

DECARBURIZATION OF MOLTEN IRON UNDER REDUCED PRESSURE

Anh-Hoa Bui , Thanh-Hai Le, and Bao-Trung Nguyen

School of Materials Science and Engineering, Hanoi University of Science and Technology, Hanoi, Vietnam,
Tel: 84-4-38680409, e-mail: hoaba-lkd@mail.hut.edu.vn

Received Date: October 8, 2012

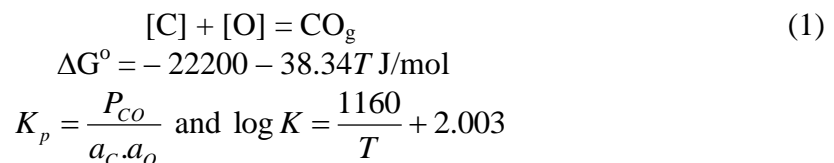
Abstract

One of the most important problems in steelmaking process is an increase of decarburization in molten iron, especially at ultra low level of carbon content. In order to achieve this, it is required a reduced pressure or vacuum atmosphere or a combination of both with a low oxygen source. From this point of view, the paper presents an experimental work of decarburization of molten iron with oxygen in air under reduced pressure. The investigation was performed in the range of 1623-1723K from 0-120 minutes. The results show a high decarburization of molten iron. The carbon content decreased to 0.016 weight percent (wt. %) after 120 min at 1723 K. In the present work, reaction constant for the decarburization at 1673 K and 1723 K were calculated as 0.0252 min^{-1} and 0.0470 min^{-1} , respectively. Optical microscopy observation of the sample containing 0.016 wt. % carbon showed a typical ferrite microstructure of ultra low carbon steels. It was concluded that decarburization of molten iron could be conducted in reduced atmosphere to lower the carbon content to an ultra low level.

Keywords: Decarburization, Molten iron, Reaction constant, Reduced pressure

Introduction

Exposing molten iron to an oxidizing environment (e.g. unkilld steel, slag or oxygen injection) will reduce carbon content of the iron. Reaction of oxygen provided from several sources, namely iron ore, rolling scale, blowing air/CO₂/H₂O/O₂ or mixture gases with carbon in molten iron plays an important role in steelmaking and refining technology. The interaction of carbon with oxygen in molten iron can be written as reaction (1) [1].



where K_p is equilibrium constant for reaction (1), P_{CO} is partial pressure of CO in equilibrium, a_{C} and a_{O} are activities of C and O respectively, T is absolute temperature.

Relationship of carbon content and oxygen at 1873 K was shown in Figure 1. The figure point out that carbon content is unable to be lowered down to 0.02 wt. % unless the atmospheric pressure is lower than 1 atmosphere (atm). Therefore, the carbon content is not easily decrease in the production of automobile body sheets where carbon content below than 0.01 wt. % are needed [2,3]. Vacuum processes are important in the production of high quality steels, particularly ultra low carbon steels with less than 20 ppm carbon. The RH degasser is a secondary refining process that uses vacuum treatment of liquid steel and provides a high productivity [3,4]. Before the existence of vacuum treatment in the production of steels with ultra low carbon content, producers coped with considerable increase in the iron melting loss [2]. In order to achieve carbon content with a value of

about 0.002 wt. %, it requires a supersaturation of oxygen in liquid steel [4]. This resulted in steel with high oxygen content after high decarburization. This is undesirable because of a high consumption of deoxidizers and metal contamination with oxide inclusions. Therefore, the development of an effective method to remove carbon from the molten iron is desired. An important feature of the novel technology is the possibility of the simultaneous achievement of very low concentration of carbon and oxygen in steels.

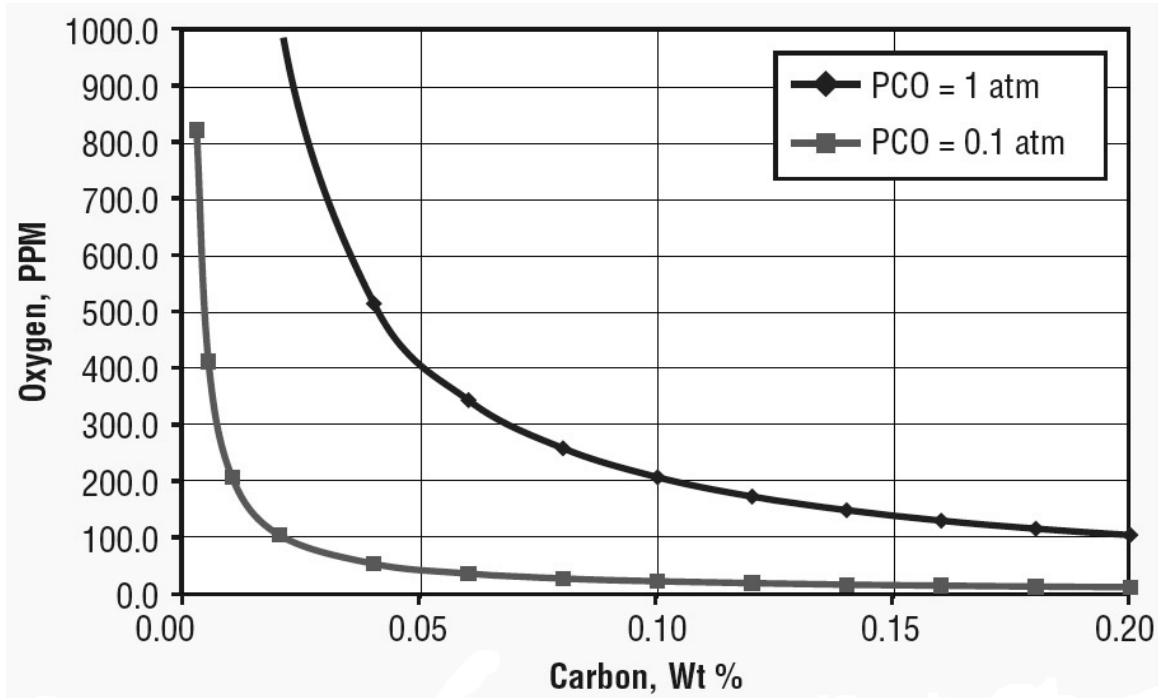


Figure 1. Relationship of carbon and oxygen at 1873 K [4]

It has been reported, several researchers on decarburization of molten iron used injection of iron oxide, oxidizing gases (CO_2 , H_2O) and vacuum chamber [2-9]. Even, Ji-Ook Park *et al* has performed decarburization of Fe-C alloy in solid state with the purpose of decreasing energy, cost, CO_2 emission and time for production of steel sheets [10]. The use of either oxidizing gases or reduced pressure/vacuum atmosphere is effective in increasing the decarburization rate. However, study on the decarburization process in air under reduced pressure has been limited. In the present work, the decarburization of molten iron in reduced atmosphere is investigated.

Experimental

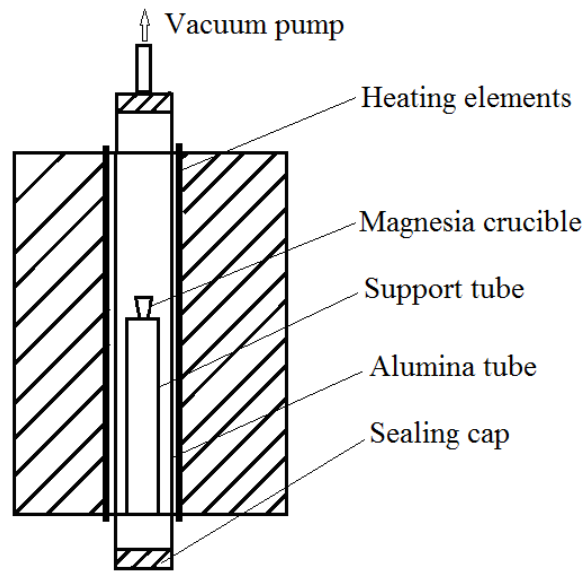


Figure 2. Experimental setup

Experimental setup is illustrated in Figure 2, in which a magnesia crucible (38 mm in I.D.) containing 50 g of iron with 3.959 wt. % carbon was put in a resistant furnace (Brother XD-1600VTF). After the alumina tube was sealed, air was evacuated using a vacuum pump until the inside pressure was stable at 0.79 atm. The iron sample was then heated to the temperature of the experimental condition with the rate of $10 \text{ K}\cdot\text{min}^{-1}$, maintained for a given time and quickly cooled down to room temperature. Since the melting temperature of the iron was measured as 1431 K using Fluke 744 temperature calibrator, the investigation temperature was carried out in the range of 1623-1723 K. Three trials were done for each experimental condition of the same heated temperature and maintained time. After the experiments, carbon contents were analyzed and microstructure was examined using optical microscope (Axiovert 25). In the present study, carbon contents were determined by employing a carbon – sulfur analyzer (Leco - CS230).

Results and Discussion

Analyzed carbon contents are listed in Table 1 and Figure 3, which indicates that the initial carbon content (3.959 wt. %) decreased drastically to 3.290 wt. % and 2.615 wt. % when the temperature reached to 1673 K and 1723 K, respectively. This means that decarburization reaction has occurred as soon as the iron started melting at 1431 K. For both temperatures, decarburization occurred quickly at the beginning stages and slowly as the time increased. After 120 min at 1723 K, the carbon content decreased to a very low value as 0.016 wt. %. It is measured that at higher temperature, the lower carbon content was obtained. It was attributed to a better fluidity of the molten iron and higher activation energy for the decarburization reaction [11]. This data is also consistent with the fundamentals of molten iron which states that liquid iron becomes more viscous at lower carbon content [12]. Figure 4 shows carbon contents at the various temperature when the maintained time fixed at 60 minutes. Thus, it can be concluded that the decarburization rate in the experiments are strongly dependent on the temperature, time and carbon content of the molten iron.

Table 1. Analyzed Results of the Carbon Content

Temperature (K)	1623			1673			1723		
Time (min)	60	0	30	60	120	0	30	60	120
C Content (%)	0.881	3.290	0.658	0.422	0.261	2.615	0.592	0.058	0.016

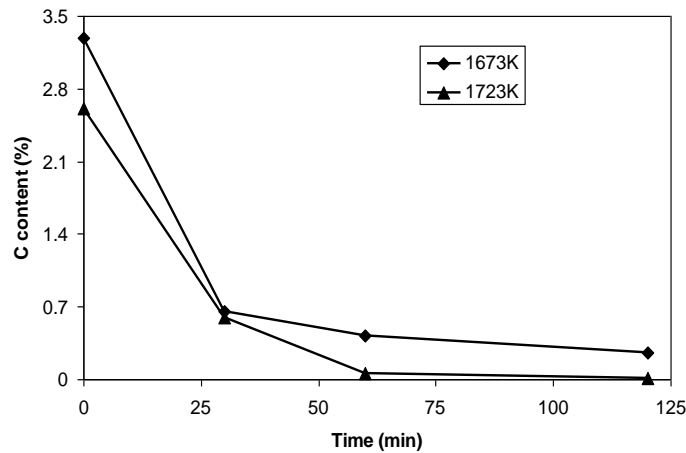


Figure 3. The carbon contents at various time and temperature

Decarburization is known as a complicated heterogeneous process consisting of several stages of reactions. Each of which can theoretically control the overall reaction rate. No common opinions has been formed to date concerning both the limiting stage and mechanism of this reaction [5]. The hypothesis of a diffusion character of decarburization explains the existence of the main stages of the reaction. This is true during the decarburization of Fe–C melts with oxygen-containing gases [8]. According to the Fe-C diagram, the used iron stays in liquid at beginning and becomes viscous the solid at some time later during these experiments. The decarburization rates vary for each stage. The rate is speculated to be much higher in liquid, lower in viscous and very low in solid. Therefore, temperature or time must be increased in order to raise the decarburization rate.

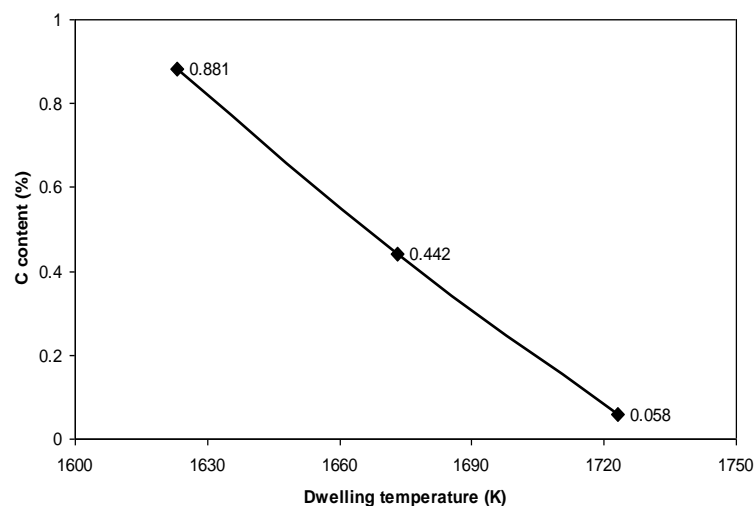


Figure 4. The carbon contents at different temperature for 60 minutes

According to the thermodynamics of decarburization reaction [2,11], there is a correlation between final and initial carbon content. The carbon content (C_t) at any given

time of the reaction in relation to initial carbon content (C_0) of the molten iron can be written as equation (2).

$$C_t = C_o \cdot \exp(-kt) \quad (2)$$

(k is reaction constant, min^{-1}).

From equation (2), a correlation can be written as equation (2).

$$\ln\left(\frac{C_t}{C_o}\right) = -kt \quad (3)$$

Figure 5 shows the reaction constant (k) was calculated as 0.047 min^{-1} at 1723 K. The same calculation was done at 1673 K and the value of 0.0252 min^{-1} was obtained. Variation in the reaction constants indicated that temperature is an important factor for the decarburization. Other factors affecting the reaction may include surface area of the molten iron exposed to the reduced atmosphere, vacuum level, amount of the molten iron and treatment time [3, 5, 8].

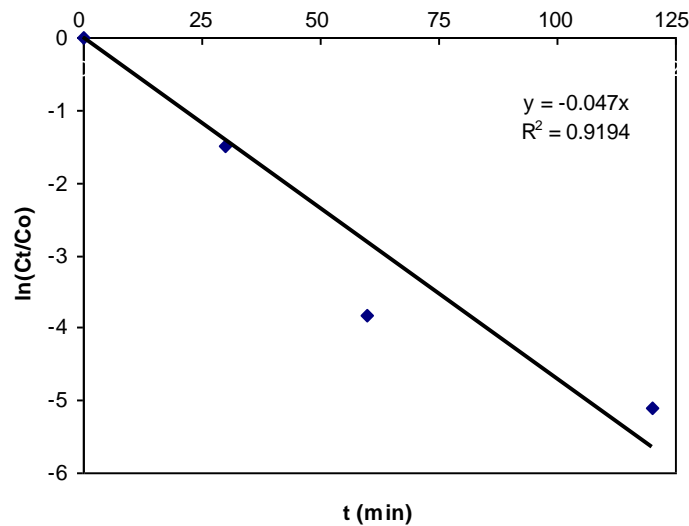


Figure 5. Relationship between $\ln (C_t/C_0)$ and time

Figure 6 shows the microstructure of the decarburized sample with 0.016 wt. % C. It was found that the 0.016 wt. % C sample had a microstructure of as-casted ferrite grain of ultra low carbon steel [13-15]. As seen in Figure 6b, the grain size is smaller and more homogenous owing to rolling and annealing processes. There were some voids (in black color) which may be caused by release of carburizing gases in the present study. These kinds of defects would have a negative effect on the steel quality. M. A. Makarov *et al* remarked that it was difficult to solve the existence of pores without the treatment in high vacuum [2]. At a carbon content of 0.01 wt. %, activity of carbon becomes so low that a further decrease in the activity is possible only at a high oxygen activity. A high vacuum was required to decarburize the steel even further.

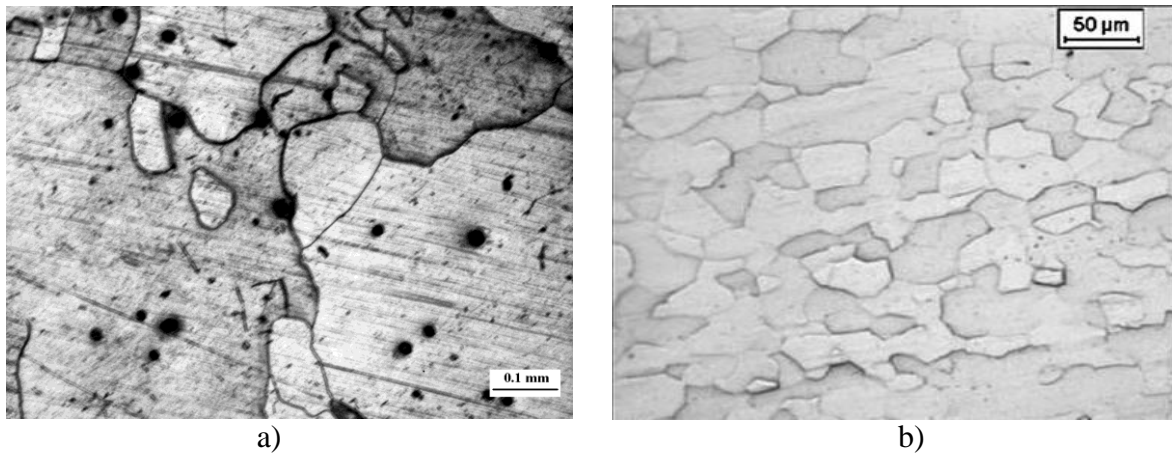


Figure 6. Microstructure of (a) the decarburized sample containing 0.016 wt. % C, and (b) the rolled and annealed ultra low carbon steel with 0.004 wt. % C [15]

It is noted that a decrease in the gas pressure above the molten iron was shown to increase the deoxidizing capacity of carbon to a certain extent [3, 4]. The decarburization proceeds by the reaction between carbon and oxygen gas in the reduced atmosphere. The CO gas formed by the reaction (1) was easily to be removed out of the molten iron, and hence the decarburization degree was greatly increased. Since the amount of evolution of CO from the iron melt was negligible, the oxygen concentration at the interface should be approximately equal to the initial value. In the steelmaking industry, the vacuum suction degassing method is also possible method to decrease the carbon content. This is due to the creation of additional reaction surfaces in the volume of the melt under vacuum conditions. The effect of exposing molten iron to a low-pressure atmosphere (i.e. vacuum) has other benefits to the steelmaker such as the reduction of dissolved gases.

Conclusions

The decarburization of molten iron in reduced atmosphere has been investigated in the range of 1623-1723 K. The results are summarized as follows.

1. Carbon content of the molten iron could be decreased easily in a reduced atmosphere without injection of any oxygen source. A high decarburization rate caused the carbon to decrease to a low content of 0.016 wt. % when it was heated to 1723 K for 120 minutes.
2. The reaction constants at 1673 K and 1723 K were calculated as 0.0252 min^{-1} and 0.0470 min^{-1} respectively. This indicated that the temperatures was an important factor for the decarburization. Further research on others factors on this decarburization must be performed.
3. The decarburized metal contained 0.016 wt. % carbon. It had a typical microstructure of ferrite grain which was associated with ultra low carbon steels. The existence of voids caused by evolved gases or solid oxide inclusions in the 0.016 wt. % C could be prevented in a high vacuum. The problem of making steels with ultra low (0.002-0.01 wt. %) carbon content could be solved through the reaction of carbon with oxygen in air under reduced pressure.

Acknowledgement

The authors would like to thank POSCO (Rep. of Korea) for financial support of this research.

References

- [1] The Japan Society for the Promotion of Science and the 19th Committee on Steelmaking, *Steelmaking Data Sourcebook*, Gordon and Breach Science Publishers, New York, USA, 1988.
- [2] M.A. Makarov, A.A. Aleksandrov, and V.Y. Dashevskii, "Deep decarburization of iron-based melts," *Russian Metallurgy*, Vol. 2007, No. 2, pp. 91-97, 2007.
- [3] L. Neves, H.P.O. de Oliveira, and R.P. Tavares, "Evaluation of the effects of gas injection in the vacuum chamber of a RH degasser on melt circulation and decarburization rates," *ISIJ International*, Vol. 49, No. 8, pp. 1141-1149, 2009.
- [4] K. Shoop, "Vacuum degassing for the steel industry," *The International Journal of Thermal Technology*, pp. 861-867, 2006.
- [5] K. Taguchi, H. Ono-Nakazato, T. Usui, and K. Marukawa, "Desiliconization and decarburization behavior of molten Fe-C-Si(-S) alloy with CO₂ and O₂," *Metallurgical and Materials Transactions B*, Vol. 34B, No.6, pp. 861-867, 2003.
- [6] D. Wildlund, D.S. Sama, and P.G. Jonsson, "Studies on decarburisation and desiliconisation of levitated Fe-C-Si alloy droplets," *ISIJ International*, Vol. 46, No. 8, pp. 1149-1157, 2006.
- [7] N. Dogan, G.A. Brooks, and M.A. Rhamahami, "Comprehensive model of oxygen steelmaking, Part 1: Model development and validation," *ISIJ International*, Vol. 51, No. 7, pp. 1086-1092, 2011.
- [8] H.-S. Kim, J.-G. Kim, and Y. Sasaki, "Forward and backward reaction rate constant of the reaction of $\underline{C} + \underline{O} = \text{CO (g)}$ on Fe-C melts," *ISIJ International*, Vol. 50, No. 5, pp. 678-685, 2010.
- [9] Y. Sasaki, and K. Ishii, "The decarburization of liquid iron in low carbon content by CO₂-CO gas mixture," *ISIJ International*, Vol. 37, No. 10, pp. 1037-1039, 1997.
- [10] J.-O. Park, T.V. Long, and Y. Sasaki, "Feasibility of solid-state steelmaking from cast iron - decarburization of rapidly solidified cast iron," *ISIJ International*, Vol. 52, No. 1, pp. 26-34, 2012.
- [11] M.A. Najafabadi, M. Hirasawa, and M. Sano, "Decarburization of iron melt by an immersed Al₂O₃-Fe₂O₃ porous tube," *ISIJ International*, Vol. 37, No. 1, pp. 31-37, 1997.
- [12] E.T. Turkdogan, *Fundamentals of Steelmaking*, The University Press, Cambridge, UK, 1996.
- [13] Y.-K. Lee, and O. Kwon, "Effect of strain rate of hot deformation on ferrite grain size in an ultra-low carbon steel," *Journal of Materials Science Letters*, Vol. 20, No.14, pp. 1319-1321, 2001.
- [14] A. Haldar, S. Suwas, and D. Bhattacharjee, eds., *Microstructure and Texture in Steels: And Other Materials*, Springer, Jamshedpur, India, 2008.
- [15] Y. Guo, Z. Wang, J. Xu, G. Wang, and X. Liu, "Texture evolution in a warm-rolled Ti-IF steel during cold rolling and annealing," *Journal of Materials Engineering and Performance*, Vol. 18, No. 4, pp. 378-384, 2009.