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Note

Nitrogen Absorption Rate under Plasma Arc Compared to Resistance and Induction Melting

1. Introduction

In recent past there has been increasing interest in nitrogen bearing stainless steels in view of technical and economical considerations. This has been highlighted by the authors in other papers.[1,2] Such interest has led to various studies to understand different aspects including rate of nitrogen absorption in the melt. The factors controlling the nitrogen absorption in the melt have been discussed in separate papers.[3–4] Lee and Rao[5] have given the basic steps for absorption of gas in the melt which have been mentioned in our recent publication.[6]

The rate of nitrogen absorption/desorption in liquid melt is governed by mass transfer and interfacial chemical kinetics depending on the level of surface active elements like sulphur or oxygen and have been explained by Battle and Pehlke,[7] Rao and Lee[8] and Ban-ya *et al.*[9] in their papers. The sulphur and oxygen content in the melt are well known for retarding the rate of nitrogen absorption.[10–12] In melts containing low surface active elements (SAE), the rate of nitrogen absorption is controlled by liquid phase mass transfer as demonstrated by Gallardo[13] during melting in resistance furnace (**Fig. 1**) and by Gupta and Beech[14] while melting in vacuum induction furnace (**Fig. 2**).

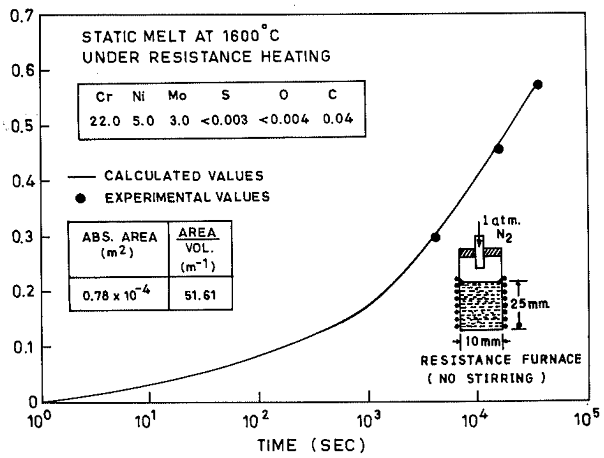

Fig. 1. Nitrogen absorption under static melt at 1600°C while melting in resistance heating furnace (Ref. 13).

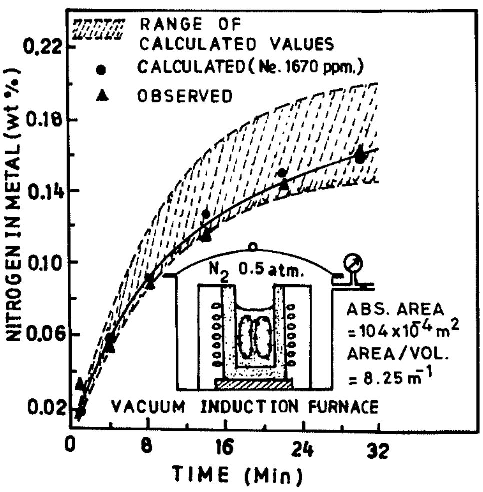

Fig. 2. Nitrogen absorption while melting in vacuum induction furnace (Ref. 14).

The good agreement between the theoretical and experimental values observed in Figs. 1 and 2 indicates that the principles of diffusion are obeyed and sulphur (0.003%) and oxygen (0.004%) in the melt at low levels did not affect the absorption rate at the gas/metal interface. The time taken to reach saturation limit (0.575 wt%) has been more (600 min) in resistance furnace due to absence of any other transport means in the melt except diffusion when compared with induction melting (30 min) where convective currents[14] helped nitrogen mass transport in the bulk.

In this study it was aimed to observe the rate of nitrogen absorption by the liquid melt when exposed to a plasma arc which is a relatively recent method[6] to rapidly nitrogenise the melt with low acoustic emission.[15] The rate of nitrogen absorption under a plasma arc has been compared with resistance[13] and induction[14] melting in order to highlight the effect of melting technique rendering rapid mass transfer attractive for industrial application. An effort has also been made to analyse the mechanism for faster rate of nitrogen mass transfer occurring in plasma arc melting.

2. Experimental

Low carbon steel scrap (0.062% C, 0.13% Si, 0.12% Mn, 0.104% O, 0.019% S and 0.009% N), commercial grade chromium (99.7% Cr), nickel (99.5% Ni), Manganese (99.7% Mn) and nitrogen gas (99.9%) were used as basic raw materials.

The plasma arc furnace fabricated[16] indigeneously having 0.08 m diameter and 0.10 m deep crucible of magnesite rammed mass for melting 3 kg steel was provided with single phase ac current (30 kVA). The nitrogen for generating the plasma was passed (8.33×10^{-6} m^3/s) through a drilled graphite electrode.

The melting and sampling procedure in plasma arc furnace described in our recent publication[6] was followed in this study.

3. Results

The nitrogen absorption behaviour of the three melts (Fe–C–Ni/Mn) with SAE ranging from 0.048 to 0.174 wt% is shown in **Fig. 3**. It can be noticed that melt

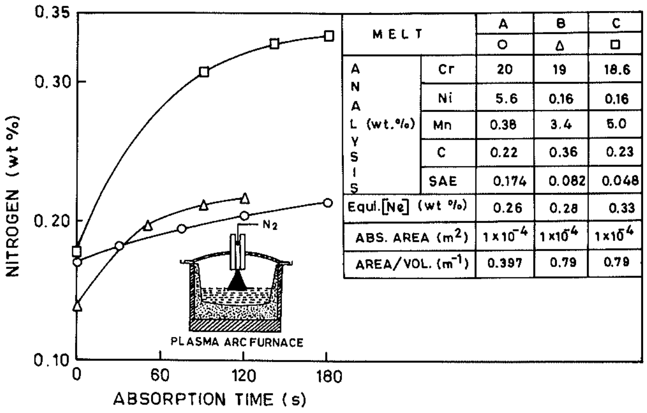

Fig. 3. Effect of melt SAE on nitrogen pick-up when exposed to plasma arc.

C (SAE 0.048%) reached equilibrium nitrogen content (0.33 wt%) in just 180 s. The other two melts (A and B) containing higher amounts of surface active element (0.082–0.174 wt%) could absorb less nitrogen compared to their respective equilibrium values (0.26 and 0.28 wt%).

4. Discussion

It is well known that the rate of mass transfer of nitrogen in liquid melt follows a first order rate law represented by Eq. (1);

$$-\frac{dN}{dt}=Ka\frac{A}{V}(N_e-N) \quad \text{.....................(1)}$$

where, Ka: Apparent rate constant for absorption (or adsorption) (m/s)

A: Absorption surface area (m^2)

V: Volume of the melt (m^3)

N_e: Equilibrium nitrogen concentration for the specified nitrogen pressure, (wt%).

Integrating Eq. (1), we get

$$-\ln\left[\frac{N_e-N_i}{N_e-N_f}\right]=Ka\frac{A}{V}t \quad \text{..................(2)}$$

where, N_i: Initial nitrogen concentration (wt%)

N_f: Final nitrogen concentrationa at time t sec (wt%).

It has been shown[6] that in the case of plasma arc nitrogenation, the experimental values followed Eq. (2) and the rate constant Ka was found to increase with higher metal temperature.

The rate constant Ka calculated for the present plasma arc melts as well as those reported by Gallardo[13] and Gupta and Beech[14] using Eq. (2), is shown in **Fig. 4**. In plasma arc melts, the nitrogen absorption rate constant (2.5×10^{-2} m s^{-1} Ka at 0.048 wt% SAE) decreases with increasing total SAE content (0.8×10^{-2} m s^{-1} Ka at 0.174 wt% SAE) in the melt (Fig. 4) since the SAE present, presumably, poison the active sites for absorption. It may be pointed here that the order of magnitude of absorption rate constant while melting under plasma arc with increasing SAE do not change (Fig. 4). While observing meltings in resistance and

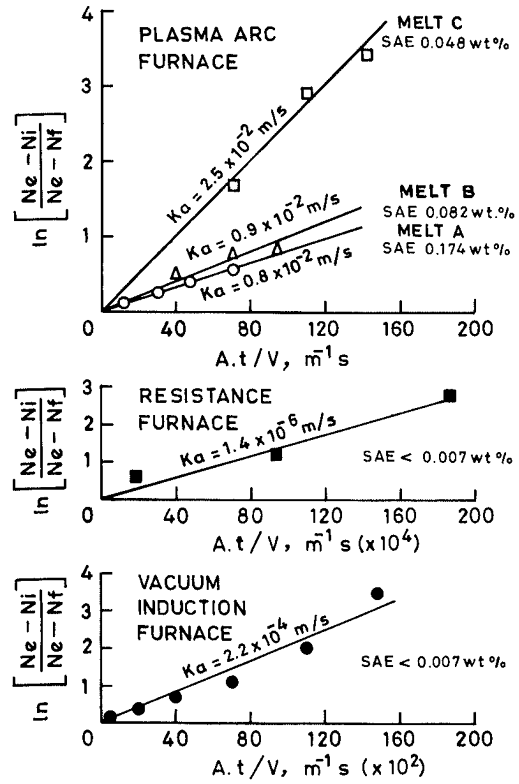

Fig. 4. Nitrogen pick-up by liquid melt under various melting conditions.

vacuum induction furnace having melts with low SAE (<0.07 wt%), the orders of magnitude were significantly different. The rate of nitrogen absorption in plasma arc melting (Ka 2.5 to 0.8×10^{-2} m s^{-1}) and induction melting (Ka 2.2×10^{-4} m s^{-1}) appear to be enhanced by four and two orders of magnitude respectively when compared with resistance melting (Ka 1.4×10^{-6} m s^{-1}). The increased absorption rate in the case of induction melting is most likely due to the effect of convective[17] currents. The cause for a higher absorption rate under plasma arc is, however, not understood clearly.

The rapid rate of nitrogen absorption by the melt under plasma arc could be attributed to the following reasons;

1) the high temperature prevailing below the arc zone, or
2) the high rate of diffusion of nitrogen ions under electric field (electrical absorption[6,18]), or
3) the high turbulence in the melt under the kinetic force of the gas stream or strong electric field, or
4) a combination of 1), 2) and 3) or all together.

The above possibilities are examined in the following lines to assign the reasons for rapid nitrogen absorption in such cases.

(1) The high temperature: If it is assumed that the high metal temperature due to plasma arc prevailing in a small plasma arc zone is rendering rapid nitrogen transportation from the bulk gas phase to the gas/liquid boundary layer leading to high nitrogen [N] concentration, it is unlikely that such a high concentration of nitrogen present in the boundary layer below the arc would be transported to the bulk melt in the absence of any other factors causing such rapid diffusion or mixing.

Thus, the higher rate of nitrogen transfer can not be attributed only to the high temperature prevailing near the arc zone or in the bulk melt.

(2) The high rate of diffusion of nitrogen ions: The linear velocity of nitrogen ions under the influence of an electric discharge is very high (200–400 m/s) as reported by Vardelle *et al.*[19] These nitrogen ions (N, N^+, N^{++}, N^{+++}) with high velocity associated with an electrical charge could get absorbed in the melt at the boundary layer resulting in a high nitrogen concentration at this position. However, in order to transport this high concentration of nitrogen atoms gathered at gas/metal boundary layer to the bulk phase, some atomic transport mechanism would be needed. In the absence of any convective current within the metal bath, it is difficult to believe that this large amount of nitrogen could be transported so quickly as recorded in the present investigation. In view of this, the high rate of diffusion of nitrogen ions in the plasma arc is unlikely to be responsible for the high rate of nitrogen absorption.

(3) The turbulence in the melt: In vacuum induction melting, the rate constant of nitrogen absorption is enhanced by about 150 times compared with resistance melting on account of the convective currents present in the melt under the influence of inductive stirring which caused the rapid transportation of nitrogen from the surface to the bulk of the liquid.

The case of a plasma melting, rendering a very rapid absorption of the nitrogen, suggests the presence of some kind of metal movement under the influence of the electric force. This could be a significant factor in enhancing the rate of nigrogen absorption. Katz and King[20] believe that the rapid absorption by the melt during the plasma arc melting could be due to the surface flow of the metal in the vicinity of jet impingement caused by "Marangoni Convection". However, no experimental evidence is possible at this stage.

The above discussion reveals that none of the above three fractors could be held responsible alone for rapid absorption of the nitrogen gas in the melt under the plasma melting and hence it is believed that all three factors combined together could be influencing absorption of nitrogen in the melt.

These observations could be of industrial significance in view of the high rate of mass transfer which could enable large scale nitrogenation of the melt in a short period. It is also important to note that the precess of nitrogenation using a plasma arc could be conducted under atmospheric conditions without the need for high pressure containers which pose problems while handling large melt tonnages. The nitrogen level in the melt could be controlled by regulating the exposure time and melt area.

5. Conclusions

(1) The rate of nitrogen absorption decreases with surface active element (SAE) in the melt exposed to plasma arc.

(2) The nitrogen absorption rate constant values are very high (0.8 to $2.5 \times 10^{-2}\,\mathrm{m\,s^{-1}}$) when melts are exposed to plasma arc.

(3) The nitrogen absorption rate constant values under plasma arc are nearly four orders of magnitude higher compared with unconvected gas/metal reaction in resistance melting.

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