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## Investigation of reduction of magnetite based carbon composite pellets under semi-fusion conditions

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**Abstract:** In this study, carbon composite pellets were exposed to a reduction test under low temperature and semi-fusion conditions in which iron was melted without a solid form of slag deteriorated. The purpose of the reduction experiments under the semi-fusion condition was to produce an iron nugget which had physical and chemical properties similar to blast furnace pig iron at lower temperatures. These nuggets were produced from pellets that were made from a mixture of iron oxide, coke, flux, and a binder. These nuggets heated in a furnace with a chamber temperature of 1330 °C. The produced dried carbon composite pellets were melted and carburated in a single-stage process. In this study, three distinct products were produced as a function of furnace residence time at fixed furnace temperature (1330 °C). These products were direct reduced iron (DRI), transition direct reduced iron (TDRI), and iron nuggets produced at residence times 8-24, 32-40 min, and 48 min, respectively. The iron nugget produced had a high apparent density (6.903 g/cm<sup>3</sup>), high micro hardness values (328 HV), high iron content (92.7% Fe), and was similar to blast furnace pig iron.

**Keywords:** iron ore, pelletizing, cold bonded composite pellet, iron nugget

### 1. Introduction

Iron-steel products are widely used as metal alloys because of their advantages such as high mechanical properties, accessibility and relevant cost. Iron-steel production has been carried out in blast furnaces at integrated iron and steel plant for centuries, and now it is one of the most used production method in the world. The purpose of a blast furnace is to chemically reduce and physically convert iron oxides into liquid iron called "hot metal". The blast furnace is a huge and steel stack lined with refractory brick, where iron ore, coke and limestone are dumped into the top, and preheated air is blown into the bottom.

The raw materials require 6 to 8 h to descend to the bottom of the furnace where they become the final product of liquid slag and liquid iron. These liquid products are drained from the furnace at regular intervals. Tapping temperatures are in the range from 1500 to 1600 °C. Due to this procedure iron steel production in the blast furnace is carried out at high temperatures, long periods of time and profit reduce. Therefore, the industry has focused on new processes to increase profit by decreasing the temperature degree.

Kobe Steel and Midrex began to study a new ironmaking process, and developed a new technology in which iron pellets of blast furnace pig iron quality are obtained by reducing carbon composite pellets formed by fine coal dusts in a rotary kiln. The process is aimed to produce highly metallized, slag free pig iron nuggets throughout a single stage heat treatment, utilizing coal as a reducing-carburizing agent. The objective of this work was to determine whether the pig iron nuggets

produced under the laboratory conditions had comparable physical and chemical properties with the blast furnace pig iron. This new ironmaking process is called as ITmk3 (Kobe Steel, 2007; Seki and Tanaka, 2008; Tanaka et al., 2008).

The main purpose of ITmk3 process is to reduce the iron oxides in the structure to the iron phase and to melt them afterwards without disturbing the rounded structure of the carbon composite pellets. The slag phase, which is composed of silicate and calcium oxides with a high melting temperature, keeps the form in the solid state sintered as it does not reach high temperature during the process. Since the melting of the slag phase is not needed, the iron nugget is formed at relatively lower temperature than the blast furnace conditions without the need to reach high temperature.

The process of obtaining the slag phase in a solid state and the iron phase in a molten state as a whole can only be achieved by the production of carbon composite pellets. Unlike conventional pellets, composite pellets are produced by the addition of coke as a reducing agent, coal and calcium oxide to provide slag formation in the composite pellet blend. Thus, during the process without a major change in the pellet form, both the iron oxides are reduced under the semi-melting conditions, and the iron nuggets formation occurs in the form of solid slag and liquid form as a result of solid-liquid phase reactions.

During the process, carbon composite pellets are reduced and melted at a relatively low temperature between 1350 and 1400 °C, and the hot metal is easily separated from the slag. This method is found in the solid-liquid co-existence phase which is different from traditional iron making processes. Since melting occurs after the reduction, FeO damage does not expose in refractory (Negami, 2001). In these processes, iron oxide and reducing agents are pelletized together, and the resulting structure is called iron oxide-carbon composite pellet (Halder and Fruehan, 2008).

The ITmk3 process has some advantages such as being a simple process, selecting various iron ore and reducing agents. Moreover, the process flow and equipment used in this method are very similar to the FASTMET process (Tsuge et al., 2002). This process can be preferred over conventional iron production technologies for some reason such as reduction of energy loss during iron oxide reduction to a minimum level, co-occurrence of reduction and slag separation, very high temperatures are not needed, requires low investment and low production costs. It is also more environmental friendly with higher energy efficient (Mazurak, 2003; Steffen and Lungen, 2004; Anameric and Kawatra, 2004; Anameric et al., 2005).

Metallic iron is formed after the reduction of iron oxides when carbon composite pellets are heated to the high temperatures, and it can be either partially or completely melted depending on the degree of temperature and carburization of the product. The success of the process depends on the change of pellet structure, furnace temperature, type and amount of the reducing agent, pellet size, residence time in the furnace as well as the gangue, ash and binder content in the mixture.

According to Han et al. (2015), the reduction of iron ore, carburization of reduced iron and the composition and quantity of slag are very important for producing iron nuggets at lower temperature. In recent past, it is discovered that small amount of nut coke addition in mixture with ferrous burden contributes to better gas permeability, enhanced reduction kinetics, lower thermal Reserve Zone temperature and good softening melting properties of the ferrous burden (Loginov et al., 1977; Yang and Yang, 1995; Mousa et al., 2010; Pishnograev et al., 2009).

In this study, unlike the ITmk3 process, coke was used instead of coal. Experimental studies were also carried out in a laboratory-type high temperature furnace (1600°C) instead of a rotary kiln. Carbon composite pellets with 1.1 basicity ratio were used, and it was aimed to obtain iron nugget from these pellets at minimum temperature by semi-melting in a laboratory-scale high temperature chamber furnace. For this purpose, the composite pellets were subjected to semi-melting conditions at 1330°C, and the iron nugget was obtained at most suitable furnace residence time.

## 2. Materials and methods

### 2.1 Materials

The iron ore used for production of pellets was a magnetite concentrate obtained from Divriği concentration plant, Turkey, with a particle size of 80% passing 45 µm. The coke was used as a reducing agent containing 88.17% free carbon, and the sodium carboxymethyl cellulose (CMC, 2%)

was used as a binder for production of composite pellets. Chemical compositions of the magnetite concentrate and coke is presented in Table 1.

Also, to produce slag formation in a composition similar with blast furnace slag composition, the CaO-SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> triple phase diagram was used, and CaO was added to the system to provide 1.1 basicity as a result of calculations.

Table 1. Chemical composition of iron ore and coke

Magnetite concentrate		Coke		
Compound	(%)	Compound	(%)	
Fe <sub>3</sub> O <sub>4</sub>	95	C	88.17	
SiO <sub>2</sub>	2.2	Ash Content	SiO <sub>2</sub>	5.35
Al <sub>2</sub> O <sub>3</sub>	0.75		Al <sub>2</sub> O <sub>3</sub>	3.59
CaO	0.6		CaO	0.46
MgO	0.58		MgO	0.17
Na <sub>2</sub> O + K <sub>2</sub> O	0.15		Others	2.26

## 2.2 Methods

The purpose of this study was to determine the residence time of nugget. The experiments were carried out with formation of carbon composite pellets produced by adding 30% coke and 2% CMC with 1.1 basicity ratio to magnetite concentrate. The prepared pellets were fired in a laboratory-scale high temperature chamber furnace at a furnace temperature of 1330 °C at the residence times of 8, 16, 24, 32, 40, 48 and 56 min. Schematic drawing of the experimental setup is shown in Fig. 1.

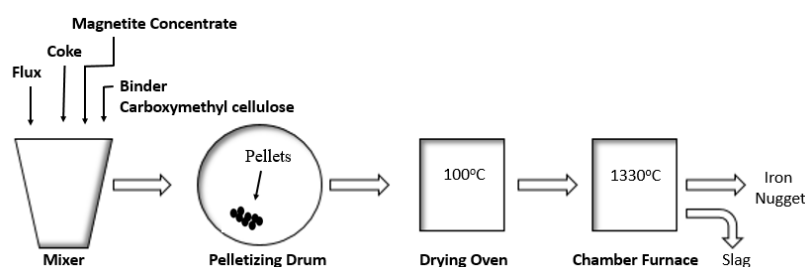


Fig. 1. Carbon Composite pellet production and reduction

During the experiments, the temperature inside of the furnace was controlled by keeping the thermocouple 5 cm above the sample. The produced iron nuggets were taken out from the furnace and cooled at room temperature.

## 2.3 Characterization

In order to standardize a surface preparation procedure for all the experiments, an ASTM standard was chosen. The macro images of the obtained iron nuggets were taken, and their apparent densities were measured based on the volume of displaced distilled water method (ASTM B 311-93, 2002). Abrasion, polishing (ASTM E3, 2001) and initial etching (ASTM E407, 1999) were applied to the cold molded iron nuggets with epoxy resin (ASTM E3, 2001), and then the microstructure examination of the samples was performed using a scanning electron microscope (SEM). In the following stage, Vickers hardness measurements (1 kg load), apparent density and chemical analysis of iron nuggets were done (ASTM B 311-93, 2002; ASTM E92-82, 1997; ASTM E384, 1999).

## 3. Results and discussion

### 3.1 Products after reduction

Three different products were obtained (Direct Reduced Iron-DRI, Transition Direct Reduced Iron-TDRI and iron nugget) depending on their residence time in the furnace and carbon content of the

system. The pictures of DRI, TDRI, and iron nugget formed as a function of the residence time at 1330°C furnace temperature are shown in Fig. 2.

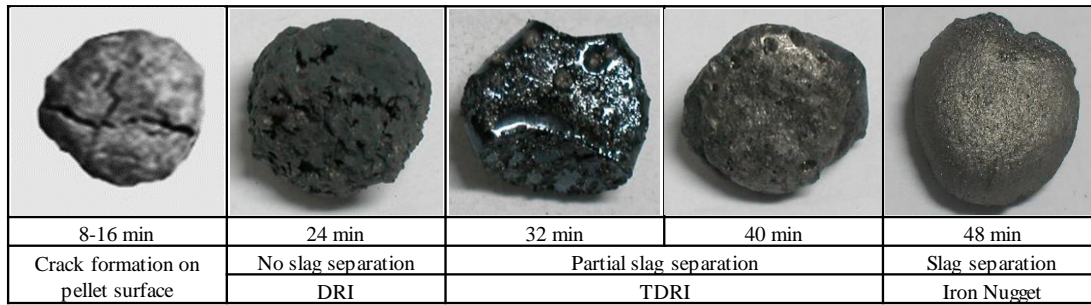


Fig. 2. Pictures of DRI, TDRI and iron nugget formed as a function of the residence time at 1330 °C furnace temperature

As seen from Fig. 2, no metal formation took place at 1330 °C temperature with 8, 16 and 24 min residence times. It was observed from the experiments that formations of DRI, TDRI and iron nugget depended on the carbon content of metallic iron. Metal formation and separation of slag occurred at 1330°C only after 32 min furnace residence time. However, the obtained metal particles could only be collected in the form of regional clusters within the structure due to the inadequate time.

The fluidity of the liquid metal increased with the increase furnace residence time. It was observed that the regional clusters were gathered together as a whole by filtering through the slag after 40 min furnace residence time. However, this furnace residence time was not enough for separation of slag and metal, and hence metal clusters in the slag were observed.

The results obtained from these experiments showed that as the furnace residence time increased, the amount of carbon diffused in the metal increased until the eutectic point containing 4.3% carbon was reached, the melting point of metallized portion decreased, and as a result formation of iron nuggets occurred (Kawatra et al., 2005). It was clearly observed that formation of iron nuggets occurred as the carbon solubility in the structure increased at 48 min furnace residence time.

### 3.2 Phase and micro-structures

Scanning electron microscopy (SEM) was used to obtain microstructure image of iron nuggets at 1330 °C for 48 min (Fig. 3). It can be seen from Fig. 3 that the structure of transformed ledeburite was formed by the mixture of ferrite and pearlite. The pearlite formed as a result of the ledeburite transformation is in small clumps in the matrix. The black small dots in the matrix are the spaces between the dendrites. Coke graphitized as plate-shape graphite. To get a general idea about the formation of cementite ( $\text{Fe}_3\text{C}$ ), graphite and pearlite, the chemical analysis was done by using energy dispersive X-ray spectroscopy (EDS). The results obtained from EDS are presented in Table 2. The XRD results showing the components in the microstructure are shown in Fig. 4.

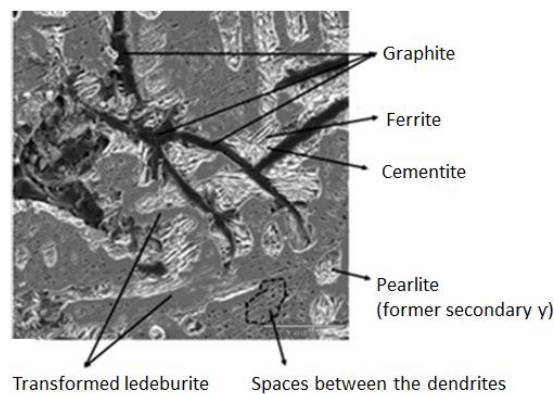


Fig. 3. SEM micro images of iron nuggets at fixed furnace temperature (1330 °C) for 48 min (micro images were taken at  $\times 500$  magnification level and nital etching)

Table 2. Energy Dispersive X-Ray Spectroscopy (EDS) analysis results of iron nuggets obtained by fired at fixed furnace temperature (1330 °C) for 48 min

Components	Fe (%)	C (%)
Matrix	98.175	0.294
Graphite	9.736	89.853
Pearlite	87.551	10.892
Cementite	75.348	23.615

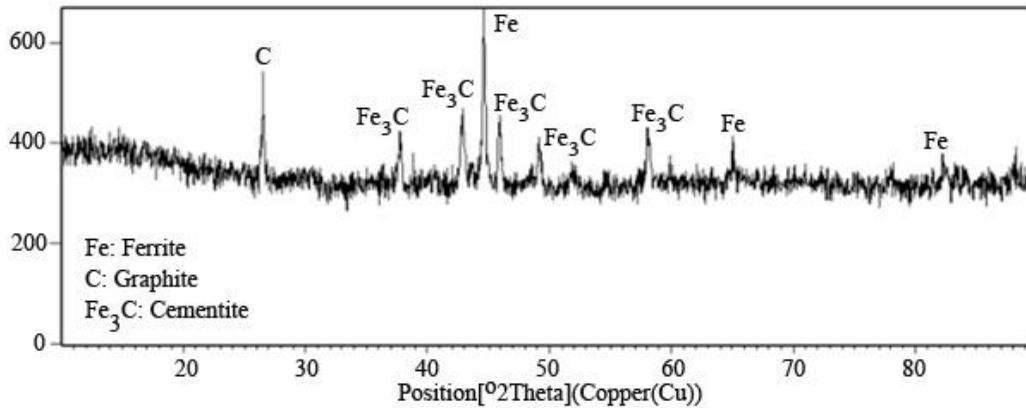


Fig. 4. XRD results showing components in microstructure of iron nuggets obtained by fired at fixed furnace temperature (1330 °C) for 48 min

### 3.3 Chemical analysis results

The chemical analysis of the iron nuggets was carried out to describe and compare the samples with the blast furnace peak iron and white cast iron. Comparison of chemical analyses of iron nugget (produced by keeping in furnace for 48 min at 1330 °C with a slag basicity ratio of 1.1), pig iron and white cast iron is given in Table 3. As shown in Table 3, the iron nuggets contained iron in either equal or greater percentages than the blast furnace pig iron. Compared to white cast iron, they contain approximately equal amounts of carbon.

Table 3. Comparison of chemical analyses of iron nugget (produced by keeping in furnace for 48 min at 1330°C with a slag basicity ratio of 1.1), pig iron and white cast iron

Element	(Peacey and Davenport, 1979)	(Smith, 1993)	(Kawatra et al., 2005)	(In this study)
	Pig Iron (%)	White Cast Iron (%)	Iron Nugget (%)	Iron Nugget (%)
Fe	90-95.5	93.3-97.3	95-97	94.9-95.4
C	4-5	1.8-3.6	1.7-3.5	3.6-3.8
S	0.03	0.06-0.2	0.2-0.8	0.6-0.5
P	<1	0.06-0.18	0.12	0.05

### 3.4 Micro-hardness measurements

The Vickers hardness measurements (1 kg load) (ASTM E 92-82, 1997; ASTM E 384, 1999) on the metallized portion were taken to detect the increase in the cementite (iron carbide) amount in the products obtained at different furnace residence times at fixed furnace temperature (1330 °C). According to Krauss (1990), the Vickers hardness increases with the increasing amounts of dissolving carbon in the metallized portion (amount of carbides). The average Vickers hardness values of the DRI, TDRI and iron nugget are summarized in Fig. 5. As seen from Fig. 5, the micro-hardness of the DRI produced varied from 70 to 80 HV, TDRI produced varied from 180 to 230 HV, and iron nugget produced varied from 328 to 338 HV. At the furnace temperature of 1330 °C, DRI, TDRI and iron nugget were obtained for varied furnace residence times: 24, 32, and 48 min, respectively.

### 3.5 Apparent density measurements

The apparent density measurements of the obtained products were made to determine the increase in the metallization and slag separation degree of the products and the decrease in porosity. The average apparent density values for DRI, TDRI and iron nugget are shown in Fig. 6.

According to Lankford et al. (1985), as the residence time in furnace increased, metallization grade and slag separation increased, while the porosity level decreased. The results obtained from the experiments showed that the similar values were found when it was compared with those obtained by Lankford et al. (1985).

If the product composed in the TDRI form within a certain period of time in the furnace was kept in the furnace for a certain time, metallization grade and slag separation increased as the residence time in the furnace increased, and as a result, the high apparent density iron nugget was obtained.

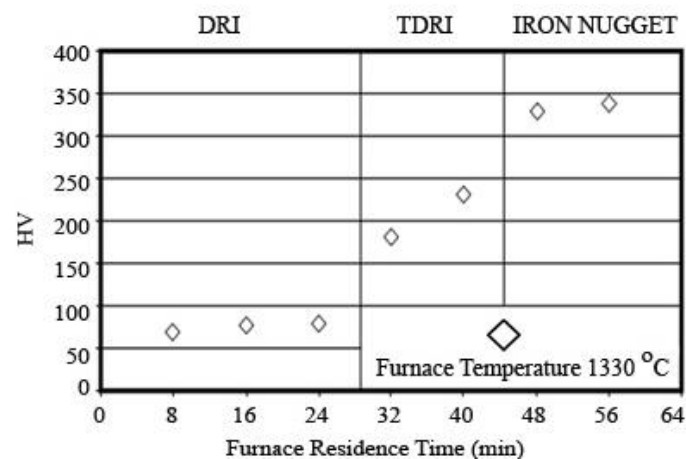


Fig. 5. Average Vickers hardness values of DRI, TDRI and iron nugget

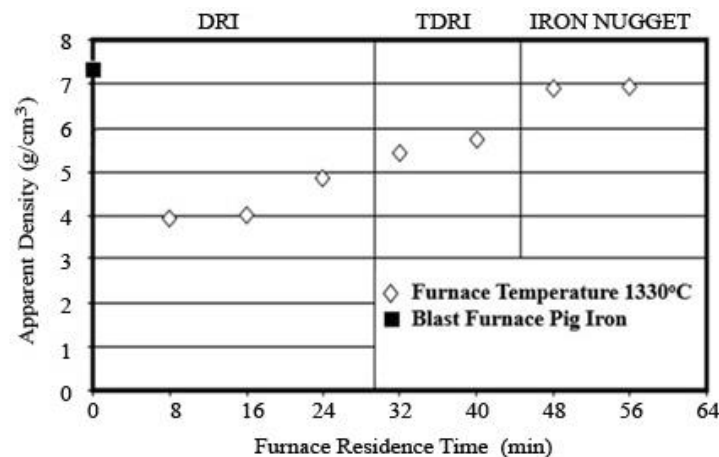


Fig. 6. Average apparent density values expressing the relation between metallization grade and porosity for DRI, TDRI and iron nugget

### 4. Conclusions

In this study, three different type products (DRI, TDRI and iron nugget) were produced as a function of furnace residence time after reduction of magnetite to iron. Direct reduced iron (DRI) products were a complete solid state product with a sponge-like structure and low apparent density. Since melting did not occur, slag couldn't be separated from metallized part in the DRI products. Transition direct reduced iron (TDRI) products had higher apparent density value than DRIs' due to the partial slag separation, lower porosity and higher degree of metallization. Resulting from partial melting, the TDRI products had better degree of metallization and more carbon solubility than the DRI products. Partial slag separation occurred due to partial melting.

It was observed that the impurities completely separated from the metal in the form of slag at a constant furnace temperature (1330 °C) for 48 min residence time. Transformation of DRI into TDRI and finally iron nugget was achieved with the increase in the furnace residence time. The results obtained from the experiments showed that as the furnace residence time increased, the amount of carbon diffused in the metal increased until the eutectic point containing 4.3% carbon was reached, the melting point of metallized portion decreased and as a result formation of iron nuggets occurred.

The Vickers hardness increased with the increasing amounts of dissolving carbon in the metallized portion. By increasing the Vickers hardness, the products metallization and the slag separation degree increased and the porosity decreased. This result was consistent with the literature.

The apparent density measurements were made to analyze the increase in the products' metallization and slag separation degree and the decrease in porosity. The results showed that the apparent density values of DRI are lower than those of TDRI and iron. As the residence time in the furnace increased, the metallization grade and slag separation increased, while the porosity level decreased.

As a conclusion 30% coke and 2% sodium carboxyl methyl cellulose adhered basic composite pellets with a basicity ratio of 1.1 were subjected to reduction treatment at 1330 °C for 48 min in the furnace at semi-fusion conditions and the slag and metal separation were visibly observed. The iron nuggets produced under this condition had the composition and properties similar to those obtained in the blast furnace.

The results offer very advantageous working conditions according to those of conventional iron nugget production (1550 °C and 8 h). It seems to be possible to obtain more economically, than the pig iron, due to the low temperature and the short residence time in the production conditions.

## References

- ANAMERIC B., KAWATRA S.K., 2004. *A laboratory study relating to the production and properties of pig iron nuggets*, SME Annual Meeting. Preprints, 645-648.
- ANAMERIC B., KAWATRA S.K., RUNDMAN K.B., 2005. *Carburization effects on the pig iron nugget production*. Annual SME Meeting, Metallurgical Process Fundamentals: Pyrometallurgical Processing Session.
- ASTM B 311-93, 2002. *Density determination for power metallurgy (P/M) materials containing less than two percent porosity*. Annual Book of ASTM Standards, Volume 02.05 (Nonferrous Metal Products, Metallic and Inorganic Coatings, Metal Powders, Sintered P/M Structural Parts), 86-89.
- ASTM E 3, 2001. *Standard guide for preparation of metallographic specimens*. Annual Book of ASTM Standards, Volume 03.01 (Metals Test Methods and Analytical Procedures, Metals, Mechanical testing, elevated and Low-temperature Tests, Metallography), 1-11.
- ASTM E 92-82, 1997. *Standard test method for Vickers Hardness of metallic materials*. Annual Book of ASTM Standards, Volume 03.01 (Metals Test Methods and Analytical Procedures, Metals, Mechanical Testing, Elevated and Low-temperature Tests, Metallography), 229-237.
- ASTM E 384, 1999. *Standard test method for microindentation hardness of materials*. Annual Book of ASTM Standards, Volume 03.01 (Metals Test Methods and Analytical Procedures, Metals, Mechanical Testing, Elevated and Low-temperature Tests, Metallography), 418-427.
- ASTM E 407, 1999. *Standard practice for microetching metals and alloys*. Annual Book of ASTM Standards, Volume 03.01 (Metals Test Methods and Analytical Procedures, Metals, Mechanical Testing, Elevated and Low-temperature Tests, Metallography), 474-49.
- HALDER S., FRUEHAN R.J., 2008. *Reduction of iron-oxide-carbon composites: part I. Estimation of the rate constants*. Metall. Mater., 39 (B), 784-795.
- HAN H., DUAN D., CHEN S., YUAN P., 2015. *Mechanism and influencing factors of iron nuggets forming in rotary hearth furnace process at lower temperature*. Metall. Mater., 46 (5), 2208-2217.
- KAWATRA S.K., ANAMERIC B., EISELE T.C., 2005. *Single-step ironmaking from ore to improve energy efficiency*. Final Technical Report

- KOBE STEEL, 2007. *Kobe steel, Steel dynamics launch first ITmk3 project, plan to construct commercial iron making plant in Minnesota*. Tokyo, Kobe Steel Ltd. ([http://www.kobelco.co.jp/english/releases/2007/1179207\\_14779.html](http://www.kobelco.co.jp/english/releases/2007/1179207_14779.html)).
- KRAUSS G., 1990. *Microstructures, processing and properties of steels*. Metals Handbook, Properties and Selection: Irons, Steels, and High Performance Alloys, ASTM International, 10<sup>th</sup> edition, 1, 126-132.
- LOGINOV V. I., BERIN A. L., SOLOMATIN S. M., 1977. *Effect of mixing burden with coke on blast furnace fluid mechanics and operation parameters*. *Stal*, 5, 391-394.
- LANKFORD W.T., SAMWAYS N.L., CRAVEN R.F., MCGANNON H.E., 1985. *The making, shaping and treating of steel*. United States Steel, 10<sup>th</sup> edition.
- MOUSA E.A., SENK D., BABICH A., and GUDENAU H.W., 2010. *Influence of nut coke on iron ore sinter reducibility under simulated blast furnace conditions*. *Ironmak. Steelmak.*, 37, 219-228.
- MAZURAK R.E., 2003, *Ironmaking industry trends and directions*. *Min. Eng.*, 55 (4), 12-17.
- NEGAMI T., 2001. *ITmk3- Premium ironmaking process for the new millennium*. Direct from Midrex, 1, 7-9.
- PEACEY J.G., DAVENPORT W.G., 1979. *The Blast Furnace Theory and Practice, Theory and Practice*. Pergamon Press, 1<sup>st</sup> edition, ISBN: 9781483146782.
- PISHNOGRAEV S.N., CHEVYCHELOV A.V., GOSTENIN V.A., SHTAFIENKO N.S., AND GRİDASOV V.P., 2009. *Using coke fines in the blast furnaces at OAO MMK*. *Steel Transl.*, 39, 878-881.
- SEKI K, TANAKA K.S., 2008. *Changes in Paradigm Development Of Iron & Steel Industry By Applying Coal Based Dr Processes: Fastmelt & ITmk3*. *TIB Journal Articles*, 37 (4), 4-8
- SMITH W.F., 1993. *Structure and Properties of Engineering Alloys*. McGraw-Hill Materials Science and Engineering Series, 2<sup>nd</sup> Edition, 82, 1-41.
- STEFFEN R., LUNGEN H.B., 2004. *State of the art technology of direct and smelting reduction of iron ores*. *La Revue de Metallurgie*, 171-182.
- TANAKA H, MIYAGAWA K, HARADA T, 2008. *Fastmet, Fastmelt and ITmk3, Development of New Coal-based Ironmaking Processes*. RHF Technologies, ([https://www.midrex.com/assets/user/media/FASTMET\\_FASTMELT\\_ITmk3.pdf](https://www.midrex.com/assets/user/media/FASTMET_FASTMELT_ITmk3.pdf)).
- TSUGE O., KIKUCHI S., TOKUDA K., ITO S., KOBAYASHI I., URAGAMI A., 2002. *Successful iron nuggets production at ITmk3 pilot plant*. 61<sup>st</sup> Ironmaking Conference Proceedings. 61, 10-13.
- YANG Z., YANG J., 1995. *Effect of coke-ore mixed charging on reduction and gas flow characteristics in the softening-melting zone*. *Ironmak. Steelmak.*, 22, 191-195.