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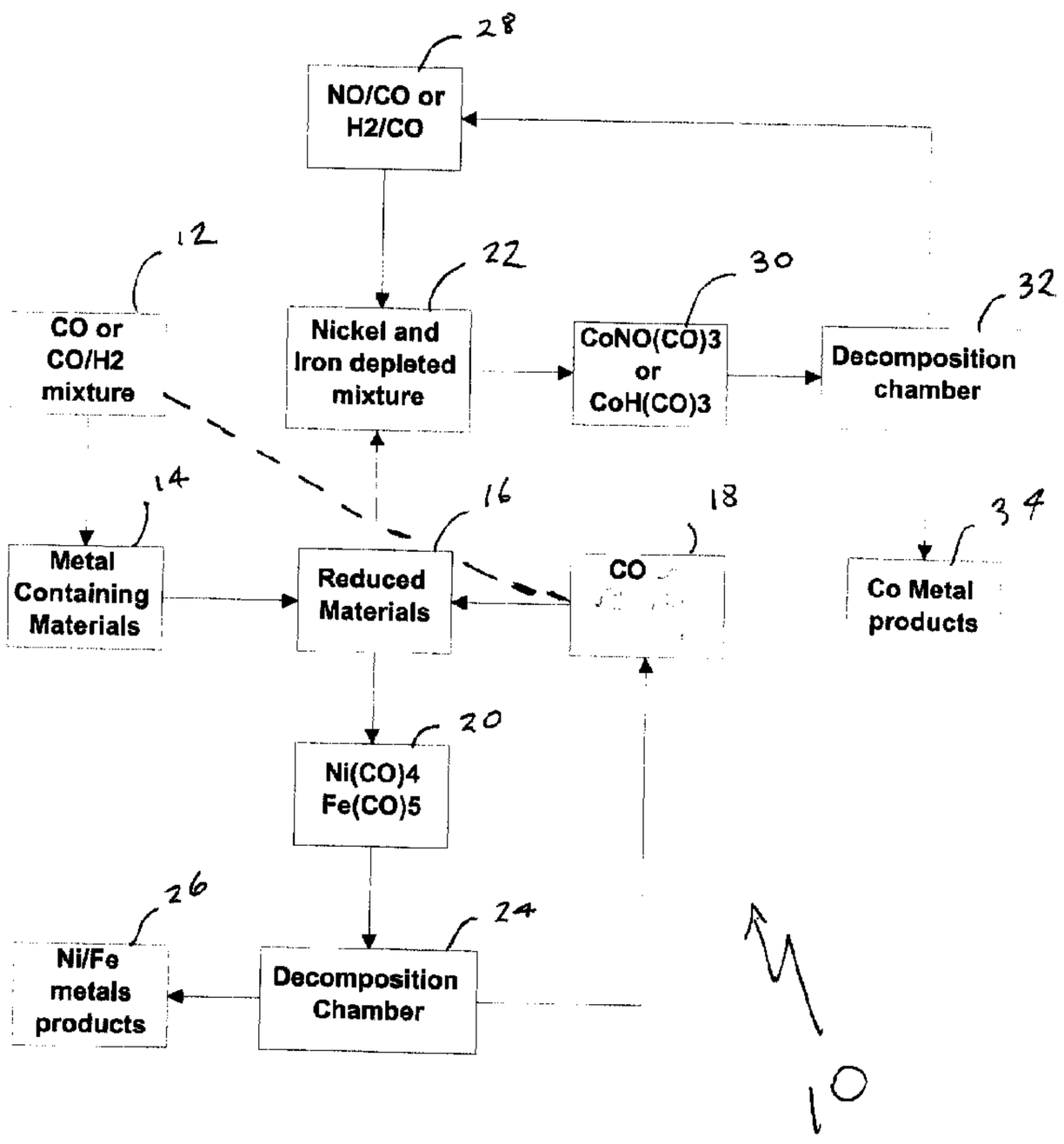
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(71) Demandeur/Applicant:
CHEMICAL VAPOUR METAL REFINING INC., CA

(72) Inventeur/Inventor:
TEREKHOV, DMITRI S., CA

(74) Agent: SMITH LYONS LLP

(54) Titre : METHODE DE RECUPERATION DU COBALT
(54) Title: COBALT RECOVERY PROCESS



(57) Abrégé/Abstract:
A process for producing purified cobalt from a mixture comprising metallic species of cobalt and metallic species of at least one of the group consisting of nickel and iron; said process comprising producing a metal carbonyl mixture of cobalt carbonyl and at least one of said nickel carbonyl and iron carbonyl from said metallic species mixture; separating said cobalt carbonyl from said nickel carbonyl and/or iron carbonyl; treating said cobalt carbonyl with an effective amount of a complexing gaseous admixture selected from a nitric oxide/carbon monoxide admixture and hydrogen/carbon monoxide admixture to produce a complexed cobalt carbonyl selected from cobalt nitrosyl tricarbonyl and cobalt carbonyl hydride; isolating said complexed cobalt carbonyl by

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(57) Abrégé(suite)/Abstract(continued):
distillation to provide purified complex cobalt carbonyl; decomposing said purified complex cobalt carbonyl to provide said purified cobalt and regenerated complexing gaseous mixture; and removing said regenerated complexing gaseous mixture. The process provides cobalt of improved quality in an optionally, continuous and closed-loop manner. Preferred process include either aqueous and/or gaseous process steps.

ABSTRACT OF THE INVENTION

A process for producing purified cobalt from a mixture comprising metallic species of cobalt and metallic species of at least one of the group consisting of nickel and iron; said process comprising producing a metal carbonyl mixture of cobalt carbonyl and at least one of said nickel carbonyl and iron carbonyl from said metallic species mixture;

separating said cobalt carbonyl from said nickel carbonyl and/or iron carbonyl; treating said cobalt carbonyl with an effective amount of a complexing gaseous admixture selected from a nitric oxide/carbon monoxide admixture and hydrogen/carbon monoxide admixture to produce a complexed cobalt carbonyl selected from cobalt nitrosyl tricarbonyl and cobalt carbonyl hydride; isolating said complexed cobalt carbonyl by distillation to provide purified complex cobalt carbonyl; decomposing said purified complex cobalt carbonyl to provide said purified cobalt and regenerated complexing gaseous mixture; and removing said regenerated complexing gaseous mixture. The process provides cobalt of improved quality in an optionally, continuous and closed-loop manner. Preferred process include either aqueous and/or gaseous process steps.

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COBALT RECOVERY PROCESS

FIELD OF THE INVENTION

This invention relates to a method and apparatus for the recovery of cobalt from impure cobalt, particularly from cobalt containing minerals, ores, scrap, slag, concentrates, metallurgical intermediates and by-products and, more particularly, nickel- and iron-containing materials.

SUMMARY OF THE INVENTION

It is an object of the present invention to provide apparatus and process for producing purified cobalt from mixtures comprising impure metallic cobalt or compounds thereof, in admixture with metallic nickel and/or iron or compounds thereof.

In its broadest aspect, the invention provides a process for producing purified cobalt from a mixture comprising metallic species of cobalt and metallic species of at least one of the group consisting of nickel and iron; said process comprising

producing a metal carbonyl mixture of cobalt carbonyl and at least one of said nickel carbonyl and iron carbonyl from said metallic species mixture;

separating said cobalt carbonyl from said nickel carbonyl and/or iron carbonyl;

treating said cobalt carbonyl with an effective amount of a complexing gaseous admixture selected from a nitric oxide/carbon monoxide admixture and hydrogen/carbon monoxide admixture to produce a complexed cobalt carbonyl selected from cobalt nitrosyl tricarbonyl and cobalt carbonyl hydride;

isolating said complexed cobalt carbonyl by distillation to provide purified complex cobalt carbonyl;

decomposing said purified complex cobalt carbonyl to provide said purified cobalt and regenerated complexing gaseous mixture; and

removing said regenerated complexing gaseous mixture.

In one preferred aspect the invention provides a process for producing purified cobalt from a mixture comprising metallic species of cobalt, and at least one of the group consisting of nickel and iron; said process comprising

(i) reacting said metallic species with carbon monoxide to form a carbonyl mixture comprising cobalt carbonyl and nickel carbonyl and/or iron carbonyl, provided that when said metallic species comprises non-elemental metal species, said mixture is, optionally, first treated with a reducing agent to reduce said non-elemental metallic species to said elemental metal;

(ii) removing said nickel carbonyl and said iron carbonyl by distillation from said carbonyl mixture to provide a nickel- and iron-depleted impure cobalt carbonyl mixture;

(iii) treating said impure cobalt carbonyl mixture with an effective amount of a complexing gaseous mixture selected from the group consisting of nitric oxide/carbon monoxide and hydrogen/carbon monoxide to produce a complexed cobalt carbonyl selected from the group consisting of cobalt nitric oxide carbonyl and cobalt hydrogen carbonyl;

(iv) isolating said complexed cobalt carbonyl by distillation to provide purified complex cobalt carbonyl;

(v) decomposing said purified complex cobalt carbonyl to provide said purified cobalt and regenerated complexing gaseous mixture; and

(vi) removing said regenerated complexing gaseous mixture.

By the term "metallic species" in this specification is meant to include the metal in the form of the elemental metal per se, sulfides, oxides, salts thereof, and minerals, concentrates, metallurgical intermediates, by-products and the like containing said elemental metal, sulfide, oxide and salts; and mixtures thereof.

It will be readily understood by the skilled person in the art that the process as hereinabove defined does not require the optional reduction step when the mixture does not contain sufficient reducable non-elemental metal compounds as hereinabove defined. The optional reduction step may be carried out by reducing agents, such as for

example, carbon monoxide, hydrogen or mixtures thereof. Any aforesaid reduction step with a CO/H_2 mixture must be carried out under such conditions that do not cause the production of volatile cobalt hydrogen carbonyl.

However, aforesaid carbonylation step (i) may be carried out simultaneously as the optional carbon monoxide reduction to elemental metal step.

Surprisingly, I have discovered that to effectively separate cobalt from nickel- and/or iron-containing admixtures according to one aspect of the present invention, that both nickel carbonyl and/or iron carbonyl must be removed first from the cobalt carbonyl containing admixture, in the complexing reaction vessel. Subsequent production and isolation of complexed cobalt carbonyl compounds, such as for example, cobalt nitric oxide carbonyl and cobalt hydrogen carbonyl provides desired pyrolysable precursors for purified metal cobalt production.

Most preferably, the nickel carbonyl and/or iron carbonyl gases of step (ii) are subsequently pyrolysed to provide regenerated carbon monoxide for recycle to step (i). Yet further, preferably, the regenerated complexing gaseous mixture of step (vi) is recycled to step (iii).

Thus, recycling of aforesaid gaseous carbon monoxide advantageously provides for a continuous closed-loop, purified cobalt production process.

The nickel carbonyl $Ni(CO)_4$, and/or iron carbonyl $Fe(CO)_5$ may be readily removed by vaporization, distillation – vacuum or otherwise, from the carbonylation reactor to leave behind cobalt carbonyl, $(Co)_2(CO)_8$.

In an alternative preferred aspect, the invention provides a process for producing purified cobalt from a mixture comprising metallic species of cobalt and metallic species of at least one of the group consisting of nickel and iron; said process comprising

(i) treating said mixture in aqueous alkaline medium with hydrogen sulfide to effect reduction of metal species to soluble metallic species;

(ii) subsequently treating said medium with carbon monoxide to produce cobalt carbonyl in admixture with nickel carbonyl and/or iron carbonyl in aqueous slurry;

(iii) removing said nickel carbonyl, if any, by volatilization from said solution; to provide a nickel carbonyl-depleted slurry;

(iv) separating cobalt carbonyl solid from said nickel-carbonyl-depleted slurry;

(v) treating said cobalt carbonyl solid with an effective amount of a complexing gaseous admixture selected from a nitric oxide/carbon monoxide admixture and hydrogen/carbon monoxide admixture to produce a complexed cobalt carbonyl selected from cobalt nitrosyl tricarbonyl and cobalt carbonyl hydride;

(vi) isolating said complexed cobalt carbonyl by distillation to provide purified complex cobalt carbonyl;

(vii) decomposing said purified complex cobalt carbonyl to provide said purified cobalt and regenerated complexing gaseous mixture; and

(viii) removing said regenerated complexing gaseous mixture.

BRIEF DESCRIPTION OF THE DRAWINGS

In order that the invention may be better understood, preferred embodiments will now be described by way of example only with reference to the accompanying drawings, wherein

Fig. 1 is a block diagram of the apparatus and process steps of one embodiment according to the invention; and

Fig. 2 is a block diagram of the apparatus and process steps of an alternative embodiment according to the invention.

DETAILED DESCRIPTION OF PREFERRED EMBODIMENTS

Fig. 1 shows generally as 10 a non-aqueous cobalt recovery process wherein a reducing agent 12 selected from carbon monoxide and a carbon monoxide/hydrogen

mixture is reacted with a cobalt oxide, nickel sulfide and iron oxide mixture 14 to produce an elemental trimetallic admixture 16, which is reacted with further carbon monoxide 18 to effect carbonylation of each of the three metals within reactor 16. Vacuum distillation of the carbonyl compounds in reactor 16 provides nickel carbonyl $Ni(CO)_4$ and $Fe(CO)_5$ 20 removal and a residual nickel- iron-depleted mixture 22. Nickel and iron carbonyls 20 are subsequentl6y pyrolysed in decomposition chamber 24 to provide metallic nickel/iron 26 and regenerated carbon monoxide recycled as source 18.

Mixture 22 containing solid polymeric, for example, dimeric cobalt carbonyl $Co_2(CO)_8$ is treated with a complexing gaseous admixture selected from the group consisting of nitric oxide carbon monoxide and hydrogen/carbon monoxide 28 to produce cobalt nitrosyl tricarbonyl or cobalt carbonyl hydride, respectively, 30.

The complexed cobalt carbonyls are transferred by distillation to decomposition chamber 32 and pyrolized therein to produce purified metallic cobalt 34. Regenerated nitric oxide/carbon monoxide or hydrogen/carbon monoxide admixtures are recycled to 28.

The aforesaid embodiment represents a closed loop gaseous recycle process adaptable to be operably continuous by the addition of impure polymetallic species feedstock and removal of purified metallic cobalt and nickel and iron by-products.

Fig. 2 shows generally as 100 an aqueous cobalt recovery system wherein a cobalt oxide, nickel oxide and iron sulfide mixture 50 is slurried in aqueous alkaline solution 52 with calcium hydroxide and hydrogen sulfide.

Carbonylation of the trimetallic species is carried out with carbon monoxide 54. Nickel carbonyl is volatilized from the mixture 54 and subsequently pyrolized 56 to produce purified nickel 58 and regenerated carbon monoxide.

The nickel-depleted slurry is filtered 60 to provide solid cobalt carbonyl 62, while iron carbonyl species remain in solution.

Cobalt carbonyl 62 is then treated with a complexing admixture selected from nitric oxide/carbon monoxide and hydrogen/carbon monoxide to produce cobalt nitrosyl tricarbonyl or cobalt carbonyl hydride, respectively, 64 which is isolated and

subsequently pyrolysed to produce purified metallic cobalt 66 and regenerated complexing admixture for optional recycle.

Example 1:

A mixture of sulfides consisting of 44% nickel, 6% cobalt and 1% iron, together with small amounts of chromium, manganese, magnesium, aluminum and silicon oxides/sulfides was mixed with 20 Kg of $Ca(OH)_2$ per 100 Kg of sulphides mixture, and formed into slurry (52). The resulting mixture was heated to 60°C and carbon monoxide introduced into the mixture and bubbled through slurry (54) under 3 bar pressure. The CO gas released from solution carried over nickel carbonyl, reclaimed (56) and recycled into process (54). The concentration of nickel carbonyl in outlet CO gas was constantly monitored to ensure complete removal of nickel from the slurry. After all of the nickel carbonyl was removed from the reactor, the resultant mixture was filtered and a NO/CO gas mixture introduced into the solution at 40°C under 3 bar pressure (62). Released NO/CO mixture was passed through the reclaim system to remove cobalt nitrosyl carbonyl ($CoNO(CO)_3$) formed in the process, and then recycled back into the process. The concentration of $CoNO(CO)_3$ in NO/CO was constantly monitored to ensure complete removal of Co. The resultant $CoNO(CO)_3$ was dried and thermally decomposed (64) into the different forms of Co metal such as powder, pellets or mesh shaped (66). Released NO/CO gas mixture from the thermal decomposition of $CoNO(CO)_3$, was pressurized and recycled into the process.

Example 2:

A mixture of Ni, Fe, Co oxides in ratios 10:1:1 (14) was reduced with CO/H_2 mixture (12) as described in B.P. 323 332 and B.P. 324 382. Carbon monoxide gas was then purged with either argon or nitrogen and the temperature of the reduced mixture of metals was lowered to 80 – 90°C. After the desired temperature was reached, carbon monoxide gas was passed through the mixture of reduced metals, under 10-20 bar pressure to produce metal carbonyls (16). The resultant nickel carbonyl, iron carbonyl and CO mixture was passed through the reclaim system (20) and metal carbonyl-depleted CO recycled into reaction vessel (160. The concentration of $Fe(CO)_5$ and

$Ni(CO)_4$ in the gas mixture was monitored to ensure complete removal of Ni and Fe. Removal of nickel carbonyl and iron carbonyl left cobalt carbonyl mixture (22). After the concentration of nickel and iron carbonyls in CO gas was reduced to the 100 ppm level, a mixture of NO/CO (28) was introduced into chamber (22) and temperature reduced to 40°C. NO/CO outlet mixture was passed through a reclaim system to remove the cobalt nitrosyl carbonyl and then reintroduced back to the reactor. The collected cobalt nitrosyl carbonyl was vaporized (32) and then thermally decomposed into metal cobalt products, such as powder, pellets or mesh shapes (32). Released NO/CO gas mixture from the thermal decomposition of $CoNO(CO)_3$ was pressurized and recycled into the process.

Although this disclosure has described and illustrated certain preferred embodiments of the invention, it is to be understood that the invention is not restricted to those particular embodiments. Rather, the invention includes all embodiments which are functional or mechanical equivalents of the specific embodiments and features that have been described and illustrated.

Claims

1. A process for producing purified cobalt from a mixture comprising metallic species of cobalt and metallic species of at least one of the group consisting of nickel and iron; said process comprising

producing a metal carbonyl mixture of cobalt carbonyl and at least one of said nickel carbonyl and iron carbonyl from said metallic species mixture;

separating said cobalt carbonyl from said nickel carbonyl and/or iron carbonyl;

treating said cobalt carbonyl with an effective amount of a complexing gaseous admixture selected from a nitric oxide/carbon monoxide admixture and hydrogen/carbon monoxide admixture to produce a complexed cobalt carbonyl selected from cobalt nitrosyl tricarbonyl and cobalt carbonyl hydride;

isolating said complexed cobalt carbonyl by distillation to provide purified complex cobalt carbonyl;

decomposing said purified complex cobalt carbonyl to provide said purified cobalt and regenerated complexing gaseous mixture; and

removing said regenerated complexing gaseous mixture.

2. A process for producing purified cobalt from a mixture comprising metallic species of cobalt and metallic species of at least one of the group consisting of nickel and iron; said process comprising

(i) reacting said metallic species with carbon monoxide to form a carbonyl mixture comprising cobalt carbonyl and nickel carbonyl and/or iron carbonyl, provided that when said metallic species comprises non-elemental metal species, said mixture is, optionally, first treated with a reducing agent to reduce said non-elemental metal species to said elemental metal;

(ii) removing said nickel carbonyl and said iron carbonyl by distillation from said carbonyl mixture to provide a nickel- and iron-depleted impure cobalt carbonyl mixture;

(iii) treating said impure cobalt carbonyl mixture with an effective amount of a complexing gaseous mixture selected from the group consisting of nitic oxide/carbon monoxide and hydrogen/carbon monoxide to produce a complexed cobalt carbonyl selected from the group consisting of cobalt nitrosyl tricarbonyl and cobalt carbonyl hydride;

(iv) isolating said complexed cobalt carbonyl by distillation to provide purified complex cobalt carbonyl;

(v) decomposing said purified complex cobalt carbonyl to provide said purified cobalt and regenerated complexing gaseous mixture; and

(vi) removing said regenerated complexing gaseous mixture.

3. A process as defined in claim 2 further comprising decomposing said nickel carbonyl and said iron carbonyl from step (ii) to provide regenerated carbon monoxide and recycling said carbon monoxide, in whole or in part to step (i).

4. A process as defined in claim 2 further comprising recycling said regenerated complexing gaseous mixture from step (vi) to step (iii).

5. A closed loop process as defined in claim 3 further comprising recycling said regenerated complexing gaseous mixture from step (vi) to step (iii).

6. A process as defined in any one of claims 2 to 5 comprising treating said non-elemental metal species with a reducing agent selected from the group consisting of carbon monoxide, hydrogen and mixtures thereof.

7. A process for producing purified cobalt from a mixture comprising metallic species of cobalt and metallic species of at least one of the group consisting of nickel and iron; said process comprising

(i) treating said mixture in aqueous alkaline medium with hydrogen sulfide to effect reduction of metal species to soluble metallic species;

(ii) subsequently treating said medium with carbon monoxide to produce cobalt carbonyl in admixture with nickel carbonyl and/or iron carbonyl in aqueous slurry;

(iii) removing said nickel carbonyl, if any, by volatilization from said solution; to provide a nickel carbonyl depleted-slurry;

(iv) separating cobalt carbonyl solid from said nickel-carbonyl-depleted slurry;

(v) treating said cobalt carbonyl solid with an effective amount of a complexing gaseous admixture selected from a nitric oxide/carbon monoxide admixture and hydrogen/carbon monoxide admixture to produce a complexed cobalt carbonyl selected from cobalt nitrosyl tricarbonyl and cobalt carbonyl hydride;

(vi) isolating said complexed cobalt carbonyl by distillation to provide purified complex cobalt carbonyl;

(vii) decomposing said purified complex cobalt carbonyl to provide said purified cobalt and regenerated complexing gaseous mixture; and

(viii) removing said regenerated complexing gaseous mixture.

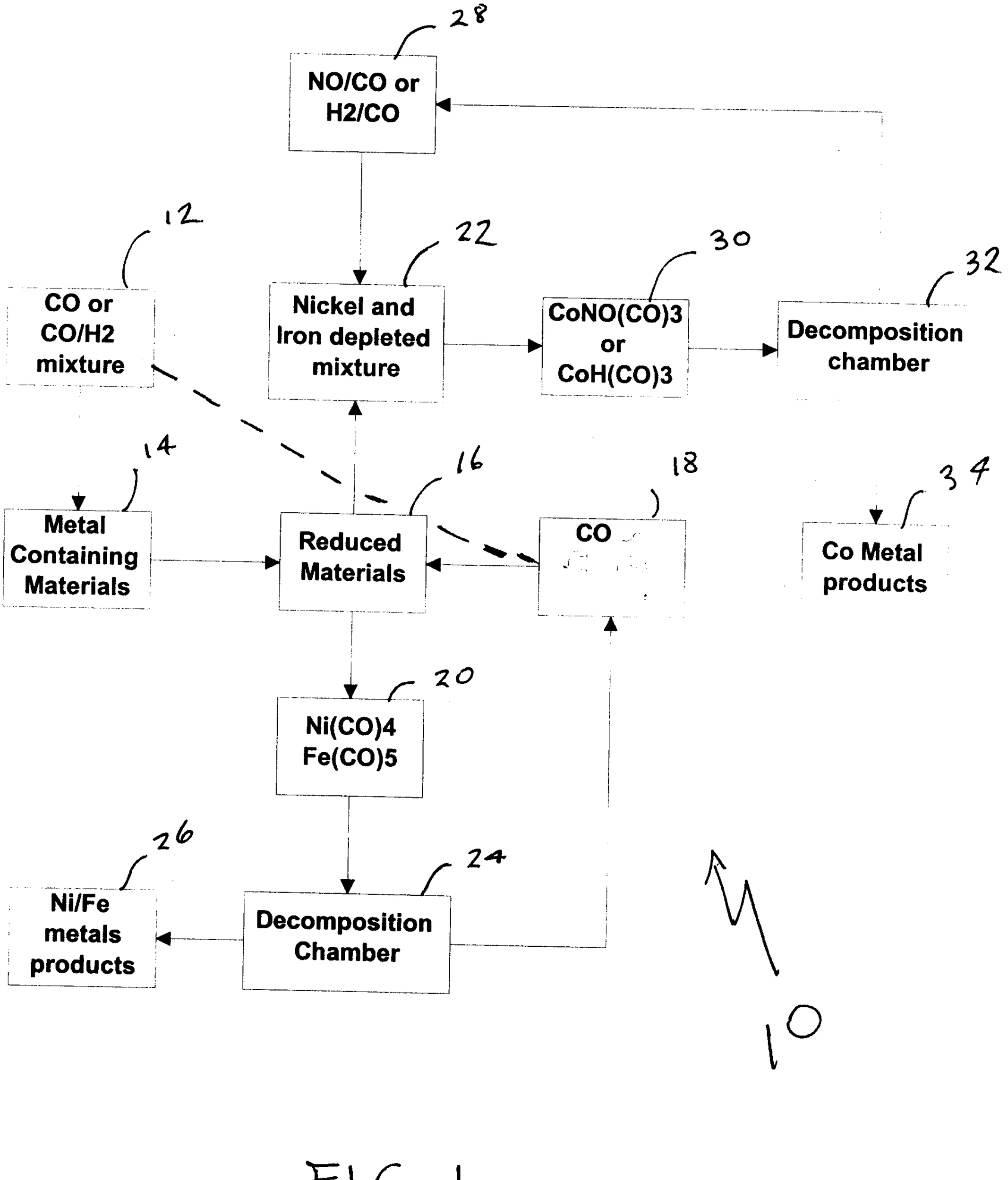

28
NO/CO or H2/CO
12
CO or CO/H2 mixture
22
Nickel and Iron depleted mixture
30
CoNO(CO)3 or CoH(CO)3
32
Decomposition chamber
14
Metal Containing Materials
16
Reduced Materials
18
CO
34
Co Metal products
20
Ni(CO)4 Fe(CO)5
26
Ni/Fe metals products
24
Decomposition Chamber
10

FIG 1.

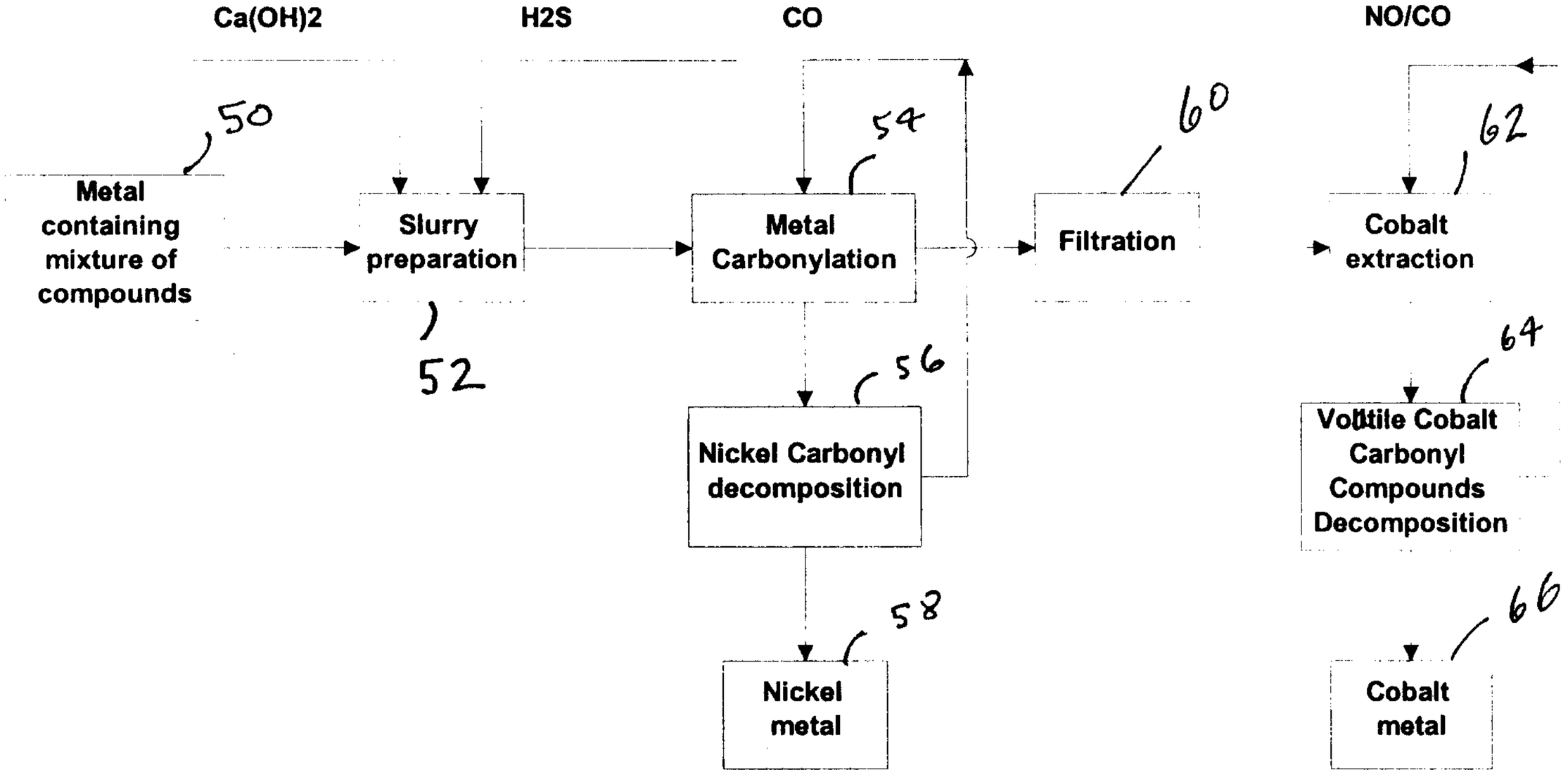
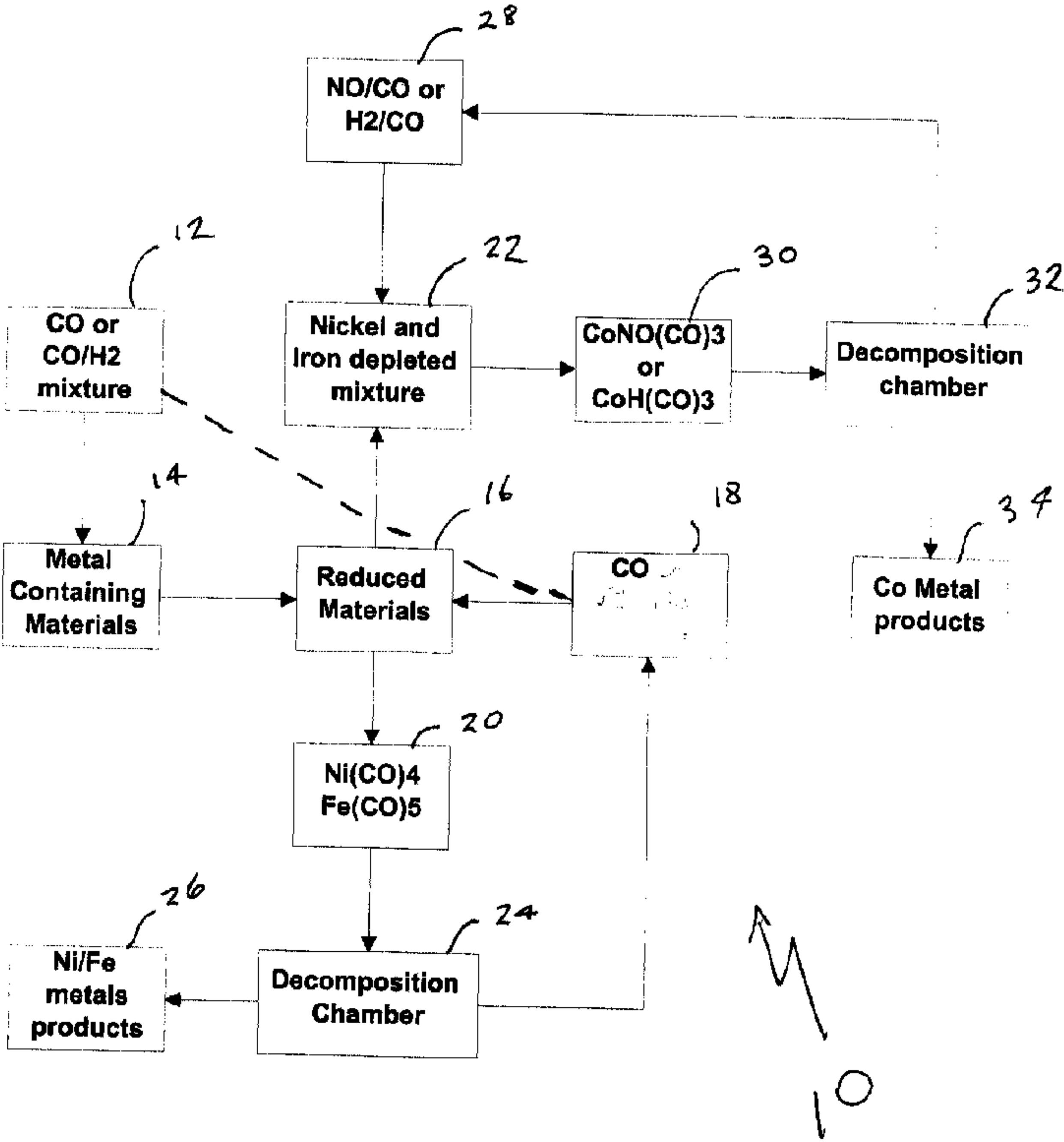

Ca(OH)2
H2S
CO
NO/CO
50
Metal containing mixture of compounds
Slurry preparation
52
54
Metal Carbonylation
56
Nickel Carbonyl decomposition
58
Nickel metal
60
Filtration
62
Cobalt extraction
64
Volatile Cobalt Carbonyl Compounds Decomposition
66
Cobalt metal

FIG 2


28
NO/CO or H2/CO
12
CO or CO/H2 mixture
22
Nickel and Iron depleted mixture
30
CoNO(CO)3 or CoH(CO)3
32
Decomposition chamber
14
Metal Containing Materials
16
Reduced Materials
18
CO
34
Co Metal products
20
Ni(CO)4 Fe(CO)5
26
Ni/Fe metals products
24
Decomposition Chamber
10