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The effect of temperature and carbon to hematite ratio on the formation of cementite during the couple of STMA and partial melting processes. A. Soleymani, M. Panjepour, M. Meratian

In this research, the role of the couple of simultaneous thermal-mechanical activation (STMA) and partial melting (PM) processes in the carbothermic reduction of hematite and cementite formation was studied. For this purpose, the STMA process was performed for 6 hours at 1073 K (800 C) on the mixture of hematite and graphite with stoichiometry ratio (22 wt pct C) in argon atmosphere in the first stage, and then this process was coupled to the PM process at 1453 K (1180 C) for 25 minutes. The results obtained showed that the percentage of cementite phase in the product of the STMA process was only about 24 wt pct and after carrying out the PM process, this value reached 77 wt pct in the final product. In the second stage, the effect of the ratio of the parameters of carbon to hematite on the initial mixture (1:1, 1:25, and 1:5 times the
stoichiometry ratio) and STMA process temperature (1073 K, 1123 K, and 1173 K (800 C, 850 C, and 900 C)) was studied. The results were indicative of the fact that by an increase in the ratio of carbon to hematite and at STMA temperature, the percentage of cementite in the final product obtained from the PM process significantly increased. In fact, the specimens obtained from the couple of the STMA and PM processes with a carbon to hematite ratio of 1.5:1 at 1073 K (800 C) and that of 1.25:1 at 1173 K (900 C) showed the greatest percentage of cementite. The mechanism regarding the processes showed that by controlling the amount and manner of free carbon distribution in the STMA product based on the parameters of the ratio of carbon to hematite and temperature, it was possible to obtain pure cementite. Therefore, the couple of STMA and PM processes can also be brought up as a new method in the production of pure cementite.

Insight into the consolidation mechanism of oxidized pellets made from the mixture of magnetite and chromite concentrates. D. Zhu, C. Yang, J. Pan, Q. Zhang, B. Shi, F. Zhang

To produce more competitive stainless steel products, the utilization of low-cost chromite concentrate is of great importance. In a previous study, a high-quality product pellet (CMP) for blast furnace smelting process made from a mixture of 40 wt pct chromite and 60 wt pct magnetite concentrates was manufactured by a high-pressure grinding rollers pretreatment. In this work, an insight into the consolidation mechanism of CMP is taken in comparison with the oxidized pellets (MP) made from 100 pct magnetite concentrate by adopting the scanning electron microscopy, energy-dispersive spectrometer, and X-ray diffractometer. The mineralogy of the pellets and the morphology of the preheated and roasted mineral particles are demonstrated. To gain better understanding of the consolidation mechanism of CMP, the thermodynamics of chromite–magnetite spinel system and hematite–sesquioxide corundum system in air are considered by using FactSage software. It can be found that the solid-state bonding is the dominant form in the consolidation of CMP, which mainly depends on the recrystallization of hematite, the solid solution bonding in adjacent areas of both magnetite–chromite particles and chromite–chromite particles. The latter two bonds rely on the formation of the miscible sesquioxide and spinel solid solution at the contact areas of particles, which is largely affected by the oxidizability of magnetite and chromite spinels. When more chromite concentrate is blended, the weak bonding among the chromite particles gradually becomes the dominant factor, which will lead to the decrease of the mechanical strength of fired pellets. The presence of a small quantity of siliceous liquid phase in CMP is believed to be beneficial to the hardening by accelerating the ion diffusion rate and forming slag bonds.

Separation of iron phase and P-bearing slag phase from gaseous-reduced, high-phosphorous oolitic iron ore at 1473 K (1200 C) by super gravity. J. Gao, Y. Zhong, L. Guo, Z. Guo

In situ observation on the morphology evolution and phosphorous migration of gaseous-reduced, high-phosphorous oolitic iron ore during the melting process was carried out with a high-temperature confocal scanning laser microscope. The results showed that 1473 K (1200 C) was a critical temperature at which the gangue minerals started to form into the slag phase while the iron grains remained in a solid state; in addition, the phosphorus remained in the slag phase. Since the separation of iron grains and P-bearing slag was not achieved at the low temperature under the conventional conditions, separate experiments of the iron phase and the P-bearing slag phase from gaseous-reduced, high-phosphorous oolitic iron ore at 1473 K (1200 C) by super gravity were carried out in this study. Based on the iron-slag separation by super gravity, phosphorus was removed effectively from the iron phase at the temperature below the melting point of iron. Iron grains moved along the super-gravity direction, joined, and concentrated as the iron phase on the filter, whereas the slag phase containing apatite
crystals broke through the barriers of the iron grains and went through the filter. Consequently, increasing the gravity coefficient was definitely beneficial for the separation of the P-bearing slag phase from the iron phase. With the gravity coefficient of G = 1200, the mass fractions of separated slag and iron phases were close to their respective theoretical values, and the mass fraction of MFe in the separated iron phase was up to 98.09 wt pct and that of P was decreased to 0.083 wt pct. The recovery of MFe in the iron phase and that of P in the slag phase were up to 99.19 and 95.83 pct, respectively.

**Sulfurization of Fe-Ni-Cu-Co alloy to matte phase by carbothermic reduction of calcium sulfate.** E. Jeong, C. Nam, K. Park, J. Park

Calcium sulfate (CaSO4) is proposed as an alternative sulfur source to convert the Fe-Ni-Cu-Co alloy to the matte phase. Solid carbon was used as a reducing agent and the influence of oxide fluxes on the sulfurization efficiency at 1673 K (1400°C) in a CO-CO2-SO2-Ar atmosphere was investigated. When CaSO4 was equilibrated with the Fe-Ni-Cu-Co alloy without any reducing agent, it was reduced by Fe in the liquid alloy, resulting in the formation of FeS. The sulfurization efficiency was about 56 pct, even though an excess amount of CaSO4 (gypsum equivalent, Geq = 1.7) was added. Adding solid carbon as the reducing agent significantly shortened the equilibration time from 36 to 3.5 hours and increased the sulfurization efficiency from 56 to 91 pct, even though the amount of carbon was lower than the theoretical equivalent for carbothermic reduction of CaSO4, viz. Geq = 0.7. Although CaS (not FeS) was formed as a primary reaction product, it continuously reacted with CaSO4, forming CaO-rich slag. Neither the carbothermic reduction time nor the sulfurization efficiency were affected by the addition of Al2O3 (SiO2) fluxes, but the equilibration time fell to 2.5 hours with the addition of Al2O3-Fe2O3 flux because the former systems produced primarily calcium silicate and calcium aluminate, which have relatively high melting points, whereas the latter system produced calcium ferrite, which has a lower melting point. Consequently, calcium sulfate (waste gypsum) can replace expensive pure sulfur as a raw material in the sulfurization of Fe-Ni-Cu-Co alloy with small amounts of iron oxide (Fe2O3) as a flux material. The present results can be used to improve the recovery of rare metals, such as Ni and Co, from deep sea manganese nodules.

**Relationship between iron whisker growth and doping amount of oxide during Fe2O3 reduction.** X. Gong, Z. Zhao, Z. Wang, B. Zhang, L. Guo, Z. Guo

Iron whisker growth during Fe2O3 doped with oxide reduced by CO was investigated by using in situ observation and scanning electron microscopy. The results indicated that the minimum doping amount (MDA) of various oxides, hindering the iron whisker growth, was different. The MDA of Al2O3, Li2O, Na2O, and K2O was 0.5, 0.4, 4, and 12 pct, respectively. From the reduction rate, it was found that Li2O, MgO, and Al2O3 had some suppressive effects on the Fe2O3 reduction process, thus, confining the growth of iron whisker. However, other oxides had some catalytic effects on the Fe2O3 reduction process (Fe2O3-Fe3O4-Fe), such as CaO, SrO, BaO, Na2O, and K2O. As long as their doping amount was enough, these oxides could inhibit the diffusion of the Fe atom. When the metal ionic radius in doped oxide was bigger than that of Fe3+, such as Ca2+, Sr2+, Ba2+, Na+, and K+, there were lots of spaces left in Fe2O3 doped with oxide after reduction, improving Fe atom diffusion. Consequently, their MDA was more than that of small radius to restrain the growth of iron whisker.

**A structural molar volume model for oxide melts part I: Li2O-Na2O-K2O-MgO-CaO-MnO-PbO-Al2O3-SiO2 melts—binary systems.** E. Thibodeau, A. Gheribi, I. Jung

A structural molar volume model was developed to accurately reproduce the molar volume of molten oxides. As the non-linearity of molar volume is related to the change in structure of molten oxides, the silicate tetrahedral Q-species, calculated from the modified quasichemical model with an optimized thermodynamic database, were
used as basic structural units in the present model. Experimental molar volume data for unary and binary melts in the Li2O-Na2O-K2O-MgO-CaO-MnO-PbO-Al2O3-SiO2 system were critically evaluated. The molar volumes of unary oxide components and binary Q-species, which are model parameters of the present structural model, were determined to accurately reproduce the experimental data across the entire binary composition in a wide range of temperatures. The non-linear behavior of molar volume and thermal expansivity of binary melt depending on SiO2 content are well reproduced by the present model.

The effects of thermal pretreatment on leaching of Yunnan ilmenite with hydrochloric acid. S. Liu, J. Xiang
The effects of thermal pretreatment on the leaching of Yunnan ilmenite ores were investigated from two aspects: the dissolution of iron and titanium, and the proportion of fine precipitations. The results indicate that high-temperature reduction or oxidization produces phase and structure transformations on ilmenite that facilitate the dissolution of iron, reduce the dissolution of titanium, and facilitate the hydrolysis of dissolved titanium. The results further indicate that oxidation at temperatures ranging from 1023 K (750°C) to 1273 K (1000°C) can significantly decrease the proportion of fine products. It is believed that the structure of oxidized ilmenite played an important role in minimizing the proportion of fine materials.

Ironmaking & Steelmaking, October 2015
Direct chromium alloying by smelting reduction of mill scale and low grade chromite ore. A. Ahmed, M. El-Fawakhry, M. Eissa, S. Shahein
Mill scale produced in rolling mills is considered a rich iron source (>67%Fe) with minimum impurities. In the present paper, iron high Cr alloy was produced by a direct alloying with chromium in carbothermal reduction using fine of low grade chromites ore and mill scale. The smelting experimental heats were carried out in a 5 kg pilot plant submerged electric arc furnace. The charging materials and reduction parameters were varied, and the optimum conditions for obtaining alloy with the highest metallic yield and the highest iron and chromium recovery were determined. When using coke as the reducing agent in stoichiometric amounts, for a mixture of mill scale (55%) and chromite ore (45%), 89.1% of the iron and 72.5% of the chromium were recovered, producing iron high Cr alloy containing 17.9Cr–3.73C–0.46Mn–1.47Si. The maximum iron and chromium recoveries obtained were 99.3 and 72.5%, respectively, when using excess carbon. The present study clarifies the possibility of using a mixture of chromite ore, mill scale and coke as the precursor for direct chromium alloying. This method offers an alternative process route with cheaper raw materials and fewer process steps (by avoiding the step of ferrochrome production) for producing high chromium iron or steel alloys.

Dephosphorisation of high phosphorus oolitic hematite by carbon composite pre-reduction and fast melting separation. G. Wang, J. Liu, J. Wang, Q. Xue
High phosphorus oolitic hematite deposit is a kind of refractory iron ore resource of huge amount. At present, it is difficult to be utilised by traditional physical and chemical technology efficiently and economically. A novel process for utilisation of the high phosphorus oolitic hematite based on carbon composite pre-reduction and fast melting separation has been put forward in the paper. High grade pig iron nugget of low phosphorus could be obtained in the present research. The influence of experimental conditions, such as pre-reduction temperature, C/O (molar ratio) and basicity, on the dephosphorisation behaviours was studied in detail. The thermodynamic basis and reduction and melting separation process were also analysed. The phosphorus content in the iron nugget decreased with the increasing of basicity and increased with the increasing of C/O. The optimum parameters were pre-reduction temperature of 1200°C for 30 min, C/O of 0.95 and basicity of 1.7. After
melting separation of molten iron and slag at 1400°C for 10 min, the iron nugget containing 0.02 wt-% phosphorus would be obtained. The dephosphorisation degree and iron yield in the form of iron nugget were 97.5% and 96.9% respectively. The iron nugget may be directly used as the raw materials of steelmaking from the view point of its high grade.

**Carbon deposition on iron surfaces in CO–CO2 atmosphere.** S. Geng, W. Ding, S. Guo, X. Zou, Y. Zhang, X. Lu

Thermodynamic calculations and thermogravimetric (TG) analysis were performed in order to understand the mechanism of carbon deposition on the surfaces of iron particles during the reduction of iron ore in a CO–CO2 atmosphere. The results of the thermodynamic equilibrium phase analysis indicate that the phases of the carbon deposition process can be predicted on the basis of the carbon potential, reaction temperature and gas pressure. The optimal thermodynamic conditions for carburisation are a low temperature (T<Tm) and a high carbon potential (ac>1). TG analysis is performed in a gas mixture of 65 vol.% CO and 35 vol.% CO2 at 650, 706 and 750 C. Cementite (Fe3C) is generated as an intermediate product, which acts as a catalyst for carbon deposition. Carbon deposition is inhibited at high temperatures (T>791 C) owing to the high stability of Fe3C. When the reaction temperature is higher than the thermodynamic limit for the formation of Fe3C, carbon deposition cannot occur. A mechanism for carbon deposition is proposed based on the experimental results.

**METEC & 2nd ESTAD, June 2015**

**High-carbon DRI with ENERGIRON DR technology.** P. Duarte, A. Martinis

Optimum Carbon content in DRI has always been a topic for debate. As the DRI-EAF route for steel production intensifies worldwide, the DRI quality requirement is of most importance for both DR plants and EAF operations. Carbon is not only a source of energy for steel production but is also necessary for the proper and optimized operation of the EAF in terms of foaming slag, continuous feeding, carbon purity, yield, etc. The form in which Carbon is present in the DRI, free or as iron carbide, is reflected in different characteristics and benefits related to stability and energy release. The wider flexibility for carbon content in DRI, ranging from 2% to 5%, is possible with the ENERGIRON ZR process scheme prevailing conditions, with minimum energy consumption in the DR plant and an optimised integration of DR-EAF operations. High Carbon DRI refers to f3.5% Carbon with a minimum of 90% as iron carbide. Benefits of this product for EAF-based steel production, as compared with conventional lower Carbon DRI are presented in the analysis. Also High Carbon DRI can be fed to the BF, improving operating conditions of both DR and BF systems. This allows increasing productivity and decreasing coke/PCI consumption while improving the environmental impact and maximising profit.

**Straw fiber utilization in rotary hearth furnace process for direct reduced iron production.** D. Duan, H. Han, P. Yuan

Straw fiber is a waste obtained by jet milling after extracting valuable substances form corn straw through steam explosion - washing - mechanical carding process. At the same time, it is also a clean and renewable reducing agent. In this study, physical and chemical characteristics of straw fiber were investigated firstly. Then the Straw fiber used in rotary hearth furnace process for direct reduced iron(DRI) production was discussed. The results show that the fixed carbon content of straw fiber is low, but the hydrogen content is high, ash and sulfur content is low, so there is little impact on production efficiency and product quality of DRI. Compared with common reducing agent, straw fiber has better reduction effect, and the straw fiber carbon-containing pellets possess higher compressive strength and larger volume shrinkage, which is conducive to increasing layer thickness of carbon containing pellets and improving production efficiency. In addition, the straw fiber carbon-containing pellets also have
advantage of low C/O and short reduction time, the appropriate C/O is 0.8, the appropriate reduction time is 15min, and the particle size of straw fiber <0.15mm has the better reduction effect. So applying straw fiber as reducing agent into the RHF process would reduce the additional amount of common reducing agent, decrease production cost, and reduce CO2 emissions. This study aims to provide theoretical and technical basis for utilization of straw fiber in rotary hearth furnace process.

The breakthrough ironmaking technologies combined with ENERGIRON, blast furnace and syngas. H. Ichikawa, T. Nakayama, P. Duarte, A. Martinis
In 2013, Nippon Steel & Sumikin Engineering Co., Ltd. (hereafter referred to as NSENGI), Tenova HYL and Danieli have entered into an agreement to combine ENERGIRON DR technology into blast furnace technology and/or with syngas technologies. This new alliance will allow the three companies to combine research and development activities with their respective expertise in ENERGIRON DR technology, Blast Furnace technology and Syngas (by-pro gas and coal gasification) technology, with the ultimate objective to develop breakthrough iron making technologies and create such EPC projects. This paper introduces the concepts and the features of our breakthrough technologies of combining of ENERGIRON DR technology, Blast Furnace technology and Syngas technology.

Trends in iron-making given the new reality of iron ore and coal resources. H. Lüngen, J. Noldin Jr., P. Schmöle
Iron ore quality has changed. Lower Fe and higher impurities are forcing blast furnaces to higher slag rates and new operational strategies. On top, iron ores are finer, impacting sinter plant productivity and economics for more pellets in the burden. This quality degradation does not seem to be a temporary phenomenon. Also, steel users are demanding cleaner steels, to improve properties, reduce weight and compete with other materials. This is a true challenge, deal with challenging raw materials to produce clean steels at very effective cost. This paper shows the evolution of raw materials and implications in Europe, discussing how the players are reacting and the most acceptable trends.

Recovery of iron and nickel from nickel converter slag by smelting reduction process. M. Ma, Z. Pei, C. Wu, B. Li, X. Tang
A study was made on the effects of smelting reduction for Fe, Ni, Co, Cu recovery from nickel converter slag. XRD (X-ray diffraction) analysis indicated that the main mineral phase of the converter slag is fayalite (Fe2SiO4) and the minor mineral phase is NiS2. SEM (Scanning electric microscopy) observation indicated that the sulfides (NiS2) are ball like tiny particles (5-20μm) disperse in silicate. A continuous two-stage smelting reduction experiments were carried out for Fe, Ni, Co, Cu recovery from the slag. In the experiments, solid carbon was used as reducing agent, CaO as the slag modifier. In stage one, Cu, Co bearing Fe-Ni alloy and a second slag (iron-rich slag) were gotten by selective reduction. In stage two, pig iron was gotten from the second slag by deep-reduction with adding CaO as slag modifier. The effects of reducing agent dosage, smelting temperature, time and slag modifier on metals recovery were investigated. Experimental results indicated that the optimum parameters of stage one is 1400℃ for 1h, of stage two is 1450℃ for 1.5h. The total recovery rates of various metals were: Fe 95%, Ni 89%, Co 51%, Cu 67%.