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REFINING NICKEL

William J. Kroll, Niagara Falls, N. Y.

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This invention relates to metallurgical processes and more particularly to a process for refining nickel contaminated with metallic impurities to remove the metallic impurities therefrom.

Heretofore in the art, the preparation of substantially pure nickel or nickel containing relatively small amounts of metallic impurities has been exceedingly difficult and has required the practice of complicated and costly processes.

The object of the present invention is to provide a process for the elimination of associated metal impurities from metallic nickel.

Another object is to provide a process for treating finely divided or comminuted metal consisting principally of nickel and containing associated metallic impurities to eliminate the associated metallic impurities therefrom.

Still another object is to provide an economical process of treating impure nickel to refine the same to a nickel product having a high degree of purity.

Other objects will be apparent as the invention is more fully hereinafter disclosed.

In accordance with the above objects I have discovered that, contrary to expectations based on known and published data relative to the same, nickel is relatively low in the displacement series of metals in molten metal chloride fusions in the system solid metal-molten chloride and that substantially all metals commonly associated with nickel in its ores and alloys, particularly the metals Cu, Fe, Co, Cr, Zn and Mn, lie above nickel in the said displacement series and will displace nickel from nickel chloride in such molten metal chloride fusions.

As a result of this discovery I have devised an improved method of treating impure nickel to eliminate therefrom substantially all associated metal impurities which consists essentially in reducing or comminuting the impure nickel to fine particle size and suspending or dispersing the same in a fused metal chloride bath containing nickel chloride for and extended time interval adapted to effect or obtain a removal of the said associated metallic impurities by a displacement reaction between the said impurities and the nickel chloride, then separating the metal from the fused bath.

There are many different ways in which the present invention may be adapted in the art of purifying nickel of its associated metallic impurities and of introducing the invention as an essential step in a process of recovering nickel from its ores. I will describe, first, the basic principles involved in the displacement reaction and, secondly, wherein this basic reaction may be adapted in the treatment of impure nickel metal powder in the elimination of certain heavy metal impurities and in the treatment of nickel scrap materials to eliminate therefrom associated metal impurities.

The basic displacement reaction of the present invention is complicated, to a certain extent by alloy and intermetallic compound formation between the nickel and the displacing metal and by the relative rates of diffusion of the two metals into and through each other. To overcome this complication and to reduce the same to a low order, it is essential to reduce the nickel to a small particle size or thin section thereby to reduce the diffusion path to the smallest distance that is economically practical to obtain.

The reaction involved is essentially one of displacement according to one or more of the reactions below indicated:

$$2Cu+NiCl_2 \rightleftarrows Ni+2CuCl$$
$$Fe+NiCl_2 \rightleftarrows Ni+FeCl_2$$
$$Co+NiCl_2 \rightleftarrows Ni+CoCl_2$$
$$Cr+NiCl_2 \rightleftarrows Ni+CrCl_2$$
$$Mn+NiCl_2 \rightleftarrows Ni+MnCl_2$$

(etc.)

This reaction will occur at all temperatures at which the $NiCl_2$ and the resultant chloride compound of the displacing metal may be maintained in a liquid anhydrous phase but the rate of the reaction increases markedly with increase in temperature and is most rapid at temperatures above about 700° C. and below the boiling point of the chloride compound of the displacing metal when this boiling point lies below that of nickel chloride (975° C.).

I have found, however, that by melting nickel chloride in a metal chloride fusion consisting principally of one or more of the chloride compounds of the most stable metal chlorides, such as the alkali and alkaline earth metal chlorides, a wide range of liquid anhydrous metal chloride fusion mixtures may be obtained that are highly stable and resistant to oxidation decomposition when heated in the open air to temperatures as high as 975° C. to 1000° C. and which are operative in accordance with the present invention at temperatures as low as 500° C.

In general, though, I prefer to employ a metal chloride fusion mixture consisting of potassium and sodium chlorides mixed in the ratio of 60% KCl and 40% NaCl and having a melting point of 650° C. To any given volume of this fusion mix I add $NiCl_2$ in the total amount desired relative to the associated metal impurities of the comminuted nickel dispersed therein, usually adding the said nickel chloride in such increments as may be necessary to maintain a large

excess of $NiCl_2$ over that theoretically required and preferably between 25 to 50% $NiCl_2$ (by weight) in the fusion mix. The addition of $NiCl_2$ to this preferred fusion mixture or base chloride fusion normally lowers the melting point to below 500° C. and temperatures as high as 1000° C. may be safely employed without excessive loss by volatilization of the nickel chloride.

The amount of comminuted nickel immersed and suspended in the molten metal chloride bath may be varied widely without essential departure from the present invention as one skilled in the art will recognize, and is primarily dependent upon the total amount of impurities it is desired to eliminate in one treatment. As the displacement reaction involved results not only in a solutioning of the associated metal impurities but also in an enrichment of the metallic residue with precipitated nickel, in many instances it may be only necessary to lower the percentage of contained associated impurities materially to obtain an intermediate purified nickel product containing the remaining impurities within tolerance percentages suitable, in some instances, for use in the trade. Again, it may be desired only to selectively remove one or more of the associated impurities, it being apparent that where two or more associated metal impurities are present in the nickel, the one higher in the displacement series will be dissolved out in major proportion before solutioning of the second impurity appreciably initiates.

In this connection, my investigations indicate the following approximate descending order for the various metals, commonly found associated with nickel, in the displacement series of metals in molten metal chloride baths containing nickel chloride: V, Mn, Zn, Cr, Fe, Co, Cu, Ni.

The alkali and alkaline earth metals and magnesium lie to the left of the list or above V and only a few metals lie to the right or below Ni. The metals Ag, Pb, Sn, Cd, Al, Be, U, Th, all lie above Ni in this displacement series and if present in Ni also would be removed along with any of the metals in the series above noted.

With respect to the above series, some of the metals form intermetallic compounds which resist decomposition in accordance with this series. As an example, the intermetallic compound nickel silicide is more noble than Ni and very difficult to break down, and in most cases the silicon content of nickel alloys is largely retained.

In the practice of the present invention, I prefer to maintain a temperature substantially below the boiling point of the chloride compound of the displacing metal, but not over the boiling point of nickel chloride (975° to 1000° C.), and a temperature approximating 700° C. whenever practicable. However, temperatures as low as 500° C. have been employed in the practice of the present invention with good results.

The melting and boiling points of the chloride compounds of the more common metal impurities are as follows:

	M. P., °C.	B. P., °C.
$CuCl$	425	1,366
$FeCl_2$	674	1,023
$MnCl_2$	650	1,190
$CoCl_2$	735	1,049
$CrCl_3$	815	1,343
$ZnCl_2$	313	732

As one specific example of the present invention, but not as a limitation thereof, nickel powder containing 2% cobalt obtained by the hydrogen reduction of mixed nickel and cobalt oxides was reduced by mechanical means to a particles size passing 60 to 100 mesh and suspended in about 3 times its weight of a molten bath consisting of a 60/40 mixture of KCl and NaCl containing about 15% $NiCl_2$. The temperature of the bath was maintained for about one hour at 650° C. at the end of which time the metal powder was separated from the fusion mixture and the cobalt content remaining therein determined by chemical analysis. The chemical analysis showed that 70% of the cobalt content of the nickel metal powder had been removed in this relatively short time of treatment.

By extending the time interval of treatment to two hours; or by increasing the amount of $NiCl_2$ in the fusion mixture to increase the rate of the displacement reaction; or by reducing the particle size of the nickel powder to below 200 mesh; or by repeating the above treatment, the amount of cobalt removed from the nickel powder may be varied widely. It is not always desired to effect a substantially complete removal of the cobalt in one extraction treatment, except where, in addition to cobalt, the metal powder contains undesired amounts of other impurities lower than Co in the displacement series. In that event substantially all of the Co must be removed before any of these other metals may be removed.

In general, I prefer to employ higher concentrations of $NiCl_2$ in the fusion mixture of alkali metal chlorides than given in the above example and concentrations within the range 25–50% are preferred so as to obtain as rapid a rate of displacement as possible at an operating temperature of 650°–750° C., thereby to materially shorten the required time interval of treatment. With this high concentration of $NiCl_2$ in the fusion mixture I find that the amount of nickel powder incorporated therein for treatment may be greatly increased, the precise amount of increase depending upon the total amount of associated impurities present therein, and the total percentage thereof it is desired to remove.

I have found that with most of the metals displacing Ni from $NiCl_2$ in metal chloride fusions, an equilibrium is reached between the chloride compound of the displacing metal and the $NiCl_2$ at any given operating temperature at which the displacing reaction practically ceases or is reduced to an exceedingly low rate. This equilibrium ratio is higher the closer the metal lies to Ni in the displacement series. With Cu, for example, a large excess of $NiCl_2$ must be present in the fusion, whereas with Zn and Mn relatively a small excess is required. By maintaining such an excess, however, from 70 to 80% of any given metal may be removed in each treatment and by repeating the treatment several times a substantially complete removal may be effected.

Where substantially complete removal of these associated impurities only is desired, a second treatment using a molten flux substantially free of the displacing metal chloride is generally effective where the original amount of the contaminating metal is not excessive.

As a second specific example, a metal powder passing about 100 mesh and consisting principally of nickel but containing copper in about the percentage usually present in Monel metal which powder was obtained by the hydrogen reduction of mixed Ni and Cu oxides, was suspended in a

molten bath consisting of a 60/40 mixture of KCl and NaCl containing about 25% nickel chloride, the mixture being about two parts fusion mixture to one part metal powder. The bath temperature was maintained at 700° C. and the time interval of treatment approximated one-half hour. After separating the metal powder from the fusion mixture, chemical analysis of the metal powder showed that 72% of the copper had been removed in this short time interval of treatment. Longer time intervals of treatment have resulted in substantially complete removal (90–95%) of the copper content of this metal powder, and a second treatment in a similar fusion mixture usually resulted in an even greater purity nickel powder product.

As another example, nickel metal powder containing Fe (15%) as an impurity when added to the fusion mixture used in the above second example in about the same relative proportions and under substantially the same time and temperature conditions resulted in the removal of 80% of the iron within one-half hour and 90 to 95% of the iron at the end of an hour.

From the above examples, it is believed apparent that the removal of Co, Cu and Fe from nickel may be easily effected by the practice of the present invention. The metals Al, Zn and Mn, are even more easily removed in the same manner and under the same conditions, as these metals are higher than Cu, Co and Fe in the displacement series as hereinbefore noted. In general, Mn, Zn and Al will be removed in higher percentages in one treatment than is usually obtainable with Cu, Fe or Co.

The adaptation of the invention to the treatment of nickel scrap is of particular importance in the art, inasmuch as it is known that it is extremely difficult in remelting scrap nickel to eliminate therefrom many of the metals associated therewith in alloy or occluded form. Some of these metals may be removed in major part from the molten alloy by oxidation but some contaminating metals, such as iron and copper, may not be separated from nickel in this manner.

In accordance with the present invention, the scrap nickel following reduction in particle size to pass 60 to 100 mesh in any convenient manner, is subjected to extended heat-treatment in a molten metal chloride bath consisting of highly stable metal chlorides such as one or more of the chloride compounds of the alkali and alkaline earth metals and containing 25 to 50% $NiCl_2$, the relative amounts of the metal to the flux being proportioned to provide a relatively large excess of $NiCl_2$ over that theoretically required to remove, by displacement reaction, substantially all of the associated metal impurities in the metal. The temperature of the bath is maintained, preferably at about 700° C. but may be as high as 975° C. (the B. P. of $NiCl_2$) and as low as 500° C. without essential departure from the present invention, the specific temperature being selected with respect to the impurities present to obtain the most economically practical rate of displacement with consequent shortest time interval of treatment to obtain the desired percentage of removal of impurities in the first treatment.

In general, from 60 to 70% of the associated metal impurities may be removed from the nickel by means of the above fusion mixture, within a time interval of treatment approximating one hour. In general, I prefer to end the treatment after one hour and after separating the metal cake from the fusion mixture, subject the metal to a second treatment in a fresh batch of the fusion mixture under substantially the same conditions for another hour, thereby effecting a removal of 90 to 95% of the associated metal impurities.

Whether or not a third treatment is to be given depends in part upon the particular impurity remaining and in part upon the particular use to which the refined nickel may subsequently be put. My experience shows that copper and cobalt are the last of the metallic impurities to be eliminated by the practice of the present invention. Where the refined nickel metal powder is to be used in forming Cu-containing nickel alloys, as an example, the refining operation, of course, may be terminated when copper content of the nickel is within the tolerance limits of the alloy to be formed therefrom.

As an alternative practice a sequence of treatments may be practiced on the scrap nickel whereby each of the contaminating metals are selectively removed.

Alternatively, also, the scrap nickel may be melted, subjected to an oxidizing blast to remove some of the contaminating metals, cast into ingots, fragmented and comminuted to the desired particle size, and then treated in accordance with the present invention to remove the remaining impurities.

In the treatment of scrap metal in the form of chips and turnings in accordance with the present invention, it is not always necessary to comminute the metal to small particle size when the section of the metal is relatively thin. For convenience in handling and treating, however, it is preferable to break the thin sectioned chips and turnings into relatively small fragments before treating in accordance with the present invention regardless of section.

Various other modifications and adaptations of the present invention will be apparent to one skilled in the art from the above disclosure of the present invention but all such are contemplated as may fall within the scope of the following claims.

What I claim is:

1. The method of treating a molten metal chloride bath containing nickel chloride to remove the nickel content of said bath as metallic nickel which comprises incorporating in said bath a finely divided metallic material having a melting point above the temperature of the bath and consisting at least in part of a metal higher than nickel in the solid metal-molten metal chloride displacement series at the temperature of heating.

2. The method of treating a molten metal chloride bath containing nickel chloride heated to temperatures within the range 500–1000° C. to remove the nickel content of said bath as metallic nickel which comprises incorporating in said bath a finely divided metallic material having a melting point above the temperature of the bath and consisting at least in part of a metal selected from the group of metals Al, Mn, Zn, Cr, Fe, Co, and Cu.

3. The method of treating a molten metal chloride bath containing nickel chloride to remove a good part of the nickel content of said bath as metallic nickel which comprises heating the bath to a temperature within the range 500–1000° C. and incorporating a finely divided alloy of nickel and copper in said bath the amount of the copper in said alloy being substantially less than that theoretically required to dis-

place substantially all of the nickel from the chloride combination.

4. The method of removing metallic impurities from nickel which comprises reducing the impure nickel to small particle size and dispersing the small particle sized material in a molten metal chloride bath consisting of a mixture of nickel chloride and metal chloride compounds of metals relatively high in the displacement series in the system solid metal-molten metal chloride, and heating the said bath to a temperature within the range 500–1000° C. for a time interval promoting the removal of at least a major portion of said impurities by a displacement reaction of the same with the said nickel chloride present in the bath.

5. The method of removing metal impurities from metallic nickel which comprises reducing the impure nickel to relatively small particle size and suspending the small particle sized material in a metal chloride fusion mixture consisting of highly stable metal chloride compounds and nickel chloride, said highly stable metal chlorides being selected to provide a fusion temperature within the range 500 to 1000° C.

6. The method of removing metal impurities from metallic nickel which comprises reducing the impure nickel to relatively small particle size and suspending the small particle sized material in a metal chloride fusion consisting of a mixture of alkali metal chlorides and nickel chloride having a temperature within the range 500–1000° C.

7. The method of claim 6, wherein the amount of said nickel chloride is maintained in large excess of that theoretically required to remove substantially all of the said metal impurities by a displacement reaction.

8. The method of claim 6, wherein the amount of said nickel chloride is maintained in large excess of that theoretically required to remove substantially all of said metal impurities by a displacement reaction and wherein the time interval of treatment is limited to that effecting a removal of the major portion of said impurities within an economically practical short time and wherein the said treated metal is subjected to at least one other treatment in at least one more bath of said fusion mixture to obtain a removal of the greater portion of the remaining metal impurities.

9. The method of treating metallic nickel to eliminate therefrom associated metallic impurities of the group consisting of Cu, Co, Fe, Cr, Zn and Mn, which comprises reducing the impure nickel to fine particle size and suspending the said fine particle sized material in a molten metal chloride bath containing nickel chloride and metal chlorides higher than Mn in the displacement series of solid metals in fused metal chlorides at temperatures within the range 500–1000° C.

10. The method of claim 9, wherein said molten metal chloride bath consists of a mixture of KCl and NaCl.

11. The method of claim 9, wherein the amount of said nickel chloride is in large excess of the theoretical amount required to obtain substantially complete removal of said metal impurities by a displacement reaction.

12. The method of claim 9, wherein the time interval of immersion in said bath is limited to a time interval providing for the removal of the major proportion of said metal impurities within a relatively short time interval and wherein the metal is given further treatments in new batches of said fusion mixture to remove the major portion of the remaining impurities.

WILLIAM J. KROLL.