ENHANCED EVAPORATION OF COPPER BY NH_3 GAS BLOWING

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Enormously high rate of evaporation from liquid pure copper was found when NH_3 gas was top-blown. Smoke of fine spherical particles of Cu was observed by laser light sheet method. Nitrogen in the melt was supersaturated during NH_3 gas blowing. The formation of an unstable and volatile copper compound such as CuN_x or CuH was suggested in addition to the cooling effect due to endothermal decomposition of NH_3.

1 Introduction

Significant evaporation from copper melt was observed when atmospheric pressure of NH_3 gas was blown[1,2]. By blowing NH_3 gas onto the molten steel at the reduced pressures, the dissolved copper could be removed to a few hundreds ppm level[1,2]. Because the Cu removal was difficult by the conventional steel refining procedures, NH_3 gas blowing holds a potential for industrial application of iron scrap recycling. The mechanism of Cu evaporation by NH_3 gas blowing was experimentally studied here using the pure Cu melt.

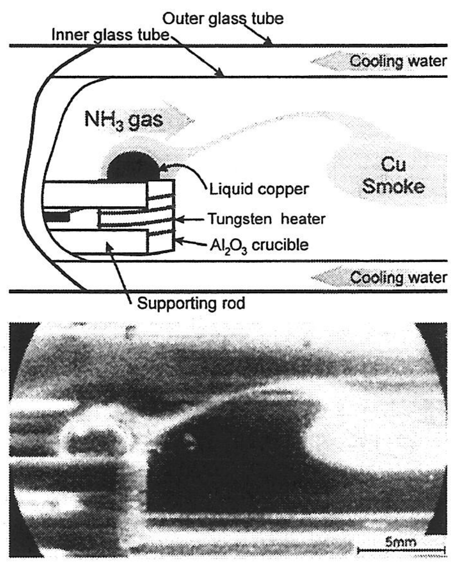

Figure 1: Smoke from Cu melt in NH_3 gas.

2 Fume Observation

Evaporation by NH_3 gas blowing was visualized by laser light sheet method: a 0.2 mm thick sheet of laser light was irradiated for 10^{-7}second to observe a two-dimensional slice in the tree-dimensional space. A distribution of fine particles in the 2-D space could be reflected without interfere from the heat radiation. A copper droplet heated in the Al_2O_3 crucible. Cooling water was flown in the gap between two transparent glass tubes. 2.5×10^{-6} m^3/s of NH_3 gas was blown to the Cu melt at 1573 K in the inner tube. The image of "fume" like cigarette smoke was taken as shown in Figure 1. This smoke could not be found in Ar gas. The initiation of smoke was found at 75-120μm above the melt surface, and this smoke piled on the glass tube surface.

Scanning electron micrograph (SEM) of the particles adhered to the tube was shown in Figure 2. All the particles were spherical and smaller than a few μm. X-ray diffractions (XRD) identified them as metallic pure copper.

3 Evaporation rate

During NH_3 gas top-blowing at atmospheric pressure, the surface of molten copper was wavy and the intense boiling with sparkling splashes was sometimes observed. The evaporation rate was evaluated by the mass change of molten copper as shown in Figure 3, where NH_3 gas was top-blown through the water-cooled alumina lance. The maximum evaporation rate in vacuum can be calculated by Langmuir equation and equilibrium vapor pressure of metallic copper[3]. This theoretical rate can not be exceeded assuming that copper can evaporate only as Cu gas. The observed evaporation rates under NH_3 gas blowing were, however, 10-1000 times larger than the vacuum evaporation. In comparison, Ar and N_2 gas blowing suppressed the evaporation because the existence of gas is a barrier for free evaporation of Cu.

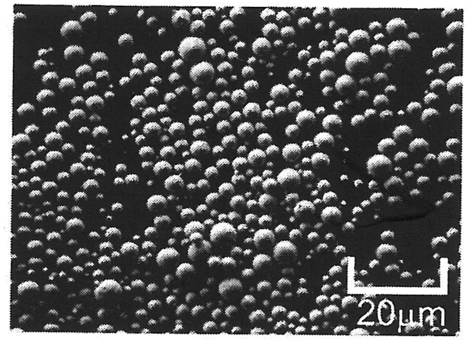

Figure 2: Evaporated Cu particles.

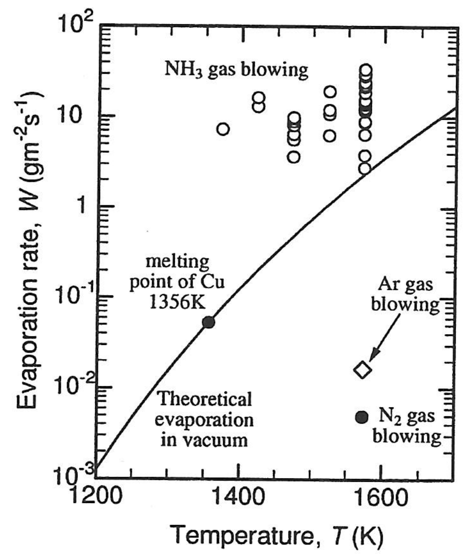

Figure 3: Evaporation rates under gas blowing at 10^5 Pa.

4 Nitrogen solubility in Cu melt

Nitrogen dissolution was chemically analyzed in the rapidly quenched specimens that were molten under gas blowing at 10^5Pa of NH_3 and N_2. As shown in Figure 4, only about 1 mass ppm nitrogen can dissolve in equilibrium with 10^5Pa of pure nitrogen at 1740K, which corresponds well with the previous works[4,5]. However, 40-75 ppm nitrogen dissolved under NH_3 gas blowing.

NH_3 gas at high temperatures decomposes into gas mixture of N_2 and H_2. When NH_3 gas was forced to be introduced onto the molten Cu, an excited state of NH_3 gas relaxes to an equilibrium state with time. In this relaxation process,

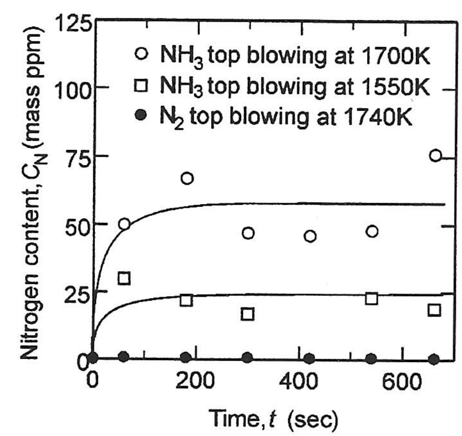

Figure 4: Nitrogen dissolution on gas blowing.

"nascent nitrogen and hydrogen" decomposed from NH_3 are highly reactive and hold a high thermodynamic potential. They may dissolve from the melt surface to liquid Cu to a steady super-saturation value, and combine as N_2 and H_2 in the melt. The evolution of these gases causes the boiling.

Based on the boundary layer theory, evaporation can occur after the metal atoms have passed the boundary layer through diffusion driven by a gradient in partial pressure, and the diffusion may become the rate determining factor[4,5]. If the thickness of the boundary diffusion layer for Cu vapor decrease by the cooling effect of a gas flow towards the Cu melt surface, the evaporation rate will be increased. Because the decomposition of NH_3 gas is endothermic, the temperature decrease of the melt by 20-30K was experimentally recorded. This cooling effect may promote the precipitation as Cu particles just above the Cu melt, as in Figure 1.

5 Dilution of NH_3 gas

Blowing the gas mixture of NH_3 and, H_2, N_2 or Ar, the evaporation of Cu at 1573K was studied as shown in Figure 5. For example, 10 vol% addition of NH_3 to Ar (total pressure = 10^5 Pa) significantly enhanced the evaporation as well as vacuum evaporation. N_2 addition to NH_3 was more effective than Ar gas, and the evaporation in gas mixture of NH_3 and H_2 was slightly higher than that in pure NH_3.

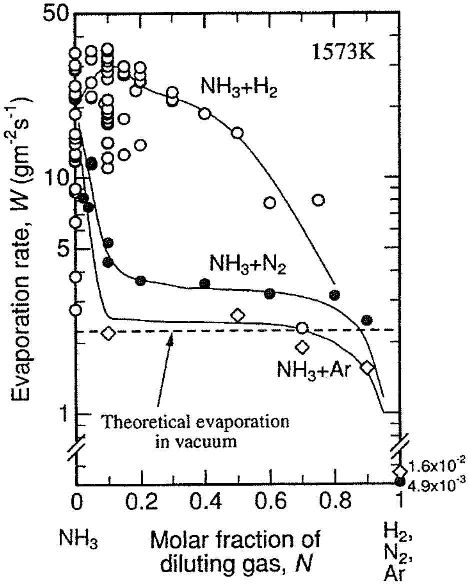

Figure 5: Copper evaporation under blowing gas mixture of H_2, N_2 or Ar with NH_3.

6 Possible Formation of CuH and Cu nitrides

The thermodynamic potential equivalent pressure of an exciting state appearing during NH_3 decomposition may be calculated by using Gibbs' free energy change, ΔG^0, for the decomposing reaction,

$$2\ NH_3 = 3\ H_2 + N_2. \tag{1}$$

Taking into account that $3\ pN_2 = pH_2$, the equivalent pressure of hydrogen, pH_2, can be deduced[1]. Figure 6 is thus calculated using HSC database[3]. For example, pH_2 and pN_2 are evaluated at 1573 K as $1.83\text{x}10^7$ Pa and $6.1\text{x}10^6$ Pa, respectively. These high equivalent pressures, i.e., high thermochemical potentials, can dissolve hydrogen and nitrogen in the Cu melt to the over-saturation values, and form a gaseous copper hydride or nitride.

The thermodynamic data of CuH was reported by the effusion cell-mass spectrometric measurement[6]. Using ΔG^0 for CuH formation compiled in database[3],

$$Cu + 1/2\ H_2 = CuH(g) \qquad (2)$$

the vapor pressure of CuH, p_{CuH}, is evaluated as in Figure 6. When CuH is in equilibrium with atmospheric pressure of hydrogen gas, p_{CuH} is similar with the equilibrium vapor pressure of copper, p_{Cu}. Assuming that CuH is in equilibrium with the hydrogen relieved from NH_3, p_{CuH} is about ten times higher than p_{Cu}. The comparison of these values may suggest a possible formation of gaseous copper hydride under NH_3 gas blowing. Similarly, a passing nascence of gaseous copper nitride cannot be denied. Although no thermodynamic data for copper nitride gas are available, it is known that solid copper nitrides such as Cu_3N, CuN_3 and CuN_6 can exist under high pressure nitrogen.

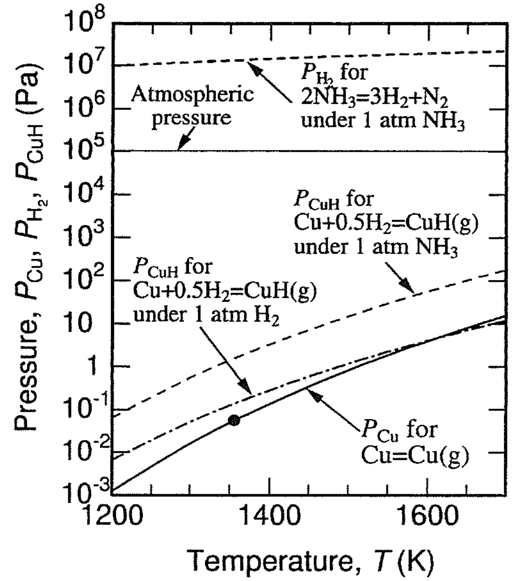

Figure 6: Equilibrium partial pressures under NH_3 gas.

The addition of a small amount of H_2 and N_2 to NH_3 gas rises the thermochemical potential of nitrogen and hydrogen, respectively, according to Eq. (1). For example, 1 vol% H_2 in NH_3 gas gives pN_2 of 3.88×10^{19} Pa at 1573K. This high potential of nitrogen in gas mixture of NH_3 and H_2 has been applied on iron nitride formation for surface hardening. Therefore, the higher evaporation rate of Cu in NH_3 and H_2 gas mixture (Figure 5) is strongly related with the high pN_2. Although some experimental evaporation rates were larger than the evaporation rate expected by mass balance and CuN_6 formation, nitrogen relieved from NH_3 plays an important role for evaporation.

7 Acknowledgement

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8 References

[1] K. Ono, E. Ichise, R. O. Suzuki and T. Hidani, steel research **66**, 372-76 (1995).

[2] K. Ono, R. O. Suzuki, T. Hidani, and K. Takemura, Tetsu-to-Hagane **82**, 135- (1996).

[3] A. Roine, in HSC Chemistry, Ver.4.0, Outocumpu Research Oy, Poli, Finland (1999).

[4] E. T. Turkdogan, P. Grieveson and L. S. Darken, J. Phys. Chem., **67**, 1647-54 (1963).

[5] K. Ono and R. O. Suzuki, J. Mass Spectrom. Soc. Jpn., **47**, 38-41 (1999).

[6] A. Kant and K. A. Moon, High Temper. Sci., **11**, 55-62 (1975).