

UNITED STATES PATENT OFFICE

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SEPARATION OF NICKEL CONTAINED IN
NICKELIFEROUS COBALT ALLOYS

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This invention relates to a process for the separation of nickel contained in nickeliferous cobalt alloys or other metallic substances.

The said alloys or other metallic substances may contain other metals than nickel, such as iron, zinc, manganese, copper, lead.

The object of the present invention is to effect a separation as complete as possible of the nickel from the cobalt contained in the primary materials.

It has previously been proposed in a process for the separation of copper from other metals, more electropositive than copper, such as zinc, tin, nickel or cobalt, contained in alloys or other metallic substance, to fix the copper in the form of insoluble cupric sulfide by treatment with an acid in the presence of elemental sulfur, whilst the more electropositive metal or metals pass into solution.

The present invention consists in a process for the separation of nickel from cobalt contained in primary materials, which comprises forming a nickel-cobalt alloy and adding a dilute acid and sulfur to the primary material, heating the mixture, precipitating nickel in the form of nickel sulfide, and separating the precipitate from the resulting solution containing the major part of cobalt.

For the present process, the presence of metallic iron may be advantageous; the presence of other metals may also be beneficial.

It may be advantageous for obtaining cobalt solutions very poor in nickel, to effect the selective dissolution of cobalt stepwise, that is by successive partial treatments with acid and sulfur, and separation after each partial treatment of a solution free or almost free from nickel, by filtration, settling or otherwise.

The acid used for dissolving the primary material is preferably sulfuric acid or hydrochloric acid.

It may be advantageous to use both the sulfur and the primary material in a finely-divided form, but whatever the form may be, an intimate contact of all the substances present should preferably be ensured.

The pH of the solution during the treatment should be maintained below 7, preferably between 1 and 5. At the end and/or during the treatment (or each partial treatment when the process is carried out stepwise), it is advantageous to allow the pH to rise once or several times to 3 or more.

The amount of sulfur used may vary within wide limits according to the percentage of Ni and of other metals capable of becoming combined with the said metalloid and which are present in the alloy or other metallic substance.

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The sulfur may be added either wholly at the beginning of the operation or after partial dissolution, or progressively during the whole operation or part of it. If the treatment is carried out stepwise, the addition of sulfur may be effected in any of the said ways during each partial treatment.

When the sulfur is added in powder form, a wetting agent may be added in order to facilitate the dispersion of the metalloid. For instance, about 0.1% of an alkyl-sulfonic compound may be used.

Instead of elemental sulfur, use may be made of a compound of sulfur producing insoluble nickel sulfide during the reaction. For instance, use may be made of SO₂-gas injected into the solution, or of a sulfide or hyposulfite. The elemental sulfur or sulfur compound necessary for the reaction may already be present in the primary material used.

It is also possible to use an acid solution containing cobalt and nickel and eventually also iron and/or other metals for treating a nickeliferous cobalt alloy or other metallic substance so as simultaneously to separate the Ni from the Co contained by the solution and the Ni from the Co contained in the alloy or other metallic substance. In this case, the precipitation of Ni from the solution takes place first, the dissolution of the metallic substance being only partial. It may be advantageous for obtaining cobalt solutions very poor in nickel, to separate the said solution (by filtration, settling or otherwise) and to continue the extraction of Co from the metallic substance by means of fresh acid and with a fresh addition of sulfur. The later extraction of cobalt may be carried out stepwise.

By the present invention, a solution may be obtained containing a ratio of Ni/Co as low as 0.05/100 or even lower.

The yield of the cobalt extraction in the form of a solution free or almost free from Ni varies, among other factors, with the solubility of the alloy or other metallic substance. It may exceed 90 to 95%.

The cobalt contained in the nickel precipitate may be separated by any known method, for instance by means of chlorine or hypochlorite after dissolution of the nickel precipitate.

Example 1

400 grams of an alloy containing:

41.6 %	Co	} Ni/Co=0.8/100
0.36 %	Ni	
36.5 %	Fe	
12.8 %	Cu	

and of the following granulometric analysis:

15% larger than 100 mesh A. S. T. M.
50% larger than 200 mesh A. S. T. M.
35% smaller than 200 mesh A. S. T. M.

were treated in 2.5 liters of water with strong stirring at 95° C. with 20 grams of flowers of sulfur of about 270 mesh A. S. T. M. and with addition of 2.5 cc. of a wetting agent. 437.5 grams of H₂SO₄ were progressively added thus maintaining the pH=1.3 to 1.5.

The duration of the operation was 4 hours 30'. The product of the reaction was filtered and washed. 2.6 liters of a solution were obtained, containing per liter 50.9 grams of Co, 49.2 grams of Fe, and 0.07 gram of Ni.

About 80% of the cobalt of the original alloy were thus extracted with a ratio Ni/Co of about 0.14/100.

Example 2

200 grams of the same alloy as in Example 1 were introduced into 2 liters of a solution containing per liter:

41.6 grams of Co
0.21 grams of Ni
36.0 grams of Fe

10 grams of flowers of sulfur of 270 mesh were added together with 1 cc. of a wetting agent.

The mixture was strongly stirred during 2 hours 40 minutes at 90° C. 175 grams of H₂SO₄ were progressively added, thus maintaining a pH between 1.3 and 1.7. After all the acid was added, the mixture was allowed to digest for one hour at the same temperature, and the pH rose to 4.1. The mixture was filtered and washed. 2.5 liters of a solution were obtained containing per liter:

58.1 grams of Co
0.05 gram of Ni
48.1 grams of Fe

About 85% of the cobalt of the original alloy and primary solution were thus extracted with a ratio Ni/Co equal to 0.08/100.

Example 3

200 grams of an alloy as in Example 1 were introduced into 2 liters of a solution as in Example 2, and were treated at 95° C. with 16 grams of flowers of sulfur of 270 mesh and 2 cc. of a wetting agent. 24 grams of H₂SO₄ were added and the solution was stirred for one hour at the same temperature. The pH rose to 3.4 and the mixture was filtered and washed. A first solution was thus obtained containing 53.7% of the total cobalt in the alloy and in the primary solution, with a ratio Ni/Co of 0.05/100.

The residue was treated with one liter of water and with 170 grams of H₂SO₄ which were progressively added during two hours thus maintaining the pH between 1.5 and 2.0. 4 grams of flowers of sulfur were then added together with 1 cc. of a wetting agent. Stirring was continued for one hour. The pH rose to 3.3 and the mixture was filtered and washed. A second solution was thus obtained containing 31.8% of the total cobalt present in the alloy and in the primary solution with a ratio Ni/Co of 0.02/100.

The residue was treated with one liter of water and with 30 grams of H₂SO₄ which were progressively added during one hour thus maintaining a pH at about 1.5. One gram of flowers of sulfur was added together with 0.5 cc. of a wetting

agent. Stirring was continued during one hour. The pH remained at 1.5 during the whole stage of the operation. A third solution was thus obtained containing 6% of the total cobalt contained in the alloy and in the original solution with a ratio Ni/Co equal to 0.53/100.

The final residue contained 8.5% of the total Co of the alloy and of the primary solution with a ratio Ni/Co of 8.38/100.

The two first solutions mixed together contained 85.5% of the total cobalt of the alloy and of the primary solution with a ratio Ni/Co of 0.04/100.

The three solutions mixed together contained 91.5% of the total cobalt of the alloy and of the primary solution with a ratio Ni/Co of 0.07/100.

Example 4

(a) 400 grams of an alloy containing:

46.63% Co
2.43% Ni
31.65% Fe
12.17% Cu

and of the following granulometric analysis:

10% larger than 100 mesh A. S. T. M.
51% larger than 200 mesh A. S. T. M.
39% smaller than 200 mesh A. S. T. M.

are treated in 1.5 liters of water with strong stirring at 85° C. for 5 hours. 505 grams of H₂SO₄ are progressively added, thus maintaining a pH of about 0.8-1 in order to avoid too violent a reaction. At the end of the operation, the pH is allowed to rise to 1.2.

(b) By filtration and washing an insoluble residue is separated. This residue weighs 134 grams and contains:

Co: 21% (which corresponds to 15% of the Co contained by the alloy)
Ni: 1.5%
Fe: 11.3%
Cu: 37.5%

The solution with washwater brought to 2 liters ("Solution I") contains:

64.0 grams/liter Co
2.3 grams/liter Ni
42.5 grams/liter Fe

(c) This Solution I is stirred at 95-100° C. for one hour, with addition of 400 grams of the original alloy, 40 grams of flowers of sulfur of about 270 mesh A. S. T. M. and 2.5 cc. of a wetting agent. The pH rises to 3.9.

Ten grams of H₂SO₄ are then added together with 20 grams of flowers of sulfur and 2 grams of a wetting agent; the pH decreases to 1.5. Stirring is continued for one hour, and the pH rises to 4.5.

(d) After filtration and washing, a solution ("Solution II") is obtained, containing 0.08 Ni/100 Co. The residue of this filtration ("Residue I") is attacked as in (a) by H₂SO₄ at 85° C.

(e) A new residue ("Residue II") and a new solution ("Solution III") are obtained by filtration. The Solution III contains per liter:

63.9 grams Co
2.3 grams Ni
42.3 grams Fe

This Solution III is practically identical with the Solution I and its nickel is removed as in the case of Solution I.

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The Residue II contains:

Co:15% (which corresponds to 21% of the Co present in the alloy used in (c)).
Ni:2.2%

After dissolution of this residue, its cobalt is extracted by means of hypochlorite.

What I claim is:

1. In the separation of nickel from cobalt contained in a cobalt-nickel alloy, the process which comprises heating such an alloy with a suspension of sulfur in a dilute aqueous inorganic acid solution having a pH within the range of from about 1 to 5, starting the treatment with a low pH value within said range and permitting it to rise during dissolution of the alloy to the upper end of the range, whereby the nickel precipitates in the form of nickel sulfide and the cobalt goes into solution, and removing the precipitate.

2. In the separation of nickel from cobalt contained in a cobalt-nickel alloy, the process which comprises heating such an alloy with a suspension of sulfur in a dilute aqueous solution of sulfuric acid having a pH within the range of from about 1 to 5, starting the treatment with a low pH value within said range and permitting it to rise during dissolution of the alloy, whereby nickel precipitates in the form of nickel sulfide

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and the cobalt goes into solution, removing the precipitate, adding additional cobalt-nickel alloy, additional acid and additional sulfur, heating this mixture while permitting the pH to rise to the upper end of the said pH range, and again removing the precipitate containing nickel sulfide from the remaining solution containing cobalt.

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