

[54] SEPARATION AND RECOVERY OF METAL ALLOYS FROM SUPERALLOY SCRAP

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[58] Field of Search 423/53, 55, 140, 58, 423/54, 139

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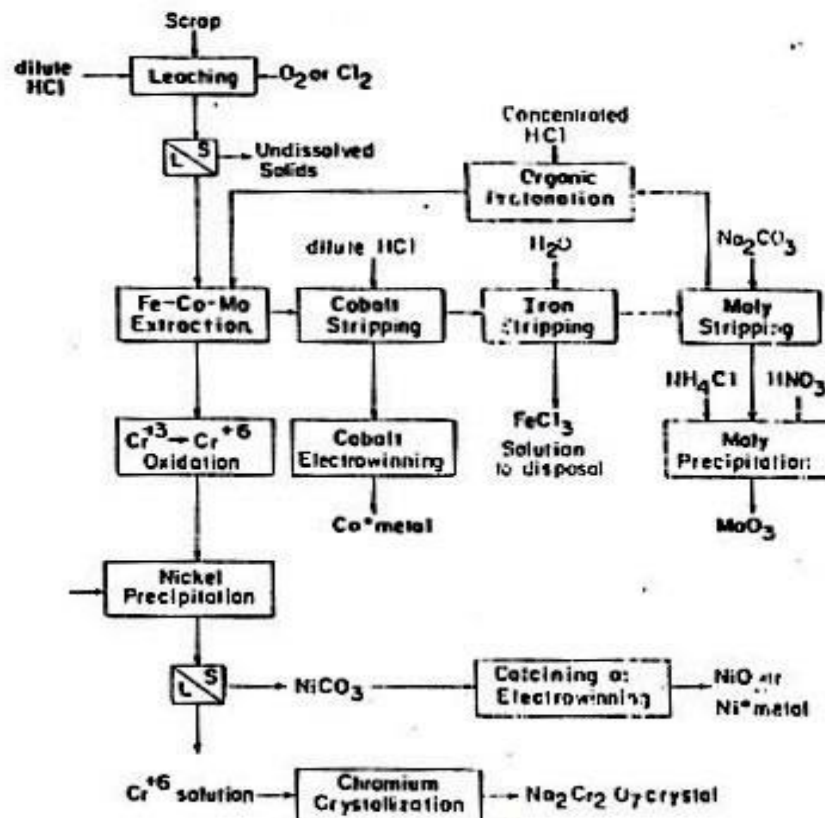
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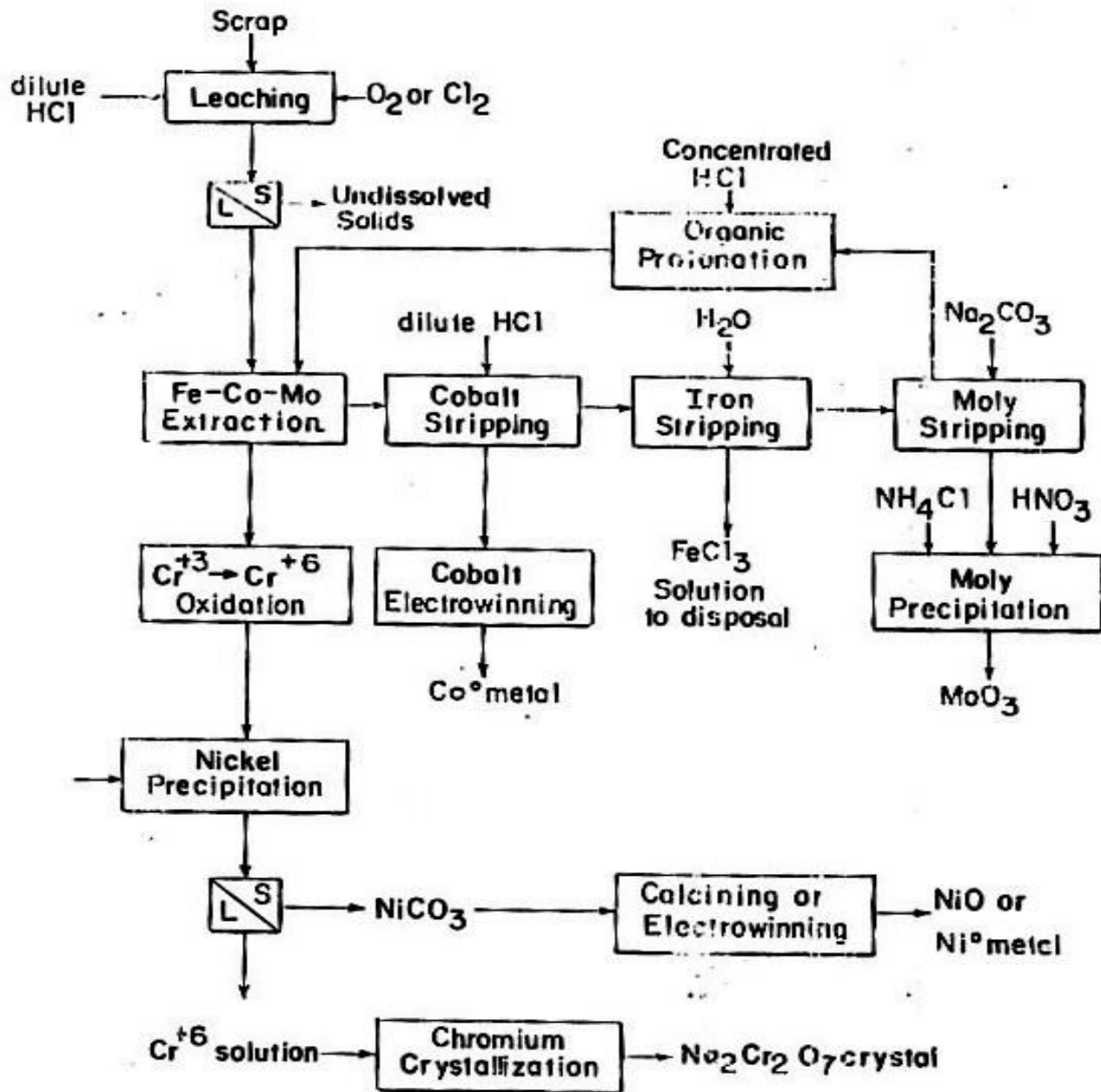
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[57] ABSTRACT

A method for recovering superalloy scrap is disclosed. The method involves oxidizing superalloy scrap in an aqueous acidic medium. The aqueous acidic medium has an oxidation potential sufficient to oxidize nonferrous additive superalloy elements to insoluble oxides thereof and to oxidize major superalloy constituents to aqueously soluble species. The insoluble solids from the aqueous solution are separated when the aqueous solution is extracted with an aqueously substantially insoluble tertiary amine to form an organic phase and an aqueous phase. The aqueous phase contains essentially nickel and chromium values. The organic phase is sequentially extracted with aqueous solutions which selectively solubilize individual metal value species to form individual aqueous solutions having substantially single metal value species therein. The metal value species solutions are processed to obtain substantially pure metals.

7 Claims, 1 Drawing Figure





## SEPARATION AND RECOVERY OF METAL ALLOYS FROM SUPERALLOY SCRAP

### BACKGROUND OF THE INVENTION

This invention relates to the recovery of metal values from superalloy scrap and more particularly to the separation of metal values from superalloy scrap in substantially pure form.

### DESCRIPTION OF THE PRIOR ART

In recent years "superalloys" have found increased utility and great increases in volume of production due to the need for articles having the special properties afforded by these materials. Among these properties are high temperature strength, high temperature oxidation resistance, corrosion resistance and the like. As the use of these superalloys grows, so does the amount of scrap and other waste containing them. The form of the scrap includes off-quality products, turnings, grindings, pouring skulls, mold gates, flashings and waste products such as sludges and the like.

Typically, superalloys are based upon chromium, nickel, cobalt, molybdenum, small amounts of iron, aluminum, silicon, titanium, columbium, tantalum and the like. The superalloys are predominantly composed of chrome and nickel as major constituents, and in most instances cobalt.

In many instances, the scrap superalloy as hereinbefore described is discarded in landfills and similar disposal methods because the individual metal values cannot be isolated for reuse. More particularly, it is desirable to recover and reuse the cobalt, chrome and nickel values so that they can be reused in producing superalloys. While it is recognized that turnings and grindings can be recycled for use in heats having the same alloy composition, a large portion of the scrap is generally downgraded and in many instances discarded. Further, the turnings and grindings, if they are to be used in heats of the same alloy composition, must be isolated and classified so that the alloymakers place these turnings and grindings in the appropriate heat.

Metallurgical methods have been used to treat superalloy scrap, but it has generally only been possible to produce a metal of iron, cobalt, nickel and possibly chrome and molybdenum while the refractory metals such as tantalum, titanium and columbium are lost in the slag. Although these metal values are recovered, they are in a form which is unsuitable for use in superalloy production.

The skilled artisans have attempted many methods to recover metal values from superalloy scrap with varying degrees of success. Exemplary of such efforts are those processes disclosed in U.S. Pat. Nos. 4,138,249; 4,193,968; 3,083,085 and 3,544,309.

In accordance with the present invention, a method of separating metal values from superalloy scrap is provided wherein the major constituents of the superalloy, such as nickel, chromium, cobalt and molybdenum, are separated from each other and recovered. Such recovery allows for isolation of these values in substantially pure form so that they can be reused in the manufacture of superalloys, thus conserving valuable raw materials.

### BRIEF DESCRIPTION OF THE INVENTION

A method for recovering superalloy scrap is provided. The method involves oxidizing superalloy scrap in an aqueous acidic medium. The aqueous acidic me-

diem has an oxidation potential sufficient to oxidize nonferrous additive superalloy elements to insoluble oxides thereof and to oxidize major superalloy constituents to aqueously soluble ionic species. The insoluble solids from the aqueous solution are separated and the aqueous solution is extracted with an aqueously substantially insoluble tertiary amine to form an organic phase and an aqueous phase. The aqueous phase contains essentially nickel and chromium values. The organic phase is sequentially extracted with aqueous solutions which selectively solubilize individual metal value species to form individual aqueous solutions having substantially single metal value species therein. The metal value species solutions are processed to obtain substantially pure metal values.

### DETAILED DESCRIPTION OF THE INVENTION

"Superalloys" as used herein means and refers to alloy compositions containing nickel and/or chromium and cobalt and at least one metal selected from the group consisting of molybdenum, aluminum, titanium, tantalum and columbium.

"Valve metals" as used herein means and refers to refractory metals such as titanium, tantalum, columbium and the like which form oxide films stable enough to serve as capacitors or electronic valves.

The superalloy scrap useful in the practice of the invention is in the form of high surface area per unit weight material, such as grindings and other particulate matter. Preferably, the material has a mesh size of 20 to 200, and more preferably a mesh size of 100 to 200. The high surface area is desired so that it will readily react in the aqueous acid medium. Although very large pieces of superalloy scrap, i.e. on the order of one-eighth to one-half inch in diameter may be used, it is preferred that they be reduced in size in order to allow for ready reactivity with the acid solution.

Preferably, the scrap is first degreased by an appropriate organic solvent and/or otherwise treated to remove particulate impurities such as dirt and the like from the scrap prior to treatment in the process in accordance with the invention.

The scrap is then contacted with the aqueous acidic medium. The aqueous acidic medium useful in the practice of the invention is one which is rich in chloride ion so that it readily reacts with the metal values in the scrap. The chloride concentration in the aqueous acidic medium should be in the range of 150 to 350 grams per liter corresponding to 4.2 to 10 molar HCl. The aqueous acidic solution can be provided by hydrochloric acid per se or with chlorine gas to provide the desired acidity and chlorine concentration to the media.

Further, a hydrochloric acid solution can be enriched by the addition of chlorine gas thereto.

The solution potential is preferably controlled in the range of above +500 millivolts in order to provide a rapid leaching, i.e. reaction of the metal values with the acidic medium. Further, the solution potential should be at least about 750, and more preferably at least about 800 millivolts prior to solvent extraction in order to have any iron present as  $Fe^{+3}$  and molybdenum as  $Mo^{+6}$ . Although these valence states for iron and molybdenum can be maintained at potentials less than 800 millivolts, it is desired to maintain the potential at or about 800 millivolts in order to ensure these valence states. In addition, the oxidation potential should be

TABLE I-continued

	ELEMENT										Form/ Compound
	Ni	Cr	Co	Mo	Fe	Water	Cl	H	O	Total	
Solid	13647.2	4874.0	3168.1	1218.5	243.7	1218.5				24370.0	Grinding
All <sup>1</sup>							43009.0	1211.5		44220.5	HCl
H <sub>2</sub> O <sup>1</sup>								9124.9	72998.0	82123.8	H <sub>2</sub> O
Water <sup>2</sup>								4254.0	34032.2	38286.2	H <sub>2</sub> O
Total	13647.2	4874.0	3168.1	1218.5	243.7	1218.5	43009.0	14590.4	107030.2	189000.5	
Input											
Output											
Solution	12635.0						15204.8			27839.8	NiCl <sub>2</sub>
		4693.0					9611.6			14304.6	CrCl <sub>3</sub>
			2931.3				7055.0	99.4		10085.7	H <sub>2</sub> CoCl <sub>4</sub>
				960.3			1775.5	20.0	160.0	2915.8	H <sub>2</sub> MoOCl <sub>5</sub>
					231.0		585.9	8.3		825.2	H <sub>2</sub> FeCl <sub>4</sub>
							7725.2	217.6		7942.8	HCl
								13358.9	106871.1	120230.0	H <sub>2</sub> O
								886.2		886.2	H <sub>2</sub>
Crystals <sup>3</sup>	485.9	0.02	113.7		6.1		1051.0			1657.9	Mixed crystals
Undissolved	526.3	94.1	123.1	134.3	6.6	45.5				930.9	Grindings
Solid											
Fine Black		86.88		123.9		1172				1382.8	Fine Black
Material <sup>4</sup>											Material <sup>4</sup>
Total	13647.2	4874.0	3168.1	1218.5	243.7	1218.5	43009.0	14590.4	107030.2	189000.5	
Output											

<sup>1</sup>Input is 15 percent HCl<sup>2</sup>Water to make 29 percent HCl<sup>3</sup>Mixed chloride crystals of Ni, Cr, and Fe<sup>4</sup>Fine Black Material is valve metals and other impurities

The final solution properties of the combined reaction products were as follows:

87.50 grams/liter Ni  
 32.50 grams/liter Cr  
 20.30 grams/liter Co  
 6.65 grams/liter Fe  
 294.60 grams/liter Cl  
 2.00 molar HCl  
 Density: 1.280 grams/cm<sup>3</sup>  
 Potential: +177 mv

It was noted during the running of Examples I through V that it was necessary to keep the chloride ion concentration at about 280 to 300 grams/liter for effective dissolution of grindings.

Although Examples I through V were conducted using HCl as an oxidant, other oxidants such as oxygen, ozone, chlorine, chromate ion or ferric ion can also be used in the practice of the invention.

The combined reaction products of Example I through V were raised to an oxidation potential of about +800 with H<sub>2</sub>O<sub>2</sub> and were filtered free of solids and used as the base material for the remaining examples.

#### EXAMPLE VI

To a 5 gallon glass reactor equipped with an agitator and a thermometer was charged 1 gallon of combined reaction product along with 1 gallon of 30 percent by weight Atamine 336 (trioctylamine), 40 percent by weight isodecanol and 30 percent by weight kerosene. The organic phase and the aqueous phase were heated to 40° C. and agitated to ensure intimate contact of the two phases for 4 minutes. The organic phase was drawn off and 1 gallon of amine solution was charged to the reactor and contacted and separated as previously described. Again, 1 gallon of amine solution was charged, contacted and separated as previously described. Thus, 1 gallon of reaction product had the cobalt, molybdenum and iron extracted therefrom into 3 batches of organic phase.

The 3 batches of organic phase were combined and extracted by 4 successive extractors with 1 gallon of

aqueous HCl solution having a pH of 2. The aqueous phase contained the cobalt and the organic phase contained Fe and Mo.

The organic phase, which has the Co removed therefrom, was extracted by contacting with 1 gallon of water to remove Fe in the aqueous phase. The organic phase, which now contained only Mo, was adjusted to a pH of 10 to 12 by the addition of a 22 percent by weight aqueous solution of sodium carbonate, and the molybdenum was stripped from the organic phase as Na<sub>2</sub>MoO<sub>4</sub>. The organic phase was protonated by the addition of HCl and used for subsequent extractions.

The process of Example VI was repeated several times in order to treat 10.5 gallons of combined reaction product.

In the process of Example VI, 95 percent of Co, 98 percent of Mo, 99 percent of Ni and 94 percent of Cr were recovered from the combined reaction product.

#### EXAMPLE VII

The cobalt solution recovered in accordance with Example VI was filtered and neutralized to a pH of 5.5 with sodium carbonate to remove nickel and iron. The cobalt was recovered by electrowinning the cobalt solution.

#### EXAMPLE VIII

The molybdenum solution formed in Example VI as Na<sub>2</sub>MoO<sub>4</sub> was converted to MoO<sub>3</sub> by reaction with ammonium chloride and then with nitric acid.

#### EXAMPLE IX

The aqueous solution containing Ni and Cr formed in Example VI was adjusted to a pH of 7 to 10 with sodium carbonate, thus precipitating NiCO<sub>3</sub> and Cr(OH)<sub>3</sub>.

The precipitate was stirred in water and reacted with H<sub>2</sub>O<sub>2</sub> to oxidize Cr<sup>3+</sup> to Cr<sup>6+</sup>, thus providing soluble sodium chromate and precipitated NiCO<sub>3</sub>. Once precipitated, the nickel can be electrowon. The chrome can be precipitated as CrO<sub>3</sub> or as Na<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>.

Thus, precipitate can also be calcined to remove  $\text{CO}_2$  and aluminothermically reduced to an alloy of Ni and Cr.

In order to provide maximum recovery of metal values from the superalloy scrap, certain parameters must be observed during the process.

Thus, prior to extraction with the organic phase, the reaction product must be carefully oxidized so that iron is present as  $\text{Fe}^{+3}$ , Mo is present as  $\text{Mo}^{+6}$ , cobalt is present as  $\text{Co}^{+2}$  and chromium is present as  $\text{Cr}^{+3}$ . Further, to ensure the extraction of  $\text{Co}^{+2}$ , the  $\text{Cl}^-$  content of the solution must be at about 250 grams/liter to ensure complete formation of the  $\text{CoCl}_4^{-2}$  ion.

Although the specific examples herein are directed to a batch recovery process, the process of the invention is adaptable to performance of a continuous basis using known countercurrent methods.

Thus, the process of the invention provides a method of recovering a substantial amount of the valuable metal values in superalloy scrap.

Although the invention has been described with reference to specific processes and specific materials, the invention is only to be limited so far as is set forth in the accompanying claims.

We claim:

1. A method of recovering metal values from superalloy scrap comprising the steps of:

- (i) oxidizing the superalloy scrap in an aqueous acidic media, said aqueous acidic media having an oxidation potential sufficient to oxidize valve metals to insoluble solid oxides thereof, and to oxidize non-valve metals to aqueously soluble ionic species wherein the chromium values are oxidized to the +3 valence;
- (ii) separating the insoluble solids from the aqueous solution;
- (iii) extracting the aqueous solution with an aqueous substantially insoluble tertiary amine to form

an organic phase containing the non-valve metal values except for the nickel and chromium values and an aqueous phase containing nickel and chromium values; and

- (iv) separating the aqueous phase containing the nickel and chromium values from the organic phase wherein the improvement comprises the steps of:
  - (v) oxidizing the chromium +3 to aqueous-soluble chromium +6;
  - (vi) deacidifying the aqueous phase to a pH of about 7-10 with a soluble carbonate to form insoluble nickel carbonate;
  - (vii) precipitating the nickel carbonate from the chromium-containing solution;
  - (viii) recovering the nickel from the nickel carbonate precipitate; and
  - (ix) recovering the chromium from the solution.

2. The method of claim 1 wherein the aqueous phase is deacidified to form insoluble nickel carbonate and chromium hydroxide before the chromium is oxidized to form aqueous-soluble chromium +6.

3. The method of claim 1 wherein step (v) comprises oxidizing the chromium with hydrogen peroxide.

4. The method of claim 1 wherein step (vi) comprises deacidifying with sodium carbonate.

5. The method of claim 1 wherein step (viii) comprises the recovery of nickel from the carbonate by calcining to form nickel oxide.

6. The method of claim 1 wherein step (ix) comprises recovering chromium as a chromate by crystallization.

7. The method of claim 1 wherein the aqueous acidic phase containing the chromium and nickel ionic species is a chloride solution and is deacidified with a soluble carbonate, and the nickel carbonate is formed in a chloride salt solution.

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