ADVANCED TECHNOLOGICAL SOLUTIONS FOR QUALITY STEEL PRODUCTION WITH COPPER CONTAMINATED SCRAP

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ABSTRACT

Recyclability is an important feature of steel as material. There are not still exist reliable methods to control the copper content during steelmaking process with the scrap contaminated by copper except dilution technique. Numerous trails have been made to create a technology for dissolved copper removal from the iron-base melts, but the tested variants were not competitive at the commercial level. Refining steel melts by special solid agents lets to remove a great deal of dissolved copper by means of adsorption (up to 70-80% for one treating). Promising material for refining agent is spinel on the base of alumina and zinc oxide. But this method has not studied properly until now. Other perspective way to refine iron-based melts from copper is method of sulfidizing. Investigations let us developed special techniques for realization of the mentioned methods including in combination. Successful experiments allow us to say about real possibility to design a commercial technology.

Steady tendency of electric steelmaking growth in total crude steel production is observed in the last decade of years. In the circumstances as the quality steel scrap quantity is limited, an increase in consumption of the obsolete scrap takes place in steelmaking. The problem is that the obsolete scrap accumulates tramp elements like Cu, Sn, As, Sb etc. [1,2]. The ensuring of the necessary level of residuals in produced steel assumes a vital importance for steelmakers.

Copper is one of the most troublesome contaminants in steel. It is not removed when steel making and it frequently presents in the obsolete scrap in large concentration up to 0.5 % and even more high percentage [2,3]. Special investigations show that it is required to maintain a copper proportion in high grade steels less than 0.2% to ensure guaranteed quality level of products [4]. Now in the most cases the upper level of copper percentage for steel used in machinery sector is to be around 0.3%, although it may actually decrease in future. Moreover copper is the element related to surface defects that may appear during steel casting or steel hot rolling.

Thus on the background of fluctuation of the steel scrap quality, steelmakers should focus attention to the metal charge chemistry. Because there are not still exist reliable methods to perfectly control of copper content during steelmaking except maybe dilution [3,5,7]. Alternative charge materials like DRI, hot iron, ferric carbide allow producing steel with the assured low content of tramp elements in EAF [6]. Steady rising of scrap prices makes steelmaking technologies with alternative charge materials attractive for producers. Today in the world more than 25 electric arc furnaces work with hot iron in charge [7]. New advanced steelmaking technologies on the base of electric arc melting process are developed to ensure flexibility in charge materials choice [6-8]. Though these are technologies directed on the virgin materials utilization therefore they mainly compete with the blast furnace-BOF route.
Up to date steelmakers try to remove copper mainly at the stage of steel scrap preparation via careful separation or special treatment. There are a few commercial methods of mechanically removing of mixed residuals by an enhanced shredding process and coating removing by electrolytic leaching or vacuum heating [2]. However it is possible for physically distinct metallic copper only. As for dissolved copper, numerous trails have been made [10], but the tested methods are not competitive at the commercial level yet.

Copper removal into gas phase and extraction into sulfides fluxes consider as promising ways in some publications [2].

At the conditions of steelmaking process vapor pressure of copper is higher than that for iron. Thus there is a possibility to remove copper into gas phase by vaporization. However special investigations show that without vacuum above the iron melt surface the technology is not effective [11]. For example to decrease copper concentration from 0.6% to 0.3% under vacuum 100 Pa it need expose 160 ton ladle during five hours, but vigorous gas agitation can appreciably reduce an exposure time. The weak oxidizing powder blowing method was proposed in order to enhance the mass transfer rate in copper evaporation from molten iron [12]. The results demonstrated that the technique was applicable under practical reduced pressure of about 130 Pa. In case of SiO₂ powder blowing, removal percentages of copper were 20-30% at initial content 0.4% in two hours treatment. Some adding acceleration in the copper evaporation is achieved after silicon and carbon addition in molten iron to adjust the activity coefficient of copper [13]. Next noteworthy decision is treatment of the molten steel by NH₃ gas blowing under reduced pressure [14,15]. Under a vacuum of 1300 Pa the copper with initial concentration of around 0.4% could be removed to 0.1% level during 30 minutes blowing and as little as 2 ppm level during 90 minutes blowing. The method may be realized at RH vacuum units. As a variant of the described idea may consider the ammonium compounds addition to the liquid metal [15,16]. The technique allows achieve acceptable results without noticeably pressure reducing. However the last year’s publications don’t allow saying about any implementation of the mentioned technological decisions into a real production even in the pilot scale. Obviously the requirement in a long treatment under vacuum, specific technical troubles and some ecological limitations restrains it.

Second widely investigated method of dissolved copper removal from the iron melts is treatment by sulfide fluxes [17]. To get the higher values of the copper distribution coefficient it needs keep up the high sulfur potential in the system and try decreasing the copper sulfide activity coefficient in a sulfide phase. In equilibrium the copper distribution ratio amounts to 9 between the flux on the base of pure iron sulfide and iron melt at the equilibrium sulfur concentration about 1.9% and temperature 1400°C [18]. But adding of some alkaline or alkaline earth sulfides to a flux increases the copper distribution ratio up to about 30 and decreases the equilibrium sulfur concentration in the metal up to four times more. Similar results observe for aluminum sulfide additions [19], and even special technological schemes were developed for iron melts treatment with Al₂S₃–FeS flux.

In some cases direct addition of alkaline earth sulfides to get a flux with the necessary chemical composition is not obligatory. For instance in metallurgical processes sodium sulfide forms during interaction between Na₂CO₃ and iron melts that contains enough of sulfur at presence of carbon [20]. It was reported a treatment by mixtures on the base of soda, NaF, NaCl ensured removing up to 10-40% of copper from iron melt according to initial sulfur percentage (0.2-1.5%).

Authors have conducted special laboratory investigations to study a potential of technique with sulfur and soda injection into the iron melt [21]. In laboratory experiments 350 g of
iron melt was treated by the reagents in different variants under argon atmosphere. The duration of treatments was up to 5-7 minutes. The copper removing level changed in limits 25-45% for different tests at the initial copper concentration about 1%. The lowest final copper was 0.49% at final sulfur percentage 0.51%. In the metal the final copper concentration correlates with the sulfur percentage. The final sulfur in the metal was on the level 0.3-0.6% in different trials.

The next stages of the experimental work were made on the 200 kg induction furnace. Iron melts with copper contents of about 1-2% were treated with powder mixtures on the base of sulfur and soda according to different schemes. The mixture was blown into iron melt via a submerged lance in the argon stream. Developed technique ensures reducing in copper percentage up to 50-60% after one stage of the treatment (figure 1). During mixture injection the sulfur concentration in the metal rises up to 1.5% and more (figure 1, point 2). To increase the efficiency of treatment was developed a technique with aluminum addition after blowing [22]. It allows some increase in copper extraction into sulfide phase (figure 1, point 4; figure 2). The excessive aluminum in the metal reduces final sulfur content, to the level about 0.25% for the represented experiment, but not the copper concentration at the same time (figure 1, point 5).

Aluminum addition conduces to considerable increasing of sulfide inclusions size and transforms them to globular form (figure 3). All of that promotes the inclusions floating to the surface of metal where they are assimilated by sulfide flux.

The investigations have uncovered serious troubles inherent to work with sulfide fluxes. It is necessary restrict interaction of the sulfide flux layer on the metal surface with oxidizing atmosphere to avoid sulfur oxidation and copper recovering back into metal phase. A cover on the induction furnace crucible has solved the problem partly. But next trouble is concerned with sulfide flux removing from the metal surface. It was proposed to do it by means of addition of granular material on the surface of metal to absorb sulfide flux and then easily remove it away.
**Fig. 1** Changing of concentration of copper and sulfur during a test (1 – initial percentage; 2 – in the middle of blowing; 3 – at the end of blowing; 4, 5 – after adding of aluminum)

**Fig. 2** View of sulfide inclusions are made via an electron microscope in the reflected electrons (a) and the characteristic rays of elements (according the figure 1: I – control point 2; II – control point 3; III – control point 4)
Moreover some layer of the material can restrict interaction of liquid sulfides with air. As a sorptive material was tested some crushed refractory materials on the base of alumina, silica and lime. Workability of the method was confirmed during special tests but it needs further investigation to define parameters more exactly.

In whole the results demonstrate that it is not necessary to create and maintain a considerable layer of sulfide flux on the surface of liquid metal for copper removal. Saturation metal with sulfur, creation propitious conditions for sulfide inclusion formation and agglomeration in the volume of metal is more effective way.

In Fe-S-C ternary phase a separation between FeS and iron melts is observed in the certain range of concentrations [23]. The content of sulfur in iron melt equilibrated with molten FeS becomes the lowest at carbon saturation, and increases with decreasing carbon content until the critical composition where immiscibility disappears to a single homogeneous phase. Moreover carbon raises the copper activity coefficient in the metal, and thereby it promotes the cooper accumulation in the sulfide phase in addition. Thus a sulfidizing treatment for copper removal is effective for high carbon iron melts only, and do not work for steel melts.

Injection of powdered or granulated materials in an inert gas stream makes favorable condition for a quick saturation of the melt with sulfur due to intensive agitation. Test with forming sulfide flax layer on the metal surface without of blowing were shown low effectiveness of the treatment. In addition inert gas constrains atmosphere air effect.

Refining metal from the precipitated sulfides and effective removing of the sulfide flux away from the liquid metal surface is the next key point of the technology.

Effective refining of the iron melts from sulfide inclusions is very impotent because it allows thoroughly separate the sulfide phase from metal and improves results. Filtration technique was employed to clean a liquid metal. Melted and treated by blowing in the induction furnace iron melts were filtered during the casting process. A filter was placed at the entry to a casting mold. The filter was made with a refractory tube filled by shards of
alumina refractory with fraction 2-10 mm. The filtering units were heated before casting. Tests demonstrated filtration ensures complementary refining of the metal due to more complete removing of sulfides that hardly possible at a gas rinsing. Due to filtration copper concentration in the melt was reduced up to 50%. For example it was reduced from about 0.7% to 0.32% in the best test. Some decreasing in sulfur percentage was observed too.

It was discussed a proposition to use some modified technique of filtration when granules of filtering material is introduced directly into liquid metal to absorb sulfides and dissolved in the sulfides copper at the same time. After floating to the surface of the melt the refining agent forms solid layer and participating in adsorption of sulfides on the melt surface. Such approach lets refuse filtration during casting and treat whatever volumes of liquid metal. Now special equipment is under development to test the method at the experimental-industrial conditions.

Chemical composition, fraction and porosity level of a refining agent is key points of the treatment method. Some investigations demonstrate it is possible to remove copper from melts directly to the surface of a refractory material during filtration [10]. As reported spinel on the base of alumina and zinc oxide ensure the best removing of copper from iron and steel melts. At a laboratory after treatment within 5-10 minutes the copper removing level has reached more than 70% for iron melt that initially contains 3.9% C, 1%Cu and steel melt with 0.21%, 0.5%Cu. Test at the experimental-industrial condition also brought good results though not so impressive. For some reason this work has not found further development.

Our first laboratory tries with the spinel on the base of alumina and zinc oxide have shown the material porosity is a very important characteristic. Lack of experimental data doesn’t allow make any final conclusions as for mechanism of copper adsorption by the spinel sorbent. However direct adsorptions of the copper atoms on the agent surface by adhesion mechanism is hardly possible at the high temperature of the process. According to evaluate calculation recovery ZnO with CuO formation also can’t occur. Thus most likely two other schemes may be possible – formation of nucleuses of the new immiscible phase with copper atoms on the surface and copper atoms diffusion into surface layer of the refining agent.

Work of granulated refining agent during treatment the melt after blowing with sulfides is more comprehensible. Granules absorb individual sulfide inclusions and give substrate for arising new ones. Naturally it will be good refining granule’s surface could adsorb copper from attached sulfide phase, but we haven’t found evidence of that fact in our tests.

Anyhow obtained results are evidence filtration is a very perspective method for the copper removal in steelmaking. Further investigations need to uncover mechanisms and ensure necessary effectiveness of the process.

But even now the described above scheme combines a treatment by sulfides with filtration technique let obtain good results. Main feature of that development is combination of two methods for copper removal from iron melts.

LITERATURE


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