Nitrogen Removal during Continuous Electron-beam Melting of 27%Cr-Fe Alloy*

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I. Introduction

It is commercially impractical to reduce nitrogen dissolved in liquid high chromium steel to an extremely low level (less than 100 ppm) during conventional vacuum refining processes. However, continuous electron-beam melting is considered to be more potential for the removal of nitrogen than other degassing processes,^{1,2)} because of relatively higher vacuum over a melt, higher surface temperature of the melt, larger surface/volume ratio, and water-cooled copper container keeping the melt from undesired elements. It is, therefore, of great interest to know the availability of continuous electron-beam melting for the production of stainless steel with extremely low nitrogen content. Unfortunately, no quantitative study on this problem has been reported. The purpose of this short note, thus, is to present the experimental results on nitrogen removal taking place during continuous drip-type melting of 27%Cr-Fe alloy.

II. Experiment

A furnace, a mold and the intensity of electron-beam (450 mA) used in the present experiment were the same as those described in the previous work.³⁾ Alloys with different nitrogen contents for consumable electrodes were prepared by vacuum induction melting. The compositions of the alloys were shown in Table 1. Chromium content was around 26.7% and nitrogen in the range from 39 to 236 ppm. Each electrode of 55 mm in diameter was weighed before setting inside the furnace. The experimental procedure was almost similar to that of the previous work. The rate of electrode melting ranged from 35 to 105 g/min. After the remelting experiment, both of the ingot in the mold and the electrode remaining unremelted were weighed to calculate the rates of ingot growth and electrode melting. Samples for chemical analyses of carbon, oxygen, chromium, sulfur, and nitrogen were taken from the middle of vertically sectioned ingots.

Table 1. Compositions of the electrodes used

Electrode No.	Cr	C	O	S (%)	Si	N
A-10	27.49	0.030	0.027	0.012	0.04	0.0039
A-14	27.06	0.030	0.023	0.010	<0.02	0.0082
A-15	27.07	0.032	0.029	0.010	0.22	0.0125
A-23	22.56	0.023	0.026	0.009	0.03	0.0152
A-18	27.84	0.035	0.027	0.008	0.05	0.0236
AV15	25.00	0.029	0.037	0.008	0.24	0.0168

III. Results and Discussion

Carbon and oxygen concentrations in the ingots obtained from Electrode No. A-14 and A-15 are plotted against the reciprocal of the rate of electrode melting in Fig. 1. The results of the other ingots are almost similar to that shown in Fig. 1. Residual oxygen content in the ingots falls in the range from 10 to 45 ppm and for most of them less than 20 ppm. Carbon content in the ingots is approximately constant due to deficiency of oxygen necessary to prompt carbon-oxygen reaction. As for sulfur, no significant change in the concentration was observed.

The general relation between chromium content and the rate of electrode melting³⁾ is represented by a slightly curved solid line with a mark "K" in Fig. 1. The observed values of chromium concentration are found to agree well to this line. The rate of ingot growth is always smaller than that of electrode melting due to the evaporative loss. Such decrease is found to be about 4.5 ± 0.5 g/min. This observed value is in good agreement with the theoretically calculated value which varies from 4.3 to 4.6 g/min in the present range of electrode melting rate.

A plot of the logarithm of nitrogen concentration versus the reciprocal of the melting rate is shown in Fig. 2. The degree of nitrogen removal is found to increase with decreasing the melting rate and with increasing initial nitrogen content. Figure 2 shows that electron-beam melting can reduce nitrogen content from 236 to 88 ppm, while the work of Visokay, *et al.*⁴⁾ indicates that vacuum induction melting of 25%Cr-Fe alloy reduces nitrogen from 220 to 150 ppm at 0.05 Torr in 1 hr (Heat No. C-1). The comparison is rather difficult but the electron-

Fig. 1. Plot of carbon, oxygen and chromium contents against reciprocal rate of electrode melting

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Fig. 2. Relation between the logarithm of nitrogen content and the reciprocal rate of electrode melting

beam melting seems more effective for nitrogen removal than vacuum induction melting. It should, nevertheless, be noted that at lower nitrogen contents the rate of nitrogen removal is very slow.

Nitrogen removal in drip type electron-beam melting is assumed to take place at the vacuum/melt interface of the liquid metal pool in which compositions would be completely uniform. The temperature of the metal pool is 1680°C.³⁾ Nitrogen desorption occurring at the tip of electrode would be ignored because of low temperature (about 1520°C), small surface area, and relatively higher oxygen content. The material balance of nitrogen in metal stream entering and leaving the pool in a steady state may be expressed as follows.

$$(W_0[\%N]_0 - W[\%N])10^{-2} = W_N^0 - W_N = S\phi \quad \dots(1)$$

where, $[\%N]$ and $[\%N]_0$ are the nitrogen concentrations in the ingot and electrode, W and W_0 are the rates of ingot growth and electrode melting, W_N and W_N^0 are the weights of nitrogen in the metal streams leaving and entering the pool (g/sec), S is the surface area of the pool, and ϕ is the rate of nitrogen removal (g/sec cm²). ϕ may be presumed to be expressed as follows.

$$\phi = k(a_N)^n = k(f_N[\%N])^n \quad \dots\dots\dots(2)$$

where, a_N and f_N are the activity and the activity coefficient of nitrogen dissolved in the metal pool, respectively, and k is the apparent rate constant in g/sec cm²(%)². The value of n depends on the rate-controlling step, that is, unity for mass transfer across a boundary layer of the melt or two for chemical reaction.

Hence, the observed values of $\log(W_N^0 - W_N)$ are plotted against $\log(a_N)$ in Fig. 3 in order to evaluate the values of n and k . The f_N values for high chromium contents at 1680°C are calculated from an empirical equation for the solubility of nitrogen in Fe-Cr melt under nitrogen pressure of 1 atm given by

Fig. 3. Relation between the logarithm of rate of nitrogen removal and the logarithm of activity of nitrogen dissolved in the metal pool

Blossey and Pehlke.⁵⁾ Figure 3 shows that experimental results are represented by a straight line with the gradient fully close to 2.0. The obtained value of k is 1.4 g/sec cm² (%)².*

As a result, Eq. (1) can be expressed as follows.

$$[\%N]_0 - [\%N](W/W_0) = 140 \cdot S f_N^2 [\%N]^2 / W_0 \quad \dots(3)$$

Since W and f_N (or chromium concentration) can be evaluated from W_0 as described earlier, a desired nitrogen level will be obtained by the adjustment of remelting conditions (W_0 , S , $[\%N]_0$) according to Eq. (3).

IV. Conclusion

Continuous drip-type electron-beam melting can efficiently reduce nitrogen dissolved in high chromium steel to a low level (about 100 ppm) from the level (150 to 250 ppm) attainable by conventional melting methods. Lower level of nitrogen will be obtained by further decrease of the rate of electrode melting. However, the required rate is too slow to be commercially used because of low productivity and high evaporative loss of chromium.

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* This value is approximately ten times of the value estimated from a general equation proposed by Ban-ya, et al.⁶⁾