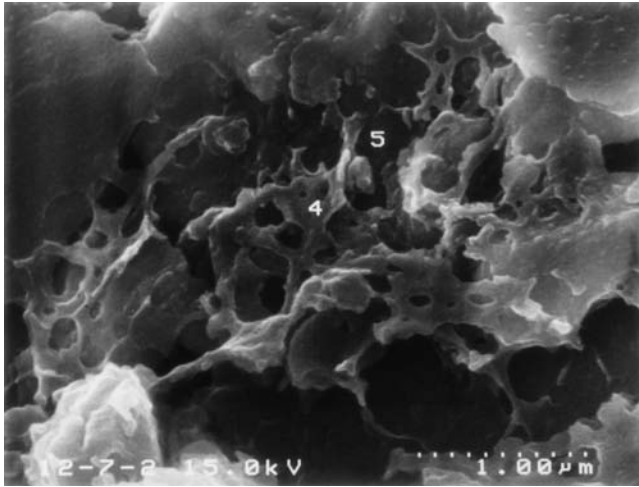
Fig. 5—SEM photomicrograph showing oxide inclusions at the bottom of the pore in 7 N copper: (4) $SiO_2$ + $Al_2O_3$ and (5) Cu.

center of the ingots (Figure 2). The solid copper–hydrogen gas interfacial energy is much larger than that of solid copper–liquid copper, and hence the formation of bubbles at the solidifying interface is impossible. In a hydrogen atmosphere, the contact angle between $Al_2O_3$ and liquid copper is 150 deg[9] and that between $SiO_2$ and liquid copper is 148 deg.[9] These oxides are, accordingly, not wetted by liquid copper. Furthermore, there are many small holes on the oxides (Figure 4 and 5), and embryonic bubbles may have grown on concave substrates of these holes.

The dew point of the exhaust from the furnace was determined to be 233 K and the corresponding partial pressure of water vapor is $1.3 \times 10^{-4}$ atm.[12] The $H_2/H_2O$ mixture exerts an equilibrium oxygen partial pressure *via* the following equilibrium:

$$H_2(g) + \frac{1}{2} O_2 (g) = H_2O (g) \qquad [1]$$
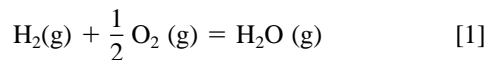
for which $\Delta G^\circ = -172,487$ J/mole[13] at 1358 K (the melting point of copper). The oxygen partial pressure, therefore, is $1.0 \times 10^{-20}$ atm when the hydrogen pressure is 0.3 atm. At the eutectic temperature, the solubility of oxygen in solid copper is 0.03 at. pct[14] and in liquid copper is 1.7 at. pct.[14] The equation for the activity coefficient of oxygen in liquid copper is given by Xue and Diekmann[15] and the value of the activity coefficient is calculated to be 0.93 when the concentration of oxygen is 1.7 at. pct. The equilibrium distribution coefficient of oxygen in copper at the eutectic temperature, therefore, is $0.03/(1.7 \times 0.93) = 0.019$. Because the eutectic temperature is close to the melting point, this equilibrium distribution coefficient can be used at the melting point.

The equilibrium for the dissolution of oxygen in liquid copper is given as follows:

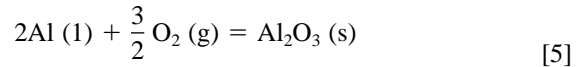$$O_2 (g) = 2\underline{O} \qquad [2]$$

Therefore, when the hydrogen pressure is 0.3 atm, the equilibrium oxygen partial pressure corresponding to the oxygen content in the liquid at the S/L interface is as follows:

$$1.0 \times 10^{-2^\circ} \times \left(\frac{1}{0.019}\right)^2 = 2.8 \times 10^{-17} \text{ atm} \qquad [3]$$

The pertinent equilibrium for the oxidation of aluminum in copper is as follows:

$$2\underline{Al} \text{ (wt pct in liquid Cu)} + \frac{3}{2} O_2 \text{ (g)} = Al_2O_3 \text{ (s)} \quad [4]$$
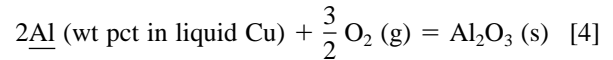
For the reaction at 1358 K the following holds:

$$2Al \text{ (l)} + \frac{3}{2} O_2 \text{ (g)} = Al_2O_3 \text{ (s)}$$
$$\Delta G^0 = -1,243,000 \text{ J/mole}^{[13]} \qquad [5]$$

Since $\gamma^\circ_{Al , in \, C^u} = 0.0055$,[16] the following holds for the change of standard state:
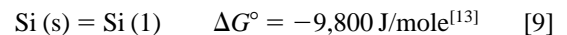
$$Al \text{ (l)} = \underline{Al} \text{ (wt pct in liquid Cu)} \quad \Delta G^\circ \qquad [6]$$
$$= -101,000 \text{ J/mole}$$

Therefore, for Eq. [4] $\Delta G^\circ = -1,041,000$ J/mole, and the concentration of Al in equilibrium with oxygen at a partial pressure of $2.8 \times 10^{-17}$ atm is $2.5 \times 10^{-4}$ ppm. The equilibrium distribution coefficient of Al in Cu is 0.83.[17] Accordingly, Al for which the initial concentration is larger than $2.1 \times 10^{-4}$ ppm is oxidized.
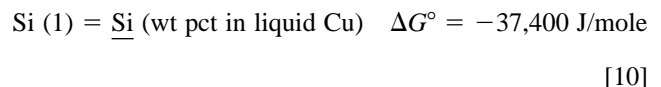
The pertinent equilibrium for the oxidation of silicon in copper is as follows:

$$\underline{Si}\text{(wt pct in liquid Cu)} + O_2 \text{ (g)} = SiO_2 \text{ (s)} \qquad [7]$$
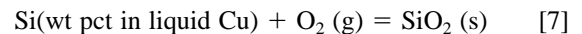
For the reactions at 1358 K the following holds:

$$Si \text{ (s)} + O_2 \text{ (g)} = SiO_2 \text{ (s)} \quad \Delta G^\circ = -668,100 \text{ J/mole}^{[13]} \quad [8]$$

$$Si \text{ (s)} = Si \text{ (l)} \qquad \Delta G^\circ = -9,800 \text{ J/mole}^{[13]} \qquad [9]$$

Since $\gamma^\circ_{Si , in \, C^u} = 1.615$,[18] the following holds for the change of standard state:

$$Si \text{ (l)} = \underline{Si} \text{ (wt pct in liquid Cu)} \quad \Delta G^\circ = -37,400 \text{ J/mole}$$
$$[10]$$

Therefore, for Eq. [7] $\Delta G^\circ = -640,500$ J/mole, and the concentration of Si in equilibrium with oxygen at a partial pressure of $2.8 \times 10^{-17}$ atm is $5.5 \times 10^{-5}$ ppm. The equilibrium distribution coefficient of Si in Cu is 0.65.[19] Accordingly, Si for which the initial concentration is larger than $3.6 \times 10^{-5}$ ppm is oxidized.

The experimental results and the thermodynamic considerations discussed previously indicate that a very small amount of Al and Si in liquid copper are oxidized by oxygen even when the partial pressure is very low.

### B. *Homogeneous Nucleation*

As discussed previously, we can be fairly certain that the pores were formed by heterogeneous nucleation in these experiments. However, it may be worthwhile to discuss the possibility of homogeneous nucleation of pores in these experiments. The classical theory of nucleation of a pore indicates that fracture pressure of liquid metal is extremely high and homogeneous nucleation is not feasible under ordinary conditions. Here, nucleation by $\alpha$ particles proposed by Campbell[3] is reviewed. Among naturally occurring $\alpha$ emitters in metals, only thorium and uranium are seen to produce significant numbers of particles.[3] The energy of the $\alpha$ particles emitted from $U^{238}$ is 4.27 MeV[20] and from

$Th^{232}$ is 4.1 MeV[20] and these particles can travel in liquid copper only very short distances; the former can travel 9.8 $\mu$m and the latter 9.4 $\mu$m, respectively.

For the nucleation of pores, the $H_2$ pressure in equilibrium with the hydrogen in the liquid must be at least 1.0 atm; therefore, the thickness of the liquid film where the nucleation of pores can occur is estimated as follows.

In the solidification model proposed by Tiller $et~al.$,[10] the solute concentration $C_1$ in the boundary layer of the liquid is expressed as follows:

$$C_1 = C_0 \left[ 1 + \frac{1 - k_0}{k_0} \exp\left(-\frac{R}{D}X\right) \right] \qquad [11]$$

where $C_0$ is the average concentration of the solute, $k_0$ is the equilibrium distribution coefficient, $R$ is the solidification velocity, $D$ is the diffusion coefficient for the solute in the liquid, and $X$ is the distance from the interface at which the concentration is $C_1$.

When the partial pressure of hydrogen in the atmosphere is 0.3 atm, because hydrogen in liquid copper obeys Sievert's law, the concentration of hydrogen that is in equilibrium with hydrogen gas at 1.0 atm is as follows:

$$\left[\frac{1.0}{0.3}\right]^{\frac{1}{2}} C_0 = 1.83 C_0 = C_1. \qquad [12]$$

As $k_0 = 1/3$,[11] $R = 1.8 \times 10^{-4}$ m/s, and $D = 5.77 \times 10^{-8}$ m$^2$/s[21] at 1356 K, $X$ is calculated as $2.83 \times 10^{-4}$ m = 0.0283 cm. The diameter of the specimen was 1.8 cm. Accordingly, the volume of the liquid film in which the concentration of hydrogen was high enough for the formation of bubbles was 0.072 cm$^3$ at the most. The numbers of decays per minute due to 1 ppm element in 1 cm$^3$ liquid metal for Th and U are 10 and 41,[3] respectively. Because the length of the ingot was about 5 cm and the solidification velocity was 0.018 cm/s, the solidification time was 278 seconds. Therefore, the number of $\alpha$ particles that could cause pore nucleation released from Th was less than $10 \times 0.072 \times 278 \times 1 \times 10^{-4}/60 = 3.3 \times 10^{-4}$, and the number of $\alpha$ particles from U was less than $41 \times 0.072 \times 278 \times 1 \times 10^{-4}/60 = 1.4 \times 10^{-3}$, respectively, when the concentrations of these elements were 0.1 ppb. As indicated in Table I, the concentrations of these elements were less than 0.1 ppb and the probability of the homogeneous nucleation of pores by $\alpha$ particles was very low. The concentrations of radioactive elements ahead of the freezing front may have increased, but the probability of homogeneous nucleation caused by radiation was still very low, because the equilibrium distribution coefficient of a metallic element in the metal is generally not much less than unity.

The surface of a specimen was liable to be contaminated by the radioactive isotopes in the air; $e.g.$, radon daughters, and $\alpha$ particles radiated from the surface of copper specimens were determined by a solid-state track detector.[22] The number of particles determined for a week was in the range of 0.4 to 0.8/cm$^2$; $i.e.$, $1.3 \times 10^{-6}$/s/cm$^2$ at the most. Some specimens were left in the atmosphere and rain fell on them. However, the number of $\alpha$ particles from such specimens was almost equal to that from the specimens with a clean surface. The surface area of the ingot was 33.4 cm$^2$. Accordingly, the number of $\alpha$ particles emitted from the surface was $4.3 \times 10^{-5}$/s. The radioactive isotopes on the surface

of the specimen may have been dissolved in the liquid specimen at the beginning of the solidifying experiment. As stated previously, the maximum volume of the liquid film in which the concentration of hydrogen was high enough for the nucleation of a bubble was 0.072 cm$^3$, and the solidification time and the volume of the specimen were 278 seconds and 12.72 cm$^3$, respectively. The probability of the existence in the film of $\alpha$ particles of high hydrogen content, therefore, is estimated to be less than $4.3 \times 10^{-5} \times 278 \times 0.072/12.72 = 6.8 \times 10^{-5}$ for each experiment, and nucleation by $\alpha$ particles could not occur.

The number of $\alpha$ particles emitted from the surface of the graphite crucible was determined to be $2.8 \times 10^{-6}$/s/cm$^2$, which is also negligible.

## V. CONCLUSIONS

1. Pores were formed when the $H_2$ partial pressure in the atmosphere was 0.3 atm or more. When the hydrogen partial pressure is 0.3 atm, the equilibrium $H_2$ pressure corresponding to the hydrogen content in the liquid at the S/L interface is calculated to be 2.7 atm.
2. Oxides of Al and Si existed at the bottom of the pores, and the pores were nucleated heterogeneously on the surface of the oxides.
3. The oxygen potential in the liquid at the S/L interface much increased during solidification, and Al and Si were oxidized even though their concentrations were very low. This is attributed to the very small value of the equilibrium distribution coefficient of oxygen in copper.
4. Homogeneous nucleation of pores by $\alpha$ particles was impossible in this study.

## REFERENCES

1. J.C. Fisher: $J.~Appl.~Phys.$, 1948, vol. 19, pp. 1062-67.
2. S. Takagi: $J.~Appl.~Phys.$, 1953, vol. 24, pp. 1453-62.
3. J. Campbell: $The~Solidification~of~Metals$, ISI Publication No. 110, ISI, London, 1968, pp. 18-26.
4. S.G. Bankoff: $Trans.~ASME$, 1957, vol. 79, pp. 735-40.
5. A.V. Bradshaw: $Le~Vide$, 1967, vol. 23, pp. 376-415.
6. J.P. Neumann, T. Zhong, and Y.A. Chang: $Bull.~Alloy~Phase~Diagrams$, 1984, vol. 5, pp. 136-40.
7. $Binary~Alloy~Phase~Diagrams$, 2nd ed, T.B. Massalski, ed., ASM INTERNATIONAL, Materials Park, OH, 1990, vol. 2, p. 1438.
8. M.B. Bever and C.F. Floe: $Trans.~AIME$, 1946, vol. 166, pp. 128-41.
9. S. Nakano and M. Ohtani: $J.~Jpn.~Inst.~Met.$, 1970, vol. 34, pp. 562-67.
10. W.A. Tiller, K.A. Jackson, J.W. Rutter, and B. Chalmers: $Acta~Metall.$, 1953, vol. 1, pp. 428-37.
11. A.J. Phillips: $Trans.~AIME$, 1947, vol. 17, pp. 17-46.
12. $Landolt$-$Boernstein~Numerical~Data~and~Functional~Relationships~in$

*Science and Technology*, vol. 4, *Physical and Chemical Properties of Air*, [G. Fisher, ed.,] Springer-Verlag, Heidelberg, 1988.

13. M.A. Chase: *JANAF Thermochemical Tables*, 3rd ed., American Institute of Physics, Inc., New York, NY, 1986.
14. J.P. Neumann, T. Zhong, and Y.A. Chang: *Bull. Alloy Phase Diagrams*, 1984, vol. 5, pp. 136-40.
15. J. Xue and R. Diekmann: *High Temp. High Pressure*, 1992, vol. 24, pp. 271-84.
16. T.C. Wilder: *Trans. AIME*, 1965, vol. 233, pp. 1202-08.
17. *Binary Alloy Phase Diagrams*, 2nd ed., T.B. Massalski, ed., ASM INTERNATIONAL, Materials Park, OH, 1990, vol. 1, pp. 141-42.
18. G. Riekert, P. Lamparter, and S. Steeb: *Z. Naturforsch.*, 1981, vol. 36a, pp. 447-53.
19. *Binary Alloy Phase Diagrams*, 2nd ed., T.B. Massalski, ed., ASM INTERNATIONAL, Materials Park, OH, 1990, vol. 1, pp. 1477-79.
20. *Table of Isotopes*, 8th ed., R.B. Firstone, ed., Lawrence Berkeley National Laboratory, University of California, Berkeley, CA, 1996, vol. II.
21. P. Sigrist, H.K. Feichtinger, and B. Marincek: *Z. Phys. Chem.-Frankfurt*, 1977, vol. 107 (2), pp. 211-18 (new series).
22. B.G. Cartwright, E.K. Shirk, and P.B. Price: *Nucl. Instrum Methods*, 1978, vol. 153, pp. 457-60.