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REDUCTION KILN

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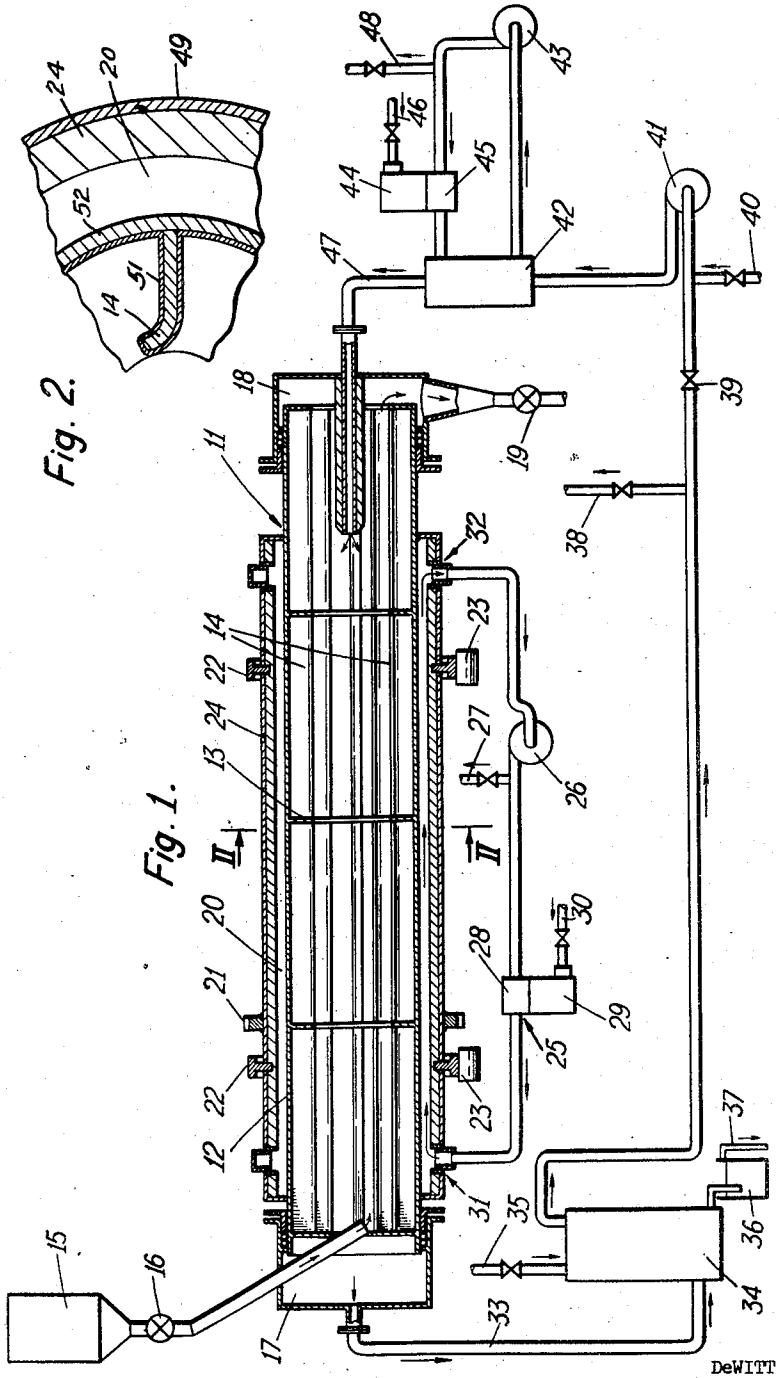

Fig. 2.

Fig. 1.

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REDUCTION KILN

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1 Claim. (Cl. 266—43)

The present invention relates to the reduction of nickeliferous materials in a rotary kiln; and more particularly to the reduction of nickel oxide and roasted nickel mattes in a rotary kiln to produce nickel metal powder.

Heretofore, the art has endeavored to reduce nickeliferous materials such as nickel oxide or roasted nickel matte to nickel metal powder by heating the material in a rotary kiln in the presence of a reducing agent, for example, hydrogen or water gas. This reduction operation may be effected as a preliminary step to the production of nickel carbonyl from the reduced nickel. For this production of nickel carbonyl, the reduced nickel is required as a fine powder. A fine nickel metal powder may be produced if the nickeliferous material fed to the rotary kiln is finely-ground, sintered nickel oxide obtained by roasting nickel matte and the rotary kiln is externally heated, e.g., by gas burners.

Rotary kilns are commonly lined with steel or cast iron. It has been found that when such a rotary kiln is used for the reduction of nickeliferous material such as nickel oxide or roasted nickel matte, the metal powder produced in the rotary kiln sticks to or cakes on the kiln wall in such a manner that it is difficult to dislodge the metal powder from the kiln wall. This sticking or caking of the metal powder to the kiln wall was found to occur regardless of whether the nickeliferous material to be reduced was fed continuously to the kiln or the reduction was conducted as a batch operation. 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 nickeliferous material such as nickel oxide or roasted nickel matte may be reduced in a rotary kiln to nickel metal powder by employing a special lining material on the kiln walls such that sticking or caking of the reduced powder product to the rotary kiln wall is substantially eliminated.

It is an object of the present invention to provide a method of reducing nickeliferous material in a rotary kiln to nickel metal powder.

It is a further object of the invention to provide a rotary kiln which, particularly in reducing nickel oxide or roasted nickel matte, will facilitate the production of fine nickel metal powder.

The invention further contemplates providing a rotary kiln structure whereby detrimental effects, resulting from contact between the kiln walls and the material being reduced or the reduced powder product, are avoided.

Other objects and advantages will become apparent from the following description taken in conjunction with the accompanying drawing in which:

Figure 1 is a schematic diagram of an embodiment of the present invention in which the tubular reduction chamber of the novel rotary kiln is externally heated.

Figure 2 shows an enlarged section of a portion of the wall of the kiln.

Generally speaking, the present invention contemplates reducing nickeliferous material such as nickel oxide or roasted nickel matte in a rotary kiln provided with a special lining whereby sticking or caking of the material and of the reduced metal product to the kiln walls is substantially wholly eliminated. The walls of the rotary kiln which are in contact with the hot material being reduced or with the hot metal powder product are lined with a metal or alloy which is capable of forming a completely continuous oxide film that is irreducible at the temperature of the reduction operation, whereby sticking or caking of the powder material in the kiln even after prolonged exposure to the reduction conditions, is substantially eliminated. The reduction operation is conducted in a suitable atmosphere such as hydrogen or water gas. The reduction temperature is maintained between about 300° C. and about 600° C. and preferably within the range of about 350° C. to about 500° C. The novel rotary kiln is rotated at between about 0.1 to about 5 r.p.m. (revolutions per minute) dependent on diameter.

Without limiting the invention to any particular theory, it appears that one of the probable causes of sticking is an alloying tendency of the freshly reduced powder with the wall of the kiln, and that this may occur if there is a discontinuous oxide film, for example, of the type that forms on an alloy such as brass.

In carrying the invention into practice, it is preferred to line the kiln with aluminum, chromium, manganese or titanium or with an alloy rich in one or more of these metals.

Commercial aluminum containing more than 99% aluminum is much preferred as the kiln lining material, because it is easily applied and no difficulty is experienced on heating up due to the differential expansion between the lining and the steel base metal, provided the aluminum is not more than 20 thousandths of an inch thick and is sprayed on or calorised.

The novel rotary kiln is provided with the aforementioned special metal lining in the following manner:

The inner kiln steel shell is shot blasted including the lifters and retention dams and the aluminum is applied by means of a spray gun to a thickness of 5 to 20 thousandths of an inch, preferably 10 thousandths. An alternative method is to calorise the steel plates, lifters and dams to bond the aluminum to the steel and then assemble afterwards but this is not thought necessary.

There is no bond between the aluminum and base metal with the sprayed on lining.

The oxide film on the metal lining of the kiln of the present invention need not be very thick, particularly in an indirectly heated kiln where the metal lining must conduct heat. Usually, the metallic lining has a very thin coating of oxide. In the use of the preferred aluminum lining the film of oxide need not be visible to the naked eye. In general the oxide film on the metal lining of this invention need be only the usual thickness for oxide films on metals such as aluminum, understood to be several hundred A.U.s (1 A.U.$=10^{-8}$cms.) However, the oxide film may be as thick as $\frac{1}{100}$ inch but, preferably, is less than $\frac{1}{1000}$ inch thick.

Referring now to the drawing, there is depicted a novel rotary kiln **11** in accordance with this invention, wherein the special, metal-lined, kiln tube or chamber **12** wherein the reduction operation takes place is externally heated. The kiln tube **12** has therein retention dams **13** to regulate the flow of the material along the kiln tube. The kiln tube **12** is also provided with lifters **14** extending longitudinally along its inner surface to effect a stirring or tumbling of the material being treated. A feed bunker **15** controlled by a rotary valve **16** supplies material to be treated such as roasted nickel matte or nickeliferous oxide into the feed end of the kiln tube **12** through a

feed head 17 closing that end of the kiln tube 12. The material moves through the tube 12 to the discharge end of the tube which is closed by a discharge head 18. The removal of the roasted and reduced matte or reduced oxide from the discharge head 18 is controlled by a rotary valve 19. The walls of the kiln tube 12, the retention dams 13 and the lifters 14 are lined or coated with the aforementioned special metal lining or coating, preferably comprising aluminum. The kiln tube or chamber 12 may be externally heated, for example, by means of the surrounding heating jacket 20 provided with thermal insulation 24 and the flue gas heating means 25 comprising flue gas circulator 26, the exhaust to atmosphere 27, the flue gas mixer 28, and the heating furnace 29, with its producer gas intake 30. The heating gases are introduced into and removed from the rotary heating jacket 20 by means of sealing connections making a sliding fit to the jacket 20 as depicted at 31 and 32. The kiln is rotated by means of the girth gear 21 around the heating jacket 20. The jacket 20 is also provided with tires 22 bearing on support rollers 23. The inner, lined kiln tube 12 is welded at the ends to the jacket 20 and rotates with the latter. A special circuit is also provided for supplying and recirculating the reducing gas such as hydrogen. As depicted in the drawing the reducing gas flow is countercurrent to the movement of the solids through the kiln tube 12. It will be appreciated, however, that the reducing gas such as hydrogen or producer gas may flow concurrent or countercurrent to the solids as desired. In the system depicted in the drawing the spent hydrogen reducing gas is removed by a hydrogen outlet conduit 33 attached to the solids feed head 17. Conduit 33 leads to the scrubber 34, wherein scrubber water is introduced at 35 and from which water is removed by means of the lute pot or water seal 36 and water exit pipe 37. The cleaned hydrogen is partly purged to atmosphere by the relief valve 38 and the hydrogen flow then controlled by valve 39, after which make-up hydrogen is added at the valved inlet 40. The hydrogen atmosphere is then pumped by means of the hydrogen circulator 41 through the hydrogen pre-heater 42 and then through the hydrogen inlet conduit 47 leading through the reduced-solids discharge head 18 into the kiln tube 12. The hydrogen preheater 42 is a heat exchanger heated by flue gas circulated through flue gas circulator 43, vent to atmosphere 48, and flue gas mixer 45. The flue gas mixer 45 in turn is heated by a heater furnace 44 which is supplied with producer gas at inlet 46.

In Figure 2 the inner steel shell 52 is shown surrounded by thermal insulation or lagging 24 and an outer steel shell 49.

One lifter 14 and the inner steel shell 52 of the kiln tube 12 are clearly shown coated with aluminum 51.

Hydrogen is the preferred reducing gas because of the risk of carbonyl formation with reducing gases such as water gas or producer gas.

Two main kiln heating methods have been used. The preferred method is to use preheated hydrogen only with countercurrent flow of the hydrogen and the solids through the kiln together with external heating of the kiln shell. It has also been found that the reduction tube of the kiln may be heated directly by feeding therein preheated roasted matte and hydrogen with no external kiln shell heating. In the latter embodiment, concurrent flow of gas and roasted matte is preferably used.

Aluminized steel prepared by calorising aluminum onto steel or just aluminum sprayed on steel are both satisfactory for kiln linings up to at least 500° C. The satisfactory working life of such a lining is at least one year.

A good material for lining kilns for temperatures up to about 500° C. is a mixture of about 90% to 95% aluminum and about 10% to 5% alumina which has been sintered, extruded and rolled into sheet. This is known as S.A.P. The mechanical properties of this material are excellent when used in the range of 350° C. to 500° C. and, moreover, it has now been established that this material can be hammer welded, the resultant weld being as strong as the parent metal. While this material is useful for lining small kilns, its relatively high coefficient of expansion may present difficulties in its application to vary large kilns.

Various types of feed material, for example, roasted nickel matte, have been successfully reduced in kilns provided with the aforementioned aluminized, aluminum and aluminum-alumina linings. The material reduced varied in particle size from relatively coarse fluid bed calcined matte having a particle size of about minus ⅛ inch to very fine partially nickel extracted concentrate No. 1 having a particle size of about minus 200 mesh.

It has been found that sulphur bearing gases increased the tendency of a roasted matte to cake in the kiln, especially with the finer roasted mattes. Hence, when treating fine materials such as roasted mattes, precautions are taken to exclude sulphur containing gases from the reduction kiln. This may be accomplished by passing water gas or producer gas through iron ore or using hydrogen gas only.

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 sample of 87 pounds of sintered nickel oxide was reduced at 380° C. in a small externally heated kiln of mild steel rotated at 4 r.p.m. with purified (i.e. no sulphur gases) water gas as the reducing agent. The rate of reduction was surprisingly slow. On opening up the kiln it was found that the fine metal powder produced by the reduction operation had caked onto the wall of the kiln, the whole charge being evenly spread and leaving no loose particles in the kiln. In comparison, when another sample of 87 pounds of the same sintered nickel oxide was reduced under the same reducing conditions in a similar kiln having the exposed surfaces within the tubular reduction chamber of the kiln provided with a lining or coating of aluminum sheet about ⅛ inch thick in accordance with this invention, the rate of reduction was normal i.e., completed in 8 hours at 400° C. and there was no sticking of the fine metal powder produced by the reduction to the wall of the kiln. When the nickel oxide was fed continuously to the kiln, similar results were obtained. Furthermore, no sticking was observed even after several months operation at 480° C. The aluminum sheet lining was unsatisfactory however because it buckled due to differential expansion in the steel tube. This difficulty was overcome by the use of a sprayed on lining of aluminum.

Example II

Two further 87 pound samples of the nickel oxide of Example I were reduced using pure hydrogen as the reducing gas at a reduction temperature of 450° C., one sample being treated in the unlined mild steel kiln of Example I and the other sample being treated in the kiln of Example I having the lining in accordance with this invention. Both of these kilns in these further tests were rotated at a speed of 11 r.p.m. The results were similar to those obtained in Example I. Moreover, the caked metal powder in the mild steel kiln was not dislodged from the kiln wall by a loose steel bar in the kiln. Similar results were obtained when nickel oxide was fed continuously to the kiln. No sticking or caking was observed with the aluminum lined kiln operating at 480° C. over a period of operation of several months. When the sheet aluminum was replaced by aluminum sprayed on trouble due to buckling was eliminated and the estimated life of a 10 thousandth of an inch lining is at least 1 year.

It is to be noted that the present invention is not to be confused with materials such as alloys sold under the trade mark "Nimonic" and containing 60% nickel, 20% chromium, 20% cobalt, 18 chromium—8 nickel stainless

steel, and other chromium alloys such as: Chromium steels containing 6.5–24% chromium; 0.75–1.5% aluminium; 0.75–3.0% silicon; 0.1% carbon steels, which did not initially have adhesion of the solids being treated and/or the reduced product to the kiln walls, but which eventually failed after prolonged exposure to reducing conditions. An example of the operation of a kiln lined with one of these materials and showing the effect of prolonged exposure to the reducing conditions is as follows:

Example III

A sample of roasted nickel matte of a particle size of −60 mesh and hydrogen were fed concurrently into a 2 inch diameter rotary kiln lined with ordinary 18 chromium—8 nickel stainless steel rotated at 2.3 r.p.m. The reduction operation was conducted at a temperature of 450° C. Initially no sticking or caking of the material on the kiln wall was observed. However, after 14 days operation under the foregoing reduction conditions the stainless steel lining developed a surface to which reduced nickel adhered blocking the kiln tube completely.

In comparison with the foregoing test in a kiln lined with stainless steel, when another sample of the same roasted nickel matte was reduced under the same reducing conditions but in a similar kiln having the exposed surfaces within the tubular reduction chamber of the kiln provided with a lining or coating of aluminum about 1/16 inch thick in accordance with this invention, the reduction operation was conducted continuously for a period of over 56 days without any sticking or caking of the material in the kiln to the kiln wall.

The present invention is particularly applicable to reduction kilns where extra heat must be supplied through the walls of the kiln. The aluminum sprayed on coating is effective in preventing adhesion of metallic particles to any apparatus under hydrogen at temperatures over 300° C. Thus Herreschoff type reducers could be internally coated with aluminum to prevent caking. Also heated conveyor elements in the roasted and reduced nickel matte could be coated with aluminum.

Fluidizers for reduction of roasted nickel matte should also be lined with aluminum as it has been found that steel fluidizers caused sticking when used for reduction of nickel oxide.

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 claim.

We claim:

A rotary kiln for reducing nickel oxide to nickel metal powder comprising a steel kiln shell having on its interior surface a very thin completely continuous aluminum oxide coating, said coating being less than about 0.001 inch thick on a base made of about 90 to 95% aluminum with the balance essentially alumina, a jacket annularly spaced from the exterior surface of the kiln shell, means for introducing heating gases into the annular space between said jacket and said kiln shell, means for charging nickeliferous oxide material into said kiln shell, and means for introducing reducing gases into the kiln shell so that the reducing gases contact the nickeliferous oxide material and cause a reduction of the nickel oxide at a temperature from about 350° C. to about 500° C., said coating characterized by being substantially irreducible within said temperature range and by being free from sticking and caking of nickel oxide and of reduced nickel powder to its surface after prolonged exposure to hot reducing conditions.

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