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METHOD OF RECOVERING METALS

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The present invention is concerned with the recovery of metal values, typically cobalt, nickel and the like, from alloys containing the same. The invention is of particular value in the recovery of metal from normally corrosion resistant scrap superalloys obtained, for example, from jet aircraft, etc. However, it will be appreciated from the ensuing description that the invention herein is capable of other applications where the recovery and separation of metal alloy components may be important.

There is a real need at the present time for an economical and otherwise effective way of separating metal values from normally corrosion resistant alloys of the type used in jet aircraft engines. The metal components of these alloys are, in most instances, expensive and the satisfactory recovery thereof is, therefore, highly desirable. However, because of the nature of these alloys, particularly their resistance to corrosion or degradation with conventional acids or other solvents, recovery of the various metal components has not been satisfactorily achieved. Present recovery practices are slow, expensive and otherwise generally ineffective, at least from the standpoint of large scale commercial operations. As a result, alloys containing valuable metal components, such as scrap superalloys obtained from jet aircraft engines, are being disposed of at far less than their actual values in the absence of some commercially feasible way of recovering these metal components.

Typical of prior efforts to recover metal values from corrosion resistant alloys in U.S. Patent 2,716,558, issued August 30, 1955, to James D. Hall. This patent describes, inter alia, a process for recovering nickel and copper from Monel metal by introducing the alloy into an aqueous solution of a strong inorganic acid, e.g. sulphuric, nitric or hydrochloric acid, and passing sulphur dioxide into the solution. This particular process, however, suffers from the fact that the rate of dissolution of the metals is too slow and resulting gases are highly toxic and undesirable. For these and other reasons, the process does not lend itself to large scale, economic commercial operations.

The principal object of the present invention is to provide a process for recovering metal values from alloys containing the same whereby prior art difficulties are effectively overcome. Another object of the invention is the provision of a process whereby metal components of superalloys or the like may be recovered in a simple, straightforward, inexpensive and otherwise highly attractive manner. A more specific object of the invention is to provide a commercially desirable process for treating scrap alloys to separate therefrom the metal components thereof. Other objects and advantages of this invention will also become apparent to those skilled in the art when reference is had to the following detailed description.

Broadly stated, the foregoing objects are realized, according to the present invention, by virtue of the unexpected discovery that normally corrosion resistant superalloys can be readily and conveniently dissolved in a dilute aqueous solution of inorganic acid and inorganic nitrate with subsequent straightforward recovery of the various alloy components.

More particularly, the present invention is directed

to the method of recovering cobalt and nickel from a cobalt/nickel alloy which comprises the steps of placing such an alloy in a suitable reaction vessel, adding a dilute acidic solution of chloride ions to the reaction vessel, adding inorganic nitrate to form a reaction mixture and conducting the reaction separating the resultant solution containing chloride ions from any remaining alloy and diluting, cooling, aerating and treating this solution to separate out other metal values, introducing more chloride ions in the form of chlorine gas into the solution and treating it again to precipitate out cobalt, followed by the continuing introduction of chloride ions to redissolve any coprecipitated nickel, and finally treating the solution to precipitate out nickel.

Specifically, the present invention is directed to the method of recovering colbalt and nickel from solid cobalt/nickel containing alloys which comprises the steps of placing solid alloys in a suitable reaction vessel, adding dilute inorganic acid to the vessel, adding inorganic nitrate to form a solution containing a reaction mixture and conducting the reaction, separating the resultant solution from any remaining alloy, diluting the reacted solution, oxidizing other metal values in the solution, adjusting the pH to precipitate these other metal values as oxides and separating the oxides from the diluted solution, simultaneously halogenating and treating the diluted solution to cause the precipitation of cobalt and separating out the precipitate, and finally adding an alkaline earth material to the diluted solution to precipitate out nickel.

The exact mechanism by which the invention operates to give the desired result is not fully understood. Whatever the mode of operation may be, it is surprising that the dilute solution of acid and nitrate used herein is effective to dissolve the alloys in question. This is particularly true when it is realized that aqua regia, comprising a highly concentrated solution of hydrochloric and nitric acids is not operative for present purposes.

For example, it is well known in the art that a quantity of aqua regia will only dissolve a small proportion of metal since a relatively great part of the aqua regia is lost by volatilization due to violent reaction. Consequently, fresh portions of aqua regia must be added to continue the reaction and ultimately, many times the stoichiometric quantity of aqua regia acids will be required to achieve results comparable to those of the present invention. Moreover, use of dilute acid according to the present invention reduces, and often eliminates the possibility of atmospheric air and fresh water pollution. Understandably, the present invention achieves an economical and very beneficial result when compared to the difficulties encountered with aqua regia and other concentrated acid solutions.

The aqueous inorganic acid solution used in the present invention to dissolve the alloys in question should comprise a constant boiling composition in which the hydrochloric acid concentration is desirably not in excess of about 20% by weight. This is to be distinguished from commercially supplied materials which contain 28 to 30% HCl. For optimum operation, the HCl concentration of this invention should be kept below 10–15% by weight and is preferably lower, e.g. 5%. Effective results can be obtained down to an acid concentration of as low as about 0.5% HCl. As far as pH is concerned, the treating bath, generally speaking should have a pH of 1 to 1.5 or lower. Not only does this diluted mixture work at a commercially attractive rate, but the dilute, constant boiling composition of this invention does not expel large proportions of the HCl, normally causing waste or necessitating a costly acid recovery as in prior art processes.

The inorganic nitrate used herein is desirably an alkali metal nitrate, e.g. sodium and/or potassium nitrate.

However, any other soluble inorganic nitrate, typically ammonium nitrate, lithium nitrate, magnesium nitrate, calcuim nitrate, barium nitrate, etc., may also be used. Nitric acid has also been used, but sodium nitrate is employed as the preferred embodiment of this invention. The amount of inorganic nitrate is desirably kept at a minimum and normally will fall within the range of about 1 to 1.5 parts by weight nitrate for every three parts of HCl.

The invention described herein is particularly useful with respect to the treatment of normally corrosion resistant nickel, chromium and/or cobalt chromium base alloys for the recovery of the nickel, cobalt and other metal values therein. Usually, such alloys include from 0 to 79% by weight nickel and/or from 0.5 to 63% by weight cobalt with various amounts of other metals, e.g. iron, chromium, molybdenum, tungsten, columbium, tantalum, etc. Specific alloys suitable for treatment herein include the well-known "S–816"; Stellites, Inconel and the like. Other alloys which are normally corrosion resistant and therefore, difficult to dissolve, for example the various alloy systems described in the above-mentioned Hall Patent 2,716,588 and the nickelferrous cobalt alloys of U.S. Patent 2,651,562 may also be successfully treated in the manner described herein.

In carrying out the present invention, the alloy to be dissolved is placed in a suitable tank or vessel which should be lined with either glass, acid-proof masonry, or some suitable corrosion resistant material which can also withstand temperatures of up to 240° F. In commerical practice several times the weight of metal to be dissolved per batch or cycle should be present. One of the unusual features of this invention is that the metal to be dissolved need not be shredded, shotted, or otherwise treated to produce a large surface to weight ratio. So-called "massive" scrap can be dissolved by this technique.

A solution of hydrochloric acid in water having a strength *below* that of a constant boiling point solution (that is a solution which boils without a change in composition, such as an azeotropic mixture, wherein the concentration of hydrochloric acid in the vapor is the same as the concentration of the hydrochloric acid in the boiling solution[1]) is then added to the vessel containing the alloy. The use of this particular hydrochloric acid solution, i.e., one having a concentration below that of the 28–30% commercially supplied azeotropic mixture, is an important feature of this invention because its use makes possible the dissolution of the metals with what approaches, and often amounts to, stoichiometric quantities of acid. A small amount of soluble inorganic nitrate is then added to initiate the reaction and smaller amounts are added as the reaction proceeds until the solution has "gone neutral." The reaction is strongly exothermic and will start itself upon addition of the nitrate to the dilute acid, but steam may be introduced into the mixture to start it more quickly on the first batch or cycle of a cold day.

The reaction is so strongly exothermic that care must exercised to control the rate in order to prevent the solution from boiling violently out of the reaction vessel. This can be done best by the rate of addition of the nitrate and by the dilution of the reacting solution with cold water as the reaction proceeds.

After the acid has become neutralized by reacting with the metals, the resulting solution of metal chlorides is drained into a suitable vessel (a wooden tank for example) and the dissolving cycle is repeated by adding an amount of metal, equal to the amount dissolved in the preceding cycle, to the metal remaining in the reaction vessel, followed by the addition of more dilute hydrochloric acid and inorganic nitrate in the manner set forth above.

The solution of metal chlorides is diluted with cold water, preferably to a concentration of 0.1 lb. of cobalt per gallon (when processing alloys in which cobalt is the major metal), and the resulting solution is aerated with compressed air through suitable spargers or other devices to facilitate the oxidation of the chromium and iron to their trivalent states.

When oxidation is complete, finely pulverized calcium carbonate is added slowly with vigorous agitation and continued aeration until all of the chromium and iron have been precipitated as hydrated oxides. The precipitate is readily filterable on a vacuum filter and can be washed practically free of soluble cobalt and nickel values.

The filtrate containing a mixture of cobalt and nickel chlorides may be treated in one of the many known ways to separate them, one from the other. The preferred way, however, according to this invention, involves treating the solution with chlorine gas introduced through a sparger under vigorous agitation, along with the slow addition of finely divided calcium carbonate, until all of the cobalt has been precipitated as the hydrated cobaltic oxide. An important feature of this invention lies in the fact that after all of the cobalt is precipitated, any nickel which has been co-precipitated with the cobalt can be redissolved from the precipitate by continuing the chlorination after the addition of the calcium carbonate until the pH of the slurry reaches approximately 3.

The cobaltic oxide precipitated in the above manner is readily filterable. Upon suitable treatment, such as that commonly used in the cobalt industry, this oxide is suitable for sale as such or for the further reduction to the metal.

The filtrate containing nickel and calcium chlorides is treated with hydrated lime to precipitate the nickel as its hydrated oxide. This nickel hydrate is further processed to a commercial grade nickel oxide by methods well known in the trade.

Periodically, the metal in the dissolving vessel is removed for physical separation of the very finely divided metallic powder which tends to coat the pieces of undissolved metal, and also tends to settle to the bottom of the tank. This powder contains columbium, tantalum and tungsten, and sometimes part of the molybdenum contained in the alloys that have been treated in the reaction vessel. The powder separates readily upon tumbling and washing into any desired settling tank. The resulting wet powder or sludge may be dried and sold or the valuable metals contained therein may be separated out by known commercial methods.

The inveniton is further described by reference to the following example.

Example

One thousand pounds of scrap cobalt/nickel/chromium alloy (S–816) consisting of 43% Co, 20% Ni, 20% Cr, 4% Cb, 4% W, 4% Mo and some iron were placed in a suitable reaction vessel line with glass or acid-proof masonry. One thousand pounds of 28–30% commercial hydrochloric acid, diluted with cold water to below 20% HCl concentration, were then added, followed by the addition of fifty pounds of sodium nitrate. The reaction started slowly at first and gradually increased in vigor. The rate of reaction was then controlled, to maintain the solution in the vessel at its boiling point, by additions of nitrate to speed it up, or by dilution with cold water to slow it down. By the time a total of one hundred and fifty pounds of nitrate had been added, the reaction showed very little response to further additions of nitrate and upon analysis it was found that a one cc. of sample of the above solution in 100 cc. of water was neutral to methyl orange indicator. The total time of reaction was about two hours.

The reacted solution was drained into a wooden tank where it was cooled and then diluted to a cobalt concentration of 0.1 pound per gallon calculated on the weight of pure cobalt. Compressed air was introduced through

[1] The Van Nostrand Chemist's Dictionary, D. Van Nostrand Co. Inc., New York (1953), pp. 56 and 179.

aerating spargers until both the chromium and iron were thoroughly oxidized to their trivalent states, and then finely ground calcium carbonate was added until the pH was between 5 and 5.4. The red color of the cobalt chloride "flashed" through the swirling greenish slurry of chromic oxide hydrate at this point indicating very clearly that the precipitation of the chromium and iron values wa complete.

The chromic oxide precipitate and the small amount of ferric oxide hydrate which accompanied it were in an easily filterable form. These materials were then filtered out in the slurry on Moore type vacuum filter leaves to produce a compact and washable product.

The cobalt-nickel-calcium chloride solution was pumped to a tall wooden tank fitted with an efficient agitator and chlorinating spargers through which gaseous chlorine was introduced into the solution at the rate at which the solution would absorb it. Finely ground calcium carbonate was fed slowly into the solution while chlorination was continued until all of the cobalt was precipitated as the hydrated cobaltic oxide. A little over fifty-two pounds of chlorine and two hundred sixty pounds of calcium carbonate were required. Chlorination was continued for a few minutes after the last of the calcium carbonate was consumed until the pH of the slurry reached a point just below 3.5 so as to redissolve the small amount of nickel which was co-precipitated.

The cobaltic oxide precipitate was filtered, washed, and dried. The yield was almost eighty pounds, calculated as pure cobalt.

The nickel-calcium chloride solution was then pumped into a wooden tank where the nickel was precipitated by chemical grade hydrated lime slurry as the hydrated nickel oxide. This precipitate was separated and refined to commercial nickel oxide. The yield of nickel was about thirty-six pounds, calculated as pure nickel.

As a result of the technique of this invention, an excellent and commercially feasible separation can be obtained in one separation cycle instead of having to use repeated separations as is commonly the case in the cobalt-nickel industry. Moreover, the process of this invention does not require any particular limitation on the ratios of cobalt to nickel which may be present in the various solutions taught herein. It will be readily obvious to those skilled in the art that this is unusual in commercial practice and constitutes one of the many novel features of this invention.

It will be understood by those skilled in the art that various changes and modifications may be made in the preceding description without departing from the spirit and scope of this invention.

It is only intended that this invention be limited by the following appended claims wherein what is claimed is:

1. The method of recovering cobalt and nickel from a normally corrosion resistant solid alloy containing cobalt, nickel, and other metal values which comprises the steps of placing said alloy in a suitable reaction vessel, adding a dilute acidic solution of chloride ions to said reaction vessel, adding soluble inorganic nitrate to form a reaction mixture and conducting a reaction therewith, separating the resultant solution containing chloride ions from remaining alloy, diluting and cooling said resultant solution, aerating and adjusting the pH of said resultant solution to precipitate other metal values as oxides and separating said oxides from the diluted solution, introducing more chloride ions in the form of a chlorine gas into said resultant solution and treating said resultant solution to precipitate out cobalt and nickel and continuing the introduction of chloride ions to redissolve co-precipitated nickel and further treating said resultant solution to precipitate nickel.

2. The method of recovering cobalt and nickel from a corrosion resistant solid alloy containing cobalt, nickel and other metal values which comprises the steps of placing said solid alloy in a suitable reaction vessel, adding a dilute inorganic acid solution of chloride ions to said reacton vessel, adding soluble inorganic nitrate to form a solution containing a reaction mixture and conducting a reaction therewith, separating the resultant reacted solution from remaining solid alloy, diluting the reacted solution, oxidizing other metal values in said diluted solution, adjusting the pH to precipitate said other metal values as oxides and separating said oxides from the diluted solution, simultaneously halogenating and treating the diluted solution to cause the precipitation of cobalt and nickel and removing said cobalt containing precipitate, and adding an alkaline earth material to said diluted solution to precipitate nickel.

3. The method of claim **2** wherein said nitrate is an alkali metal nitrate and said reaction mixture includes 1 to 1.5 parts of nitrate for every 3 parts of acid.

4. The method of claim **2** wherein said other metal values comprise a mixture of chromium and iron values in their trivalent states.

5. The method of claim **2** wherein said dilute inorganic acid contains not in excess of about 20% by weight of hydrogen chloride.

6. The method of claim **2** wherein said acid is present in an amount between about 0.5 to 15% by weight of said reaction mixture.

7. The method of claim **2** wherein said reaction is conducted until a sample of said solution is neutral to methyl orange.

8. The method of recovering cobalt and nickel from a solid alloy containing cobalt, nickel, chromium and iron, which comprises the steps of placing an amount of said solid alloy in a suitable reaction vessel, adding an amount of dilute hydrochloric acid solution equal in amount to the weight of the solid alloy, adding a soluble inorganic nitrate to initiate vigorous reaction, followed by the addition of more nitrate until the reaction subsides and demonstrates methyl orange neutrality at a one/one hundredth dilution, separating the reacted solution from any remaining solid alloy, followed by cooling and diluting the reacted solution, oxidizing said diluted solution, adjusting the pH to between about 5 and 5.4 by the addition of calcium carbonate to precipitate out said other metal values as oxides and separating said oxides from said diluted solution, chlorinating said diluted solution and slowly introducing calcium carbonate during the chlorinating step until all cobalt is precipitated, continuing chlorinating to a pH of about 3.5 until co-precipitated nickel is redissolved, separating said cobalt precipitate from said chlorinated solution, adding a hydrated lime slurry to said chlorinated solution to cause nickel to precipitate, and recovering nickel from said solution.

9. The method of claim **8** wherein the soluble inorganic nitrate is an alkali metal nitrate.

10. The method of claim **9** wherein the alkali metal nitrate is sodium nitrate.

11. The method of claim **8** wherein the soluble inorganic nitrate is selected from the group consisting of sodium nitrate, potassium nitrate, ammonium nitrate, lithium nitrate, magnesium nitrate, calcium nitrate and barium nitrate.

12. The method of claim **8** wherein the soluble inorganic nitrate is nitric acid.

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