

[54] **REDUCTION OF NICKEL AND COBALT OXIDES IN A MOLTEN METAL BATH OF CONTROLLED OXYGEN CONTENT**

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[57] **ABSTRACT**

Metal oxides, including oxides of nickel and cobalt and compounds heat decomposable thereto, and a carbonaceous reductant are introduced into a turbulent bath of the corresponding metal which bath contains at least about 0.01 percent dissolved oxygen to maintain the dissolved oxygen content of the bath at at least about 0.01 percent but less than saturation, while the carbonaceous reductant reacts to generate carbon monoxide. The metal bath is maintained in the molten state by burning above the bath carbon monoxide generated in situ and hydrocarbon fuels with an excess of free oxygen. Impurities oxidizable to volatile oxides can be eliminated by subjecting the oxygen-containing bath, or a part thereof, to subatmospheric pressures, or the metal bath can be surface blown with a free oxygen-containing gas to adjust the oxygen content of the bath before subatmospheric treatment.

24 Claims, No Drawings

REDUCTION OF NICKEL AND COBALT OXIDES IN A MOLTEN METAL BATH OF CONTROLLED OXYGEN CONTENT

This invention pertains to reducing metal oxides and more particularly to reducing and refining metal oxides, including nickel and nickel-containing materials, by pyrometallurgical and vapometallurgical techniques.

Nickel oxide is frequently an intermediate product in the commercial recovery of nickel from its ores, whether oxide or sulfide. For example, in the treatment of lateritic ores by selective reduction and ammoniacal ammonium carbonate leaching, nickel oxide is obtained by calcining precipitated basic nickel carbonate. In treating sulfide ores, nickel sulfide concentrate, obtained by matte separation including slow cooling and subsequent comminution, is roasted to nickel oxide. Nickel oxide produced by either of these processes can be employed, if it is sufficiently pure, for alloying purposes. Often, however, a more pure form of nickel is required, and nickel oxide must be reduced for further refining. Sulfur contamination problems are frequently encountered during reduction of nickel oxide, unless more expensive fuels, deficient in sulfur, are employed. If low sulfur fuels are not employed, sulfur dissolved in molten nickel must be removed therefrom, e.g., by treatment with a flux rich in lime. This latter procedure is not entirely satisfactory since it involves an additional treatment, additional fluxing materials, is time consuming and may create furnace refractory problems. Although attempts were made to overcome the foregoing difficulties and other disadvantages, none, as far as we are aware, was entirely successful when carried into practice commercially on an industrial scale.

It has now been discovered that metal oxides, including nickel oxides, cobalt oxides and compounds heat decomposable thereto, can be directly and continuously melted and refined by a combination of pyrometallurgical and vapometallurgical operations. The combination of processes allows the use of fuels containing substantial amounts of sulfur and also provides a process for lowering the content of impurities such as lead, zinc, cadmium, bismuth, antimony and other impurities which are volatile or have volatile oxides. The product obtained by the process has a low content of dissolved gases and is particularly suitable for continuous casting.

It is an object of the present invention to provide a combination of pyrometallurgical and vapometallurgical operations for refining nickel oxide and nickel-containing compounds heat decomposable to nickel oxide.

A further object of the present invention is to provide a pyrometallurgical process for the direct and continuous production of metals, including nickel and cobalt from their oxides and compounds heat decomposable to their oxides.

Other objects and advantages will become apparent from the following description.

Generally speaking, the present invention contemplates a process for reducing metal oxides. A turbulent bath of at least one metal selected from the group consisting of nickel and cobalt is established, which bath contains at least about 0.01 percent dissolved oxygen but not saturated therewith. At least one compound selected from the group consisting of nickel oxide, cobalt oxide and compounds heat decomposable thereto and a carbonaceous reductant are fed to the turbulent bath

while the dissolved oxygen content of the bath is maintained at at least 0.01 percent but less than saturation whereby the carbonaceous reductant reacts with the dissolved oxygen in the bath to generate carbon monoxide. The generated carbon monoxide and a fuel are burnt above the bath with a free-oxygen-containing gas to produce heat for maintaining the bath at operating temperatures. When it is desired to teem at least a portion of reduced metal from the bath, feeding of the compound to the bath is terminated so that the dissolved oxygen content of the bath is reduced by the carbonaceous reductant. Alternatively, a portion of the oxygen-containing bath can be teemed from the furnace and then subjected to a subatmospheric pressure treatment for final impurity elimination.

When the metal oxide or the reductant fuel contain impurities that are oxidizable to volatile oxides, the oxygen-containing bath can be directly subjected to a subatmospheric pressure treatment so that the oxidized impurities are more effectively volatilized from the bath. Alternatively, dissolved oxygen can be incorporated into the bath by surface blowing the bath with a free-oxygen-containing gas before the subatmospheric pressure treatment or by passing a free-oxygen-containing gas through the metal bath during the subatmospheric pressure treatment.

Oxides, compounds heat decomposable to the oxides of nickel and cobalt, and materials containing these compounds can be treated in accordance with the process of the present invention. Compounds heat decomposable to the oxides include, but are not limited thereto, hydroxides, carbonates, basic carbonates and nitrates of nickel and cobalt. These compounds are often produced by hydrometallurgical techniques and are contaminated by various impurities, most of which can be eliminated by practice of the process in accordance with the present invention. Impurities which can be volatilized or oxidized and volatilized include antimony, bismuth, cadmium, lead, sulfur and zinc. The total content of the aforementioned metallic impurities can amount to as much as about 0.5 percent while sulfur can amount to as much as about 3 percent, e.g., about 2 percent. Compounds produced by hydrometallurgical techniques frequently contain nuisance amounts of gangue such as alumina, calcium, magnesia and silica and the process of the present invention provides a highly effective mode for separating these constituents from nickel and/or cobalt.

A highly important feature of the present invention is the exceptionally high production rates that are achieved by maintaining the oxygen content of the turbulent bath at at least about 0.01 percent, or about 0.02 percent and even higher, when the metal oxide and the reductant are being added to the bath. In fact, when this technique is employed, commercial production rates are approached with only pilot-plant-sized apparatus. High temperatures, e.g., about 50°C. or even 100°C. above the melting point of the metal bath, and turbulence of the metal bath are the two factors that are most important in controlling the oxygen content in the metal bath. Advantageously, the metal bath is established in a top blown rotary furnace in which the bath can be independently agitated and maintained at high temperatures. Use of a top blown rotary furnace has many advantages with the foremost being the independent control of temperature, atmosphere and agitation. Further advantages flowing from the use of top

blown rotary converters include high thermal and chemical efficiencies provided by the rotating refractories and by the turbulence of the bath.

A carbonaceous reductant, such as coal, coke, charcoal or even liquid hydrocarbons, is added to the oxygen-containing metal bath to reduce the dissolved oxygen. The reduction reaction is so extremely rapid, particularly when conducted in a top blown rotary converter, that nickel oxide or cobalt oxide and the carbonaceous reductant can be added to the bath in a continuous or semicontinuous manner. The reduction reaction is so rapid and energetic that a carbon monoxide boil can be observed. Not only is the carbon monoxide boil important as a measure of the rate of the reaction; but, even more importantly, the boil agitates the metal so vigorously that the formation of a quiescent refractory oxide layer is avoided whereby briquetted nickel oxide and compounds heat decomposable thereto are rapidly wetted by and dissolved in the metal bath and do not merely float on a quiescent refractory layer. Carbonaceous reductant is added to the oxygen-containing metal bath in amounts necessary to substantially satisfy the reduction stoichiometry and to provide carbon monoxide to at least partially satisfy the heat requirements. Greater amounts of reductant can be added to insure complete reduction and to act as a source of fuel which can be burned by reaction with free-oxygen-containing gases.

In order to minimize metal losses and other problems associated with dusting, finely divided nickel oxides and compounds heat decomposable thereto are briquetted or otherwise put into an agglomerated state. During agglomeration reductant and fuel, either liquid or solid, can be incorporated in the briquettes or pellets. A highly advantageous embodiment is to incorporate into the pellets liquid hydrocarbons, such as Bunker C fuel oil during briquetting, so that at least part of the reductant and/or fuel can be added via the pellets. In addition to providing reductant and fuel, the incorporation of liquid hydrocarbons during the briquetting operation has the further addition of lowering, or even eliminating, the use of water as a binder, thereby lowering fuel costs attributable to drying and vaporizing such water. Moreover, liquid hydrocarbon, such as Bunker C oil, are particularly kinetically active reductants. The amount of reductant incorporated in the pellets can vary within wide limits. Less than stoichiometric amounts of reductant can be incorporated in the briquettes with difference being made up by the addition of coke or other solid reductant to the bath. If more than stoichiometric amounts of reductant are incorporated in the briquetted nickel oxide or other compounds heat decomposable thereto, the oxygen content of the molten nickel bath can be maintained above about 0.01 percent by surface blowing the bath with a free-oxygen-containing gas to burn the excess reductant and to incorporate oxygen in the bath, or by the addition of reductant-free briquetted oxide. The presence of excess reductant is readily ascertained since the vigor of the carbon monoxide boil rapidly diminishes.

Since the overall process is endothermic heat must be supplied to the metal bath to maintain it in a molten state. Heat can be supplied by burning above the bath carbon monoxide generated in situ or the carbonaceous reductant with a free-oxygen-containing gas and/or by burning a fuel with a free-oxygen-containing gas in a burner provided for this purpose. The fuel can be

the same as the reductant or can be gaseous (e.g., natural gas) and does not have to be sulfur free. Sufficient heat is generated by any or all of these methods to maintain the metal bath at a temperature of at least about 50°C. or even 100°C. above its melting point to promote dissolution of the oxide and to increase reduction kinetics.

An important feature of the present invention is the subatmospheric pressure treatment for final impurity elimination. A bath containing the requisite amounts of dissolved oxygen can be produced in the vacuum unit and is advantageously so done during final impurity elimination. However, when the starting material contains large quantities, e.g., about 4 percent, of impurities which are volatile or oxidized to volatile species, the demands placed on the vacuum unit render such a procedure commercially impractical. Therefore, it is preferred, in most instances, to incorporate oxygen into the molten bath by other means. From the standpoint of economy, efficiency in operation and controllability, the oxygen content of the bath can be controlled by terminating the addition of carbonaceous reductant to the bath while continuing the addition of oxides or by surface blowing the surface of the bath with a free-oxygen-containing gas.

In practice, a turbulent bath of at least one metal selected from the group consisting of nickel and cobalt and having at least 0.01 percent oxygen but not saturated therewith is established in a rotary converter that is provided with means for partially combusting hydrocarbon fuel above the bath to generate heat and means for surface blowing the metal bath with a gas containing free oxygen. The rotary converter is rotated to maintain the metal bath in a turbulent state and briquetted oxides, or compounds heat decomposable to oxides, of nickel and cobalt are fed to the turbulent metal bath to maintain the dissolved oxygen in the bath at the aforescribed levels. Carbonaceous reductants are added to the oxygen-containing metal bath to rapidly and energetically reduce the oxide fed to the bath. The amounts of oxide and reductant added to the bath are proportioned to insure that the bath contains at least about 0.01 percent oxygen and does not reach saturation levels. Precautions need not be taken to insure that the fuel has a low sulfur content since sulfur absorbed by the bath will be subsequently removed by the subatmospheric pressure treatment. Carbon monoxide generated by the reduction reactions, the carbonaceous reductant and fuel introduced via the burner are burned with an excess of free oxygen to maintain the bath at a temperature at least about 50°C. above its melting point. The additions of agglomerated oxide and solid reductants can be simultaneous or can be repeatedly alternated until the furnace capacity is approached. When the capacity of the furnace is approached, the oxygen content of the bath can be adjusted so that the metal can be cast into product form. Alternatively, the oxygen content of the bath can be adjusted for final impurity elimination during a subatmospheric pressure treatment.

When it is desirable to further purify the metal bath, the bath is subjected to a vacuum treatment for final impurity elimination. It is advantageous for thermodynamic and kinetic reasons to subject the metal bath to a vacuum of less than about 0.1 atmosphere and advantageously to a pressure less than about 0.01 atmosphere or even less than about 0.001 atmosphere. If the bath

is deficient in oxygen, additional oxygen can be added thereto. Advantageously, gaseous oxygen is introduced into the molten bath to overcome any oxygen deficiencies. The addition of oxygen during the low pressure treatment is advantageous in that it lessens the need to incorporate all the oxygen required for final impurity elimination by surface blowing during the smelting operation and thereof avoids the problems associated with possible formation of undesirable and inactive metal oxide dross. Gaseous oxygen can be added as air, oxygen-enriched air, preheated air or commercial oxygen.

Maintenance of the metal bath in a turbulent state during the vacuum treatment is highly desirable since independently induced turbulence is generally of such intensity that the bath is sufficiently mixed such that approach to equilibrium is materially increased. Furthermore, constant mixing continually provides fresh surfaces from which volatilization can occur without overcoming the pressure head of the metal bath. During the vacuum treatment, the bath can be maintained in a turbulent state by pneumatic means (e.g., by the addition of a free-oxygen-containing gas), as well as by mechanical agitation, magnetic means or electromagnetic stirring.

For kinetic reasons and to insure more complete impurity elimination, the metal bath is maintained at a temperature of at least about 50°C. above its melting point during the vacuum treatment. Even better results are obtained by maintaining the metal bath at a temperature of about 100°C. above its melting point. Higher temperatures provide better results by increasing the vapor pressure of the volatile impurities, by thermodynamically insuring more complete reactions when impurities are being eliminated as volatile oxides and by the amount of dissolved oxygen to thereby increase the driving force of this oxidizing reaction. In addition to rapid sulfur elimination down to about 0.5 percent and advantageously below about 0.01 percent sulfur, impurities such as bismuth and lead can be eliminated to almost undetectable amounts. The subatmospheric pressure treatment is advantageously continued after elimination of impurities without further oxygen additions to degas the metal.

After the refining and deoxidation operations, the metal bath can be finally deoxidized by the addition of carbon, silicon, aluminum, or calcium silicon. Deoxidation can also be effected by lancing the turbulent bath with methane or other gaseous hydrocarbons or by passing a reducing gas containing carbon monoxide, hydrogen or methane through the molten bath or by surface blowing the bath with such reducing gases. Advantageously, after both final impurity elimination and deoxidation, the melt is degassed under subatmospheric pressures to provide a final metal product that has a low content of dissolved gases which product is particularly suitable for continuous casting.

Refining and degassing can be conducted in a suitable vacuum chamber in which low pressures are maintained by mechanical pumps, steam ejector systems, or any other system capable of pumping large volumes of gas at low pressures. The vacuum chamber is equipped with means for controlling the temperature of the molten bath. For instance, the vacuum unit can be heated by induction or by carbon arc or by other means. The molten bath can be maintained in a state of turbulence

while undergoing vacuum treatment by electromagnetic stirring or by pneumatic or mechanical means.

For the purpose of giving those skilled in the art a better understanding of the invention, the following illustrative examples are given:

EXAMPLE I

A charge consisting of 1.5 inches \times 1 inch \times 1 inch briquettes of basic nickel carbonate analyzing approximately 54 percent nickel plus cobalt on a dry basis, and containing about 20 percent moisture was fed into a rotary converter operating at 20 revolutions per minute. The converter contained a bath of molten nickel maintained at about 2,950°F. and containing approximately 0.1 percent dissolved oxygen. The carbonate was added at 80 pounds per minute, and metallurgical coke at the rate of 9.6 pounds per minute. A very vigorous boil was maintained, and the carbonate and coke was almost immediately reacted. The converter was maintained at between 2,900°F. and 2,980°F. by burning natural gas within excess of the stoichiometric requirement of oxygen. The amount of oxygen was such that the gas exiting from the converter was contained between about 0 and 3 percent carbon monoxide. The carbon monoxide from the reduction of nickel oxide by carbon was therefore being largely burned to carbon dioxide in the converter, supplying a significant portion of the heat requirements for the process. Dust losses to the converter stock were negligible.

After teeming a portion of the heat, a further test on this heat was continued at a higher smelting rate. At 100 pounds per minute carbonate, the reaction of the carbonate and coke was still much faster than the rate of addition. The gas velocity out of this small converter was higher than the available gas handling capabilities of the flue system. Thus, even higher smelting rates may be possible with equipment engineered for this application.

EXAMPLE II

A heat of nickel similar to that obtained in the previous example containing 0.8 percent sulfur and just saturated with oxygen at 2,900°F. was held in a 750 kilowatt, 180 cycle vacuum induction furnace. The furnace was gradually evacuated to a fine vacuum of about 0.1 mm. of mercury using up to 6 stages of a 7-stage steam ejector. A vigorous boil occurred as the vacuum was taken below 100 mm. mercury because of the rapid withdrawal of SO₂. After a total evacuation time of approximately 2 hours, the sulfur was analyzed at 0.003 percent. The heat was then deoxidized using graphite as the reductant to produce a final metal having an analysis of 0.003 percent sulfur and about 0.01 percent carbon.

It will be observed that the present invention provides a process for reducing metal compound. The process comprises establishing a bath of at least one metal selected from the group consisting of nickel and cobalt, which bath contains at least about 0.1 percent dissolved oxygen (and advantageously at least about 0.1 percent dissolved oxygen). At least one compound selected from the group consisting of nickel oxide, cobalt oxide, and compounds heat decomposable thereto and a carbonaceous reductant are fed to the bath while the dissolved oxygen content of the bath is maintained at at least 0.01 percent (and advantageously at least about 0.1 percent) whereby the carbonaceous reductant re-

acts with the dissolved oxygen in the bath to generate carbon monoxide. The generated carbon monoxide and a fuel are burned above the bath with free-oxygen-containing gas to heat the bath to operating temperatures. A portion of reduced metal is recovered from the bath.

Although the present invention has been described in conjunction with preferred embodiments it is to be understood that modifications and variations may be resorted to without departing from the spirit and scope of the invention as those skilled in the art will readily understand. Such modifications and variations are considered to be within the purview and scope of the invention and appended claims.

We claim:

1. A process for reducing a metal compound which comprises: establishing a bath of at least one metal selected from the group consisting of nickel and cobalt, which bath contains at least about 0.01 percent dissolved oxygen; feeding at least one compound selected from the group consisting of nickel oxide, cobalt oxide, and compounds heat decomposable thereto and a carbonaceous reductant to the bath while the dissolved oxygen content of the bath is maintained at at least about 0.01 percent whereby the carbonaceous reductant reacts with the dissolved oxygen in the bath to generate carbon monoxide; burning the generated carbon monoxide and a fuel with a free-oxygen-containing gas above the bath to produce heat for maintaining the bath at operating temperatures; and recovering a portion of reduced metal from the bath.

2. The process as described in claim 1 wherein the bath contains at least about 0.1 percent dissolved oxygen but is not saturated therewith.

3. A process for reducing a nickel compound which comprises: establishing a turbulent nickel bath which contains at least about 0.01 percent dissolved oxygen but not saturated therewith; feeding at least one nickel compound selected from the group consisting of nickel oxide and compounds heat decomposable thereto and a carbonaceous reductant to the nickel bath while maintaining the dissolved oxygen level of the nickel bath at at least about 0.01 percent but less than saturation whereby the carbonaceous reductant reacts with the dissolved oxygen content in the nickel bath to generate carbon monoxide; burning the generated carbon monoxide and a fuel with a free-oxygen-containing gas above the nickel bath to produce heat for maintaining the bath at operating temperatures; and recovering nickel from the nickel bath.

4. A process for reducing a cobalt compound which comprises: establishing a turbulent cobalt bath containing at least about 0.01 percent dissolved oxygen but not saturated therewith; feeding at least one cobalt compound selected from the group consisting of cobalt oxide and compounds heat decomposable thereto and a carbonaceous reductant to the cobalt bath whereby the carbonaceous reductant reacts with the dissolved oxygen in the cobalt bath to generate carbon monoxide; burning the generated carbon monoxide and a fuel with a free-oxygen-containing gas above the cobalt bath to produce heat for maintaining the cobalt bath at operating temperatures; and recovering cobalt metal

from the cobalt bath.

5. The process as described in claim 1 wherein the compound is fed to the bath as briquettes.

6. The process as described in claim 5 wherein the carbonaceous reductant is incorporated in the briquetted compound.

7. The process as described in claim 6 wherein the carbonaceous reductant is a liquid hydrocarbon.

8. The process as described in claim 7 wherein the liquid hydrocarbon is Bunker C oil.

9. The process as described in claim 8 wherein the liquid hydrocarbon is incorporated in the briquette in amounts less than is required to satisfy the stoichiometry of the reduction reactions.

10. The process as described in claim 8 wherein the liquid hydrocarbon is incorporated in the pellets in amounts substantially equal to that required to satisfy the stoichiometry of the reduction reactions.

11. The process as described in claim 8 wherein the liquid hydrocarbon is incorporated in the briquettes in amounts in excess of that required to satisfy the stoichiometry of the reduction reactions and the surface of the metal bath is surface blown with a free-oxygen-containing gas to maintain the dissolved oxygen content of the bath at at least about 0.01 percent.

12. The process as described in claim 1 wherein the bath is maintained at a temperature of at least about 50°C. above its melting point.

13. The process as described in claim 12 wherein the metal bath is maintained at a temperature of at least about 100°C. above its melting point.

14. The process as described in claim 1 wherein feeding of the compound to the bath is terminated so that the dissolved oxygen content of the bath is reduced by the reductant before the metal is recovered from the bath.

15. The process as described in claim 1 wherein a portion of the oxygen-containing bath is teemed and then subjected to a subatmospheric pressure treatment for final impurity elimination.

16. The process as described in claim 15 wherein the teemed oxygen-containing bath is subjected to a subatmospheric pressure of less than about 0.1 atmosphere.

17. The process as described in claim 16 wherein the oxygen-containing bath is subjected to a subatmospheric pressure of less than about 0.01 atmosphere.

18. The process as described in claim 17 wherein the oxygen-containing bath is subjected to a subatmospheric pressure of less than about 0.001 atmosphere.

19. The process as described in claim 3 wherein the nickel compound is nickel oxide.

20. The process as described in claim 3 wherein the nickel compound is nickel hydroxide.

21. The process as described in claim 3 wherein the nickel compound is basic nickel carbonate.

22. The process as described in claim 4 wherein the cobalt compound is cobalt oxide.

23. The process as described in claim 4 wherein the cobalt compound is cobalt hydroxide.

24. The process as described in claim 4 wherein the cobalt compound is basic cobalt carbonate.

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