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(54) **Nickel-copper matte converters employing nitrogen enriched blast.**

(57) A process for utilizing nitrogen enriched blasts for control of oxidation and cooling of sulfide derived nickel-copper converter matte. Bessemer quality matte is produced and cooled minimizing mush formation and improving subsequent utility.

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NICKEL-COPPER MATTE CONVERTERS EMPLOYING NITROGEN ENRICHED BLAST

TECHNICAL FIELD

The instant invention relates to the pyrometallurgical production of refined nickel-copper matte from sulfide ores in general and, more particularly, to a converter process using nitrogen, air, oxygen and combinations thereof. The introduction of nitrogen or nitrogen/oxygen containing gas controls the oxidation of the resultant matte and assists in cooling it. Debilitating mush formation is substantially reduced resulting in more efficient converter operations.

BACKGROUND ART

Nickel-copper Bessemer matte is typically produced by converting molten matte from a primary smelting furnace in Peirce Smith converters which employ blowing of air or air/oxygen mixtures into the bath via tuyeres. The Peirce Smith converter is the most common type of converter used for this application and consists of a horizontally oriented cylinder which has a hooded opening at the top and is rotatable through an arc of about 180 degrees. The plurality of tuyeres are located below the normal working level of the molten matte when in the blowing position and the tuyeres are raised above the bath for pouring and holding.

The feed to the converters usually consists of a homogeneous molten matte including Ni_3S_2 , Cu_2S , FeS , and small quantities of oxygen, precious metals and other elements. Much of the rock and iron that were in the original metal bearing concentrate were eliminated in the upstream furnacing operation.

The objective of the conversion process is to oxidize the FeS in the matte to form iron oxides, liberating sulfur dioxide and leaving matte comprising nickel and copper sulfides with small but variable amounts of cobalt, precious metals and dissolved oxygen. This is accomplished by blowing an oxygen containing gas (air, oxygen enriched air or oxygen) into the matte through the tuyeres. The oxygen combines with the iron and sulfur to form iron oxide and sulfur dioxide. The sulfur dioxide passes off as a gas and is subsequently treated to prevent fugitive emissions. The iron oxide unites with added silica flux to form an iron silicate slag that floats on top of the matte now richer in nickel and copper and much lower in iron. The oxidation process is exothermic and the heat generated is usually sufficient to cause the operation to be self-

sustaining.

After removal of substantially all of the iron by blowing and skimming of the slag, the resulting matte is generally cooled, cast and further treated for recovery of valuable base and precious metals. Upon cooling, the copper and nickel in the matte form copper sulfide (Cu_2S), nickel sulfide (Ni_3S_2), and a metallic fraction containing small amounts of dissolved sulfur.

The desired composition of the Bessemer matte product is highly dependent upon the requirements of the downstream processing. Important parameters are the final iron and sulfur contents. These levels are generally controlled by the degree of blowing and the temperature of blowing. Conversion of the Ni-Cu matte is normally a batch process and is carried out in the following stages:

a) "Slag Blows", which involve filling the converter with molten matte and oxidizing FeS to iron oxides and SO_2 gas. The oxides are slagged with a siliceous flux and removed by successive skimmings (removal of the slag by pouring off the top of the matte). The iron content of the matte is kept above about 10% Fe. The temperature during this stage is generally kept between about 1150°C and 1300°C .

b) "Finishing Blows", which consist of oxidation of more FeS without taking further molten matte and then producing matte containing approximately 3% Fe.

c) "Dry-Up Blows", which are carried out by oxidizing most of the remaining FeS and simultaneously chilling the melt by the addition of excessive amounts of flux and cold dope (normally solid crust and drippings from matte and slag transfer operations) until the converter melt is at about 1% Fe. At the end of this blow, the melt temperature may vary between 1100°C and 1250°C depending upon the blowing temperature, the availability of the coolant and the matte refining technique.

d) "Cooling", is the last step in the production of Bessemer matte. In this step the residual Fe is oxidized and the melt is cooled by convection and radiation losses to 700°C - 1100°C depending upon matte composition and further processing requirements. This step typically yields a final product containing about 1% iron or less and for this stage, the melt is normally transferred to another similar converter dedicated for this purpose.

During the dry-up blow, particularly towards the end, there is a substantial amount of nickel and cobalt oxidation as well as magnetite (Fe_3O_4) formation. The result is a very viscous slag that is

difficult to remove from the converter. Excess fluxing and cold dope addition during this blow further aggravate the situation. When the melt is removed from the converter, large quantity of "mush" consisting mainly of magnetite, nickel oxide (NiO), fayalite slag ($x\text{FeO}-y\text{SiO}_2$) and undissolved flux remain in the converter. This mush must be digested by the furnace matte at the start of the next converting cycle. This imposes limitations on the grade of matte that can be produced by the upstream primary smelting units.

The function of the cooling step is two-fold; removal of most of the iron by cooling and/or minor blowing of the melt, and cooling of the converter melt to temperatures appropriate for the subsequent treatment of the Bessemer matte. Cooling takes place by natural convection and radiation and typically lasts up to four hours.

There are several disadvantages with the current procedures. First, the large quantity of mush remaining in the converter after dry-up must be redissolved during the first blow of the next converting cycle, and this imposes matte grade limitations. Enough FeS must be present in the incoming matte to provide both fuel to heat the mush and to act as a reductant to aid in dissolution. Second, the lengthy cooling period during the cooling stage places severe restrictions on the efficient use of equipment for converting operations. Third, any material added as coolant only partially dissolves in the matte and the mush also must be redissolved in the next charge.

SUMMARY OF THE INVENTION

Accordingly, molten nickel-copper mattes are finished to Bessemer quality and cooled to the appropriate casting temperature by blowing with nitrogen and/or nitrogen-oxygen (air) mixtures. Use of nitrogen promotes cooling and aids in controlled iron oxidation thus improving control over the final iron level in the Bessemer matte.

PREFERRED MODE FOR CARRYING OUT THE INVENTION

The instant invention utilizes tonnage nitrogen or nitrogen/oxygen (air) mixtures as an operating gas to both control the oxidation of and improve the cooling of Ni/Cu converter matte. More specifically, it relates to controlling the oxidation rate toward the end of the conversion cycle of Cu/Ni Bessemer matte; minimizing mush formation; regulating the converting temperature and matte com-

position during the last stages of conversion; and accelerating the cooling of the matte to a temperature consistent with good skimming, casting and the subsequent refining process.

Cooling by blowing with nitrogen enriched gas streams shortens cycle times and improves converter productivity.

The usage of nitrogen also aids in the overall cost effectiveness of the entire nickel-copper refining operation since oftentimes the site must generate and store pure oxygen for various unrelated purposes. Rather than throwing off the nitrogen as waste gas, it is collected and further utilized in the instant process.

Many of the enumerated problems can be minimized by blowing with nitrogen and/or nitrogen-oxygen (air) mixtures during the cooling cycle. By adjusting the rate of blowing and the nitrogen content of the blast, the cooling rate of the matte can be enhanced and simultaneously, the rate of oxidation and final iron and sulfur content of the matte can be controlled. Hence the need for matte transfer to a dedicated vessel and coolant addition is removed resulting in shorter cycle times, increased flexibility and increased productivity.

The addition of nitrogen to the air or oxygen blast can also be used as a control over the sulfur levels in Bessemer matte. In conventional practice, the final sulfur content in Bessemer matte is primarily controlled by blowing temperature - raising the temperature decreases the sulfur level and lowering the blowing temperature tends to increase final sulfur. Dilution of the blast with nitrogen tends to purge the bath of sulfur giving added control over the composition of the final Bessemer matte.

Nitrogen addition to the air or oxygen blast is useful for a number of different converter processes. In one instance the nitrogen/air or nitrogen/oxygen mixture may be used to finish the matte and control the iron and sulfur contents. Alternatively, the nitrogen may be used primarily for cooling the matte -- iron and sulfur control in this instance may not be a major factor.

The quantity and duration of the nitrogen addition is a function of the type, temperature and quantity of the matte.

For a typical dry-up finishing blow, the matte generally contains about 3% iron or less. Nitrogen should preferably be mixed with air in about a 0.5-2:1 volume ratio and the mixture delivered to the converter at a rate of about 2.5 - 7.5 cubic meters/minute per metric tonne of matte. In the event that nitrogen is added to oxygen, the volume ratio should be about 6-14:1 and delivery rate is about 2.5 - 7.5 cubic meters/minute per metric tonne of matte. Clearly, these parameters may be varied to adjust the conditions at hand.

For a typical cooling blow, the finished matte generally contains 1-3% iron or less at a temperature of about 1100°C - 1250°C. Nitrogen should preferably be mixed with air or oxygen in about 3-20:1 or 20-100:1 volume ratios respectively. The delivery rates should be about 2.5-7.5 cubic meters/minute per metric tonne of matte. The volumes of gas introduced into the converter should be chosen to reduce the temperature by about 50°C- 200°C. Again, the numbers may be varied depending on the circumstances.

Alternatively, nitrogen only may be used to cool the matte. Preferably about 2-4 cubic meters/minute per metric tonne of matte may be added to reduce the temperature of the matte.

Since it is generally easier to measure quantities of oxygen than quantities of nitrogen, it is most useful to employ an oxygen analyzer to calibrate and measure the gas going into the converter. By knowing the oxygen level the nitrogen level can be ascertained. Accordingly, when nitrogen containing operating gas is introduced into the converter the blast may contain about 5-15% oxygen (or about 23-70% air) for oxidizing purposes and about 1-5% oxygen (or 5-20% air) for cooling purposes.

It will be appreciated that advantages may accrue by starting nitrogen dilution immediately after the start of the finishing blows, with about 10% Fe, and progressively increasing the dilution as conversion continues. In this way, close control over matte composition and temperature throughout the final blows may be achieved leading to more consistent final product and temperature.

Three non-limiting examples describe the efficacy of the invention.

Example A: The Use of N₂-Air For The Dry-Up Blow

Approximately 120 tonnes of partially converted matte at 1230°C and assaying 2.6% Fe were transferred into a Peirce-Smith converter equipped for blowing N₂-air mixtures through the tuyeres.

The converter was turned into the blowing position and a mixture of 311.5 m³ min⁻¹ (11,000 scfm) of air and 215.2 m³ min⁻¹ (7600 scfm) of nitrogen was blown through 42 tuyeres for 21 minutes. An oxygen analyzer installed in the line indicated that the blast contained 11.6% O₂ by volume. After completion of the blow the matte assayed 1.3% Fe and was at 1150°C. About 5261 kg (5.8 tons) of mush remained in the converter in the form of an 203 mm (8 inch) layer of hard finish. The matte was transferred for further processing and the mush was sampled. Assays showed the mush to be approximately 43% matte, 26% flux

and 31% base metal oxides.

Example B: The Use of N₂ Air To Cool A Charge Of Bessemer Matte

Using the same equipment as in Example A, approximately 120 tonnes of finishing matte assaying 0.89% Fe and at 1160°C were blown with a nitrogen-air mixture to cool it to the casting temperature. The blast mixture consisted of about 31.1 m³ min⁻¹ (1100 scfm) of air and 229.3 m³ min⁻¹ (8100 scfm) of N₂ and was blown for 22 minutes through 25 tuyeres. An oxygen analyzer indicated that the blast contained 3.1% O₂ by volume. After completion of the blow, the matte assayed 0.29% Fe and had been cooled to 1000°C. The matte was cast. Only a small amount of mush remained in the converter. Assays showed this mush to be 59% Bessemer matte, 22% flux and 19% base metal oxides.

Example C: The Use Of N₂-Air For Dry-Up Followed By Cooling

The same equipment employed in Examples A and B was used. Approximately 120 tonnes of matte at 1150°C and assaying 1.3% Fe was blown with 15.7 m³ min⁻¹ (555 scfm) air and 224 m³ min⁻¹ (7930 scfm) nitrogen (2.7 volume %O₂ by analyzers) injected through 25 tuyeres. The blow lasted a total of 68 minutes and during this period 3629 kgs (4 tons) of flux was added. After the blow the matte temperature was 1000°C and the iron content equalled 0.34%. The Bessemer matte was cast leaving about 5-8 tonnes of hard finish behind. Samples of this mush assayed about 53% Bessemer matte, 28% flux and 10% base metal oxides.

The prior art has taught the use of nitrogen in pyrometallurgy. However, there has been no appreciation that the affirmative introduction of nitrogen enriched blast in a nickel-copper converter would lead to increased oxidation control, cooling and reduced mush formation. For example, U.S. patent 3,671,197 discloses the use of an inert gas, such as nitrogen, to free sulfur from pyrite to form roasted pyrrhotite. The gas is subsequently stripped of its sulfur content. The production of iron oxide is the ultimate aim. Canadian patent 973,720 (assigned to the instant assignee) discloses the use of a purge gas, including nitrogen, for refining cemented copper containing impurities. The purge gas causes the copper bath, previously treated to slag iron therein, to volatilize the impurities.

In comparison with the prior practice and the prior art, the following advantages are achieved

with the instant process:

- 1) The amount of mush remaining from the dry-up and cooling cycles is reduced, thus reducing the amount of material which must be redigested in the next cycle.
- 2) The rate of matte cooling is enhanced resulting in shorter cycle times and increased productivity.
- 3) The need for transfer to a dedicated cooling vessel is removed decreasing scrap generation and increasing flexibility and productivity.
- 4) Nitrogen cooling allows the treatment of higher grade primary mattes.
- 5) The process can use by-product nitrogen from the production of tonnage oxygen, a common commodity in many non-ferrous smelters.
- 6) The nitrogen or N₂/air or oxygen mixture can be blown through conventional tuyeres.

Claims

1. A process for treating molten nickel-copper matte derived from sulfide ores, the process comprising:

- a) Introducing the molten nickel-copper matte into a pyrometallurgical vessel,
- b) introducing an operating gas affirmatively enriched with nitrogen into the vessel; and
- c) removing the matte from the vessel.

2. The process according to claim 1 including oxidizing the matte with the operating gas and cooling the matte with the nitrogen affirmatively employed.

3. The process according to claim 1 including combining nitrogen and an oxygen containing gas to form the operating gas and introducing the operating gas into the matte.

4. A process for treating molten matte derived from sulfide ores, the matte including iron sulfide and additional metal sulfides, the process comprising;

- a) introducing the molten matte into a pyrometallurgical vessel;
- b) combining nitrogen and an oxygen containing gas to form an operating gas;
- c) introducing the operating gas into the vessel;
- d) oxidizing at least a portion of the iron sulfide contained in the matte in the presence of the operating gas;
- e) forming an iron containing slag on the surface of the matte, and
- f) separating the slag from the matte.

5. The process according to claim 4 including cooling the matte with the operating gas.

6. The process according to claim 4 including introducing an operating gas having a nitrogen-oxygen ratio of about 6-14 into the vessel at a rate of about 2.5-7.5 cubic meters/minute per metric

tonne of matte.

7. The process according to claim 4 wherein the oxygen level of the operating gas ranges from about 5-15%.

8. A process for creating molten matte derived from sulfide ores, the matte including iron sulfide and additional metal sulfides, the process comprising:

- a) introducing the molten matte into a pyrometallurgical vessel;
- b) introducing a nitrogen enriched operating gas into the vessel;
- c) cooling the matte with the operating gas; and
- d) removing the matte from the vessel.

9. The process according to claim 8 including introducing into the vessel the operating gas having a nitrogen-oxygen ratio of about 20-100:1 at a rate of about 2.5-7.5 cubic meters/minute per metric tonne of matte.

10. The process according to claim 8 wherein the oxygen level of the operating gas ranges from about 1-5%.



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EUROPEAN SEARCH REPORT

Application Number

EP 90 30 8320

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
X	SOVIET INVENTIONS ILLUSTRATED section chemistry, week C 41, abstract no. 80-72944 M/25, 19 November 1980, Derwent Publications Ltd., London, GB; & SU-A717147 (GIPRONIKEL) 25.02.1980 - - -	1	C 22 B 15/06 C 22 B 23/02
A,D	US-A-3 671 197 (N.E. MASCIIO) - - -		
A,D	US-A-3 767 383 (M.C.E. BELL et al.) - - -		
A	US-A-4 171 216 (P.J. LEROY) * claims 7,8 *	1	
A	US-A-4 504 309 (P.J. MACKEY et al.) * columns 2,3 *		
A	GB-A-2 006 180 (INCO) * claim 7 * - - - - -		
The present search report has been drawn up for all claims			TECHNICAL FIELDS SEARCHED (Int. Cl.5) C 22 B 15/06 C 22 B 23/02
Place of search Berlin		Date of completion of search 09 November 90	Examiner SUTOR W
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document			