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SMELTING PROCESS OF DIRECT REDUCTION IRON BEARING Ni AND Cu TO PREPARE Fe-Ni-Cu TERNARY ALLOY

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Abstract

The smelting behavior of direct reduction iron powder containing Ni and Cu from co-reduction followed by a magnetic separation of copper slag and nickel laterite was investigated in this paper. The results show that the perfect ternary alloy with 90.66% Fe, 5.24% Ni, 1.20% Cu and minor impurities can be prepared by smelting under optimum conditions at 1550 °C for 30 min with 1.1 slag basicity. The corresponding recoveries of Fe, Ni, and Cu were 92.77%, 96.27% and 96.24%, respectively. In addition, basicity has a significant effect on slag fluidity. The optimum basicity of slag is approximately 1.1, which is beneficial for both metal recovery and desulfuration. Compared with the direct reduction iron powder, the Fe-Ni-Cu ternary alloy contains a higher metal content and less sulfur from the smelting process and is a superior material for producing weathering steel. Hence, it is very feasible to use an electric arc furnace to smelt direct reduction iron powder to produce a high quality Fe-Ni-Cu ternary alloy.

Keywords: *Smelting; Fe-Ni-Cu alloy; Metal recovery; Desulfuration; Weathering steel*

1. Introduction

Weathering steel has a high strength and ductility as well as excellent corrosion properties and paintability[1], and therefore is widely used in many fields. As a type of low-alloys steel, it is mainly alloyed with Cu, P, Cr and Ni, etc., in a total proportion of 5 wt.% [1,2]. In particular, copper and nickel are important alloying elements required for the production of weathering steel [3-8].

Commonly, in the weathering steel-making process, the required amount of electrolytic copper and electrolytic nickel is added to adjust the chemical compositions of weathering steel [9]. However, the soaring price of electrolytic copper and electrolytic nickel has raised its production cost. At the same time, with the depletion of high grade mineral resources, the production costs of electrolytic copper and electrolytic nickel are also increasing. More low-grade laterite and secondary copper resources, such as copper slag, are used in the production of the ferroalloys replacing electrolytic copper and electrolytic nickel, providing the possibility of innovation for raw material-making technology [10-13]. However, nickel laterite and copper slag are not suitable for direct use in ferroalloy production, so a beneficiation step is indispensable. If the Ni and Cu elements can directly access the iron with the reduction of Fe minerals, it may be an effective solution to this problem. Hence, co-reduction followed by the magnetic separation of copper slag and nickel laterite to prepare the direct iron powder containing Cu and Ni was proposed in an earlier paper [14]. The copper slag and nickel laterite were effectively upgraded, and this process produced the crude Fe-Cu-Ni alloy simultaneously. However, the impurity content, especially the excessive high S content, of the crude Fe-Cu-Ni was too high, resulting in a sea of slag, high electricity consumption, long production cycle time, and high production costs.

In this paper, to obtain a high quality Fe-Ni-Cu ternary alloy for weathering steel, a smelting process for the direct iron powder containing Cu and Ni was developed. The effects of temperature, duration, and basicity on the smelting behavior of the crude Fe–Ni–Cu alloy are the subjects of this work which includes a feasibility analysis and experimental studies. This process is not only able to produce a pure alloy, but also to sharply shorten the alloy production process through bypassing the production of Fe–Ni and Fe–Cu alloys and sending ternary alloy directly to the refining step of weathering steel production.

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2. Experiments

2.1 Materials

The direct reduction iron powder containing Cu and Ni used in this paper was produced from previous co-reduction and subsequent magnetic separation experiments, and its chemical composition is shown in Table 1. The Fe, Ni, and Cu grades of the concentrates are 85.38%, 1.03%, and 4.90%, respectively, and the content of the other impurities, such as SiO_2, Al_2O_3, CaO and MgO, is as high as 8%. These impurities form a good amount of slag in the refining step of weathering steel if the direct reduction iron powder is not treated by smelting. The S content (0.18%) is also very high, exceeding the total sulfur target in weathering steel. Hence, the smelting process of this direct reduction iron powder containing Cu and Ni is crucial for obtaining the pure Fe-Ni-Cu alloy.

Table 1. *Chemical compositions of direct reduction iron powder /wt.%*

Material	TFe	Cu	Ni	SiO_2	Al_2O_3	CaO	MgO	S	P
Copper slag	85.38	1.03	4.90	3.05	0.53	1.02	0.67	0.18	0.045

Limestone containing 55.73% CaO and a 41.52% loss of ignition (LOI) was used to adjust the basicity in the smelting process.

2.2 Methods

In the smelting experiments, for each test 100 g direct reduction iron powder with Cu and Ni and a required amount of limestone were mixed evenly, and then charged into a graphite crucible with an inner diameter of 62 mm and height of 144 mm. Subsequently, the graphite crucible was put in a furnace with $MoSi_2$ heaters and then heated to a fixed temperature at a 10 °C/min heating rate under a high purity nitrogen (N_2) atmosphere, and then smelt at the fixed temperature for various durations to allow for the separation of slag and alloy. After the smelting process, the sample was cooled to the ambient temperature under the protection of N_2, and then it was removed from the furnace. Then, the crucible was broken to separate the alloy and the slag very carefully (the separation between the alloy and the slag was caused by a density difference at high temperatures, with the heavier alloy dropping to the bottom of the crucible). Finally, both the slag and the alloy were weighed and chemically analyzed by XRF, ICP-AES and chemical titration. In addition, to ensure the accurate detection result, the alloy samples were prepared by this method: 1) the alloy was crushed by rotate turning-lathe due to its high hardness; 2) The fine alloy was ground to the powder with the size of less than 0.074mm by vibrating mill (HHS6-2); 3) To determine the S, Fe, Cu and Ni content the alloy powder was subjected to XRF.

The recovery rate of iron, nickel, and Cu η was calculated from Eq. (1):

$$\eta = \frac{M_1 \times TM_1}{M_0 \times TM_0} \times 100\% \qquad (1)$$

Where η is the recovery rate of Fe, Ni, or Cu; M_1 is the mass of Fe-Ni-Cu master alloy; TM_1 is the grade of Fe, Ni, or Cu in master alloy; M_0 is the mass of direct reduction iron powder; TM_1 is the grade of Fe, Ni, or Cu in direct reduction iron powder.

The slag viscosity was calculated by FactSage7.0. However, FactSage is only suitable for calculating the viscosity of pure liquid slag, but not to directly calculate the viscosity of melt and solid mixture. Generally, the Einstein–Roscoe modeling equation has been proposed as a typical model for liquid melt with solid phase particles, which is expressed as follows:

$$\mu = \mu_0 \left(1 - af\right)^{-n} \qquad (2)$$

Where μ is the viscosity of the slag with solid particles; μ_0 is the viscosity of the pure melt; f is the volume fraction of solid particles in the melt; a and n are the constants, 1.35 and 2.5, respectively [15-17].

The phase compositions and the microstructure of the alloy were characterized by X-ray diffractometer (XRD, RIGAKU, D/Max-2500), Leica DMLP optical microscopy, FEI Quata-200 scanning electron microscope, and EDAX32 energy-dispersive spectrometer.

3. Results and discussion

3.1 Thermodynamics analysis

The slag properties have a significant effect on the smelting process control and the quality of the product. Hence, it is theoretically feasible that the slag and the Fe-Ni-Cu alloy may be successfully separated if the final slag with appropriate properties, such as good fluidity, low viscosity, and low liquid temperature, can be obtained at one temperature [18-20].

Assuming that the full Fe, Ni, and Cu elements in the direct reduction iron powder were smelted into a ternary alloy, the chemical composition of the nominal slag was estimated as follow: SiO_2 57.87%, Al_2O_3 10.06%, CaO 19.35%, and MgO 12.71%. The liquid projection of the CaO–MgO–SiO_2–Al_2O_3 in the nominal slag was determined by FactSage 7.0, and the results are shown in Fig. 1. The liquid temperature of the nominal slag is approximately 1400 °C. Generally, in the smelting process, it is necessary to maintain an approximately 100~150 °C superheat temperature of the liquid slag to ensure it has a good fluidity. Hence, the smelting temperature may be 1500~1600 °C.

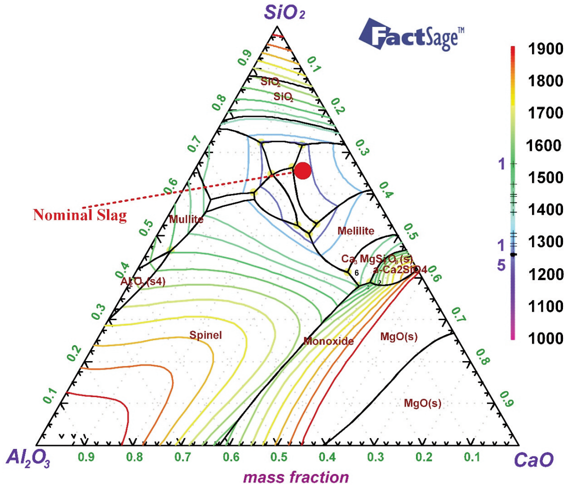


Figure 1. *Phase diagram of SiO_2-Al_2O_3-CaO with MgO=13%*

In addition, slag viscosity is also an important physicochemical property for high temperature melts, which is relevant to metallurgical processes such as extracting, refining, and continuous casting both in iron-making and steel-making [21-23]. The effects of basicity and temperature on the viscosity of the slag were evaluated by FactSage7.0, and the results are shown in Fig. 2 and the chemical compositions of slag with various basicity for calculation are shown in Table.2, which indicates that with an increase in temperature, the viscosity of the slag decreased obviously. At the same time, the minimum viscosity of the molten slag may appear to have an approximately 1.0 binary basicity, which means the slag with this basicity possesses perfect fluidity. It is well known that CaO, as a kind of alkaline oxide, can break the silicate bonds and aluminosilicate bonds and thereby increases the fluidity of the slag [24-26].

However, when CaO is added in excess and the basicity is over 1.1, various types of solid compounds, including Mg_2SiO_4 and Ca_2SiO_4 (as seen in Fig. 3), are precipitated in slags during the smelting process, and therefore the percentage of liquid phase is decreased obviously. More seriously, these compounds strongly deteriorate the slag fluidity, resulting in the poor separating effect with the slag and the alloy. Hence, it is essential to add an appropriate dosage of CaO to adjust the optimum basicity in order to realize the successful separation of the slag and the alloy.

Table 2. *Chemical compositions of slag for calculation*

Basicity	SiO_2	Al_2O_3	CaO	MgO
0.33	57.9	10.1	19.4	12.7
0.40	55.6	9.7	22.6	12.2
0.60	50.4	8.7	29.8	11.1
0.80	45.7	7.9	36.3	10.0
1.00	41.67	7.24	41.94	9.15
1.20	38.49	6.69	46.37	8.45
1.40	35.88	6.24	50.00	7.88
1.60	33.28	5.78	53.63	7.31

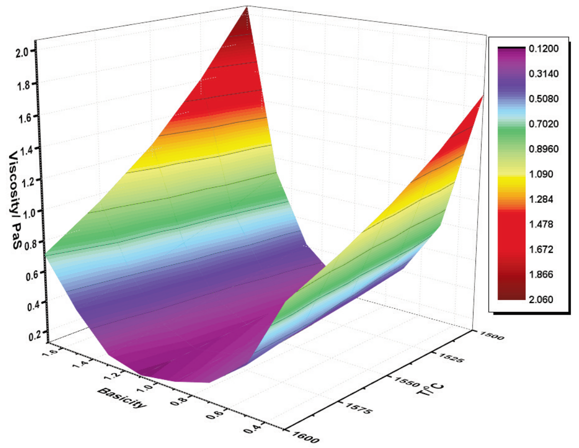


Figure 2. *Effect of basicity and temperature on the viscosity of slag*

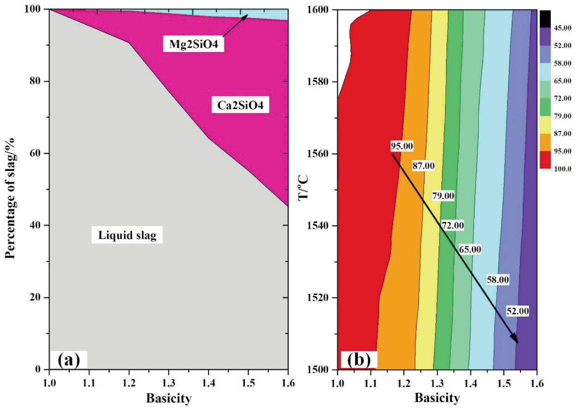


Figure 3. *Effect of basicity and temperature on the percentage of liquid phase((a)-effect of basicity on compositions of slag at 1550°C; (b)-effect of basicity and temperature on liquid percent)*

3.2 Smelting process

The results of the grades of Fe, Ni, and Cu within the alloy and the recovery rates are plotted in Fig. 4(a). When the smelting temperature increased from 1525 to 1550 °C, the recovery of Fe, Ni, and Cu obviously increased. When further elevating the temperature, all the indexes improved slightly. As seen from Fig. 2, raising the temperature was beneficial for the slag fluidity, which contributed to collision and aggregation of alloy particles and improved smelting kinetics and the separation between the slag and the alloy. In addition, it also weakened interfacial tension between the alloy and the slag, resulting in a decrease in the dissolution and mechanical inclusion of the alloy in the slag. However, further elevating temperature must be given to the increased energy consumption [27]. Hence, from a practical point of view, the smelting temperature was fixed at 1550 °C in the subsequent experiments.

The effect of smelting duration on Fe, Ni and Cu recovery and grade is shown in Fig. 4(b). The Fe, Cu, and Ni recoveries increase from 90.3% to 92.4%, 93.6% to 96.3% and 91.8% to 95.6%, respectively, as the smelting duration is prolonged from 10 min to 30 min. Then, the metal recovery remains constant even with the further increase in the smelting duration. This result implies that the full setting of the metals also requires enough time. Thus, the smelting should be performed for 30 min.

Binary basicity undoubtedly has a significant effect on the recovery of valuable metals in the smelting process. Fig. 4(c) shows the effect of binary basicity on Fe, Ni, and Cu recovery. The Fe, Ni and Cu recoveries significantly increase from 0.7 to 1.1 and reach peak values of 92.77%, 96.27%, and 96.24%, respectively, and then they significantly decline if the basicity is further increased. Accordingly, the grade of metal in the alloy changes slightly. As mentioned above, the minimum slag viscosity occurs at approximately 1.1 basicity, which means this slag possesses the best fluidity (as seen in Fig. 2). Hence, the experimental results agree well with the thermodynamic analysis of the smelting process. Therefore, the optimum basicity is 1.1.

In addition, the S content in the alloy is also an essential index that significantly influences the alloy quality. The basicity undoubtedly has a prominent effect on the desulfuration in the smelting process. Hence, the effect of the basicity on S content within the alloy was conducted, and the results are shown in Fig. 4(d). The S content in the alloy decreases obviously from 0.065% to 0.035% as the basicity increases from 0.7 to 1.3. According to an obvious model [28,29], the sulfide capacity of the slag is proportional to CaO% (see Eq. (3)). With the addition of CaO, the values of C_S can significantly increase, resulting in a higher desulfuration rate. Hence, the S content in the ternary alloy decreases.

$$\lg C_s = 1.35 \times \frac{1.79w(CaO)+1.24w(MgO)}{1.66w(SiO_2)+0.33w(Al_2O_3)} - \frac{6911}{T} - 1.649 \qquad (3)$$

where Cs is the sulfide capacity of slag; W is the mass percent of CaO, MgO, SiO_2, and Al_2O_3, and T is the smelting temperature.

Concerning kinetics, the optimum basicity can decrease the slag viscosity and facilitate S transfer from the metal to the slag-alloy interface, thereby improving the desulfuration reaction in the smelting process [30,31].

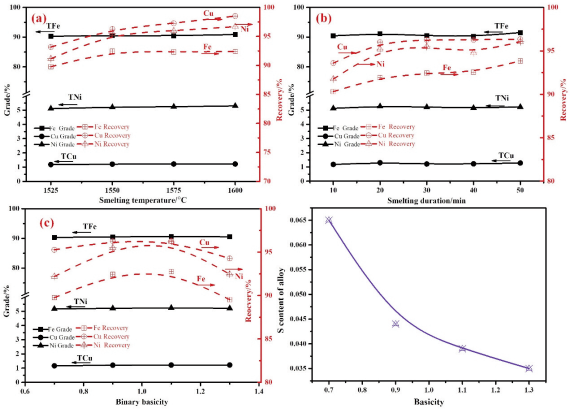
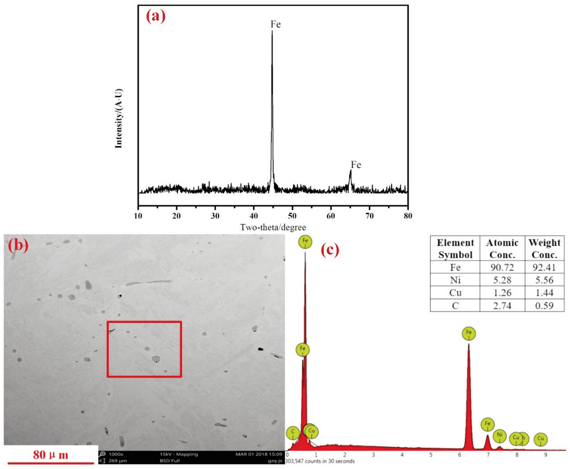


Figure 4. *Effect of smelting process parameters on grade and recovery of Fe, Ni and Cu ((a)-effect of smelting temperature; (b)-effect of smelting duration; (c)-effect of binary basicity; (d)-effect of binary basicity on S content of alloy;)*

3.3 Characterization of Fe-Ni-Cu ternary alloy

Under the optimum conditions of smelting at 1550 °C for 30 min with 1.1 slag basicity, the Fe-Ni-Cu ternary alloy was prepared. Its chemical composition and phase were determined, and the results are shown in Table 3 and Fig. 5, respectively. As seen from Table 2, the grades of Fe, Ni, and Cu are 90.66%, 1.22%, and 5.25%, respectively. The total metal (Fe, Ni and Cu) content within Fe-Ni-Cu alloy is as high as 97.12%. Compared with the direct reduction iron



Element Symbol	Atomic Conc.	Weight Conc.
Fe	90.72	92.41
Ni	5.28	5.56
Cu	1.26	1.44
C	2.74	0.59

Figure 5. *Characterization of Fe-Ni-Cu ternary alloy (a-XRD patterns, b-SEM, c-eds of map)*

Table 3. *Chemical compositions of Fe-Ni-Cu alloy/wt.%*

Material	TFe	Cu	Ni	SiO_2	Al_2O_3	CaO	MgO	Na_2O	C	S	P
Copper slag	90.66	1.22	5.24	0.10	0.15	0.16	0.039	0.011	0.15	0.039	0.008

powder, the total metals content increased significantly. In contrast, the impurity content was obviously reduced. Specifically, the S content decreases from 0.18% to 0.039% as it is believed to be conducive to the subsequent refinement of weathering steel.

As shown in Fig. 5(a), the main phase of the alloy is a-Fe solution with Ni and Cu. According to the SEM-EDS analysis of the sample in Fig. 5(b) and Fig. 5(c), the alloy mainly contains 92.41% Fe, 5.56% Ni, and 1.44% Cu, and a small amount of C, which further confirms that the product is very pure, which can be used to prepar the Cu-bearing special steels.

4. Conclusions

A feasibility analysis and relevant experiments on the smelting process for the preparation of a Fe-Ni-Cu alloy for weathering steel were conducted in this work. Based on the experimental data, the following conclusions were made:

(1) The ternary alloy with 90.66% Fe, 5.24% Ni, 1.20% Cu, and minor impurities can be directly produced from direct reduction iron powder by smelting at 1550 °C for 30 min with 1.1 slag basicity. At the same time, the Fe, Ni, and Cu recoveries were 92.77%, 96.27%, and 96.24%, respectively. Moreover, the Ni and Cu elements were very uniformly distributed in the alloy matrix. It is a superior material for the preparation of special steels, such as weathering steel.

(2) It is very feasible for the electric arc furnace to smelt direct reduction iron powder. The pure alloy can be obtained by the smelting process, which decreases the impurity content, promotes desulfurization, and improves the utilization value of the products.

Acknowledgments

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PROCES TOPLJENJA DIREKTNO REDUKOVANOG ŽELEZA SA PRIMESAMA Ni i Cu ZA PRIPREMU Fe-Ni-Cu TROJNE LEGURE

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Apstrakt

U ovom radu se ispituje ponašanje pri topljenju direktno redukovanog praha železa koji sadrži Ni i Cu dobijenog koredukcijom nakon koje je usledila magnetna separacija bakrene šljake i laterita nikla. Rezultati pokazuju da se topljenjem pod optimalnim uslovima na temperaturi od 1550 °C u trajanju od 30 minuta, i sa bazicitetom šljake od 1.1 može pripremiti odlična trojna legura sa 90.66% Fe, 5.24% Ni, 1.20% Cu i manjim nečistoćama. Odgovarajuće dobijanje Fe, Ni, i Cu bilo je 92.77%, 96.27% i 96.24%, pojedinačno. Uz to, bazicitet je imao značajan uticaj na fluidnost šljake. Optimalni bazicitet šljake je približno 1.1, što ima povoljan uticaj kako na dobijanje metala tako i na odsumporavanje. U poređenju sa direktno redukovanim prahom železa, trojna Fe-Ni-Cu legura ima veći sadržaj metala i manje sumpora iz procesa topljenja, i izvanredan je materijal za proizvodnju čelika otpornog na vremenske uslove. Stoga, veoma je izvodljivo koristiti elektrolučnu peć za topljenje direktno redukovanog praha železa da bi se proizvela visokokvalitetna trojna Fe-Ni-Cu legura.

Ključne reči: *Topljenje; Fe-Ni-Cu legura; Dobijanje metala; Odsumporavanje; Čelik otporan na vremenske uslove*