ENHANCED EVAPORATION OF COPPER BY NH₃ GAS BLOWING

R.O. Suzuki and K. Ono
Department of Energy Science and Technology
Kyoto University
Yoshida-Honnachi, Sakyo-ku, Kyoto 606-8501, Japan
E-mail: suzuki@energy.kyoto-u.ac.jp

Enormously high rate of evaporation from liquid pure copper was found when NH₃ 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 NH₃ gas blowing. The formation of an unstable and volatile copper compound such as CuNx or CuH was suggested in addition to the cooling effect due to endothermal decomposition of NH₃.

1 Introduction

Significant evaporation from copper melt was observed when atmospheric pressure of NH₃ gas was blown[1,2]. By blowing NH₃ 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, NH₃ gas blowing holds a potential for industrial application of iron scrap recycling. The mechanism of Cu evaporation by NH₃ gas blowing was experimentally studied here using the pure Cu melt.

2 Fume Observation

Evaporation by NH₃ 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 three-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 Al₂O₃ crucible. Cooling water was flown in the gap between two transparent glass tubes. 2.5×10⁻⁶ m³/s of NH₃ 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 NH₃ 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 NH₃ 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 NH₃ gas blowing were, however, 10-1000 times larger than the vacuum evaporation. In comparison, Ar and N₂ gas blowing suppressed the evaporation because the existence of gas is a barrier for free evaporation of Cu.

4 Nitrogen solubility in Cu melt

Nitrogen dissolution was chemically analyzed in the rapidly quenched specimens that were molten under gas blowing at 10⁵Pa of NH₃ and N₂. As shown in Figure 4, only about 1 mass ppm nitrogen can dissolve in equilibrium with 10⁵Pa of pure nitrogen at 1740K, which corresponds well with the previous works[4,5]. However, 40-75 ppm nitrogen dissolved under NH₃ gas blowing.

NH₃ gas at high temperatures decomposes into gas mixture of N₂ and H₂. When NH₃ gas was forced to be introduced onto the molten Cu, an excited state of NH₃ gas relaxes to an equilibrium state with time. In this relaxation process,
"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$_3$.

6 Possible Formation of CuH and Cu nitrades

The thermodynamic potential equivalent pressure of an exciting state appearing during NH$_3$ decomposition may be calculated by using Gibbs' free energy change, $\Delta G^0$, for the decomposing reaction,

\[
2 \text{NH}_3 = 3 \text{H}_2 + \text{N}_2.
\]

Taking into account that $3 p_{\text{N}_2} = p_{\text{H}_2}$, the equivalent pressure of hydrogen, $p_{\text{H}_2}$, can be deduced[1]. Figure 6 is thus calculated using HSC database[3]. For example, $p_{\text{H}_2}$ and $p_{\text{N}_2}$ are evaluated at 1573 K as 1.83x10$^7$ Pa and 6.1x10$^6$ 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 $\Delta G^0$ for CuH formation compiled in database[3],

![Figure 5: Copper evaporation under blowing gas mixture of H$_2$, N$_2$ or Ar with NH$_3$.](image-url)
Cu + 1/2 H₂ = CuH(g)  \hspace{1cm} (2)

the vapor pressure of CuH, $P_{\text{CuH}}$, is evaluated as in Figure 6. When CuH is in equilibrium with atmospheric pressure of hydrogen gas, $P_{\text{CuH}}$ is similar with the equilibrium vapor pressure of copper, $P_{\text{Cu}}$. Assuming that CuH is in equilibrium with the hydrogen relieved from NH₃, $P_{\text{CuH}}$ is about ten times higher than $P_{\text{Cu}}$. The comparison of these values may suggest a possible formation of gaseous copper hydride under NH₃ 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 Cu₃N, CuN₃ and CuN₆ can exist under high pressure nitrogen.

The addition of a small amount of H₂ and N₂ to NH₃ gas rises the thermochemical potential of nitrogen and hydrogen, respectively, according to Eq. (1). For example, 1 vol% H₂ in NH₃ gas gives $pN₂$ of $3.88 \times 10^{19}$ Pa at 1573K. This high potential of nitrogen in gas mixture of NH₃ and H₂ has been applied on iron nitride formation for surface hardening. Therefore, the higher evaporation rate of Cu in NH₃ and H₂ gas mixture (Figure 5) is strongly related with the high $pN₂$. Although some experimental evaporation rates were larger than the evaporation rate expected by mass balance and CuN₆ formation, nitrogen relieved from NH₃ plays an important role for evaporation.

7 Acknowledgement

This study was supported in part by Grants-in-aid for Scientific Research, under Contract No. 08555179 and 09450279.

8 References