United States Patent Office 2,946,677 Patented July 26, 1960

2,946,677

TREATMENT OF ALLOYS CONTAINING IRON GROUP METALS

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No Drawing. Filed Nov. 24, 1958, Ser. No. 775,705

5 Claims. (Cl. 75—97)

This invention relates to the recovery of metals from alloys, and more particularly to a method of producing solutions of metal salts as a step in the recovery of these metals from alloys containing the same. The invention concerns, specifically, metals of the iron group, i.e. nickel, cobalt, etc. which have been used extensively in the production of alloys of a special nature.

Exemplary of the alloys to which this invention relates, are the cobalt and/or nickel containing refractory type alloys and corrosion resistant alloys which have been developed in recent years. These may have cobalt and/or nickel concentrations ranging up to about 80% or more. With scrap containing more than about 10% nickel or cobalt, recovery of the nickel or cobalt fractions is practicable from a commercial standpoint, provided the recovery can be done in an economical manner.

Characteristically, these alloys have been prepared to have a maximum amount of resistance to corrosion, oxidization, and chemical attack. The alloys also may be quite tough and relatively hard to disintegrate. It is these very properties which distinguish the alloys and make them useful as a structural material, which have made difficult the manufacture of compounds therefrom. Thus these alloys have resisted dissolution in acids, caustic solution, fused salt baths, and other conventional hydrometallurgical recovery techniques.

In general terms, this invention contemplates as the first step in producing metal salts from such alloys the production of an intermediate "processing" alloy by melting together a mixture of the alloy from which metal is sought to be recovered and regulated amounts of aluminum. Through the introduction of aluminum, an intermetallic compound type of alloy is formed. While the original alloy may have been tough, difficult to disintegrate, and chemically resistant, the intermediate "processing" alloy is characterized generally by being (1) readily disintegrated to particle form using milling, grinding, or other conventional pulverizing techniques, and (2) markedly more reactive chemically with the usual salt forming, dissolving acids. Thus the "processing" alloy may be ground to comminuted form and the metal constituents thereof reduced to compounds of dissolving acids, using far less complex equipment than previously necessary using known recovery methods, and with considerable rapidity.

The advantages of the process outlined include considerable savings in time, faster use of processing equipment and a reduction in the extent and complexity of the equipment required, greater ease in handling and processing, savings in expense in reactants, etc.

Thus it is a primary object of this invention to provide an improved method for forming salt compounds of iron-group metals from alloys containing such metals which comprises the steps of first forming an intermediate "processing" alloy which is more reactive than the original alloy, and then subjecting this "processing" alloy to solvation with an acid. More particularly, it is an object of the invention to provide such a method which comprises melting with the initial alloy aluminum to produce a processing alloy which is friable and chemically reactive, pulverizing this processing alloy and subjecting the pulverant product to acid solvation.

The invention is described hereinbelow in conjunction wth certain specific examples, which are not intended to constitute the limits of the invention, but which are included for illustrative purposes.

Illustrative of the nickel and/or cobalt-containing alloys which may be processed according to this invention are the alloys Waspaloy (an alloy containing about 19.5% chromium, 57.0% nickel, 13.5% cobalt, 4.3% molybdenum, 3.1% titanium, 1.3% aluminum, 1.2% iron, and traces of carbon), Udimet 500 (an alloy containing about 19% chromium, 19% cobalt, 4.0% molybdenum, 3.0% titanium, 3.0% aluminum, 0.1% carbon, and the balance nickel), and Discaloy (an alloy containing about 13.5% chromium, 26.0% nickel, 54.0% iron, 3.0% molybdenum, 1.6% titanium, 0.8% manganese, and traces of carbon). These aforementioned alloys are typical of high temperature, high stress alloys finding use today in special applications, and as can be seen from the compositions given, contain substantial amounts of metals from the iron group. Corrosion-resistant alloys which may be treated according to the method of this invention are illustrated by such alloys as Monel metal (a nickel-copper alloy), Chromel (a nickel-chromium alloy), and cobalt-copper alloys. While various materials have been listed, the invention is not limited to use with these particular materials, but in general may be applied to mixtures of two or more metals wherein one of the metals is a metal from the iron group. While alloys containing relatively small percentages of nickel and cobalt may be processed as contemplated by this invention, as a practical matter usually such processing is not justified from an economic standpoint unless the percentage of nickel and cobalt in the alloy is more than about 10%.

In practicing the invention, generally optimum results were obtained when sufficient aluminum was incorporated with the original alloy to produce an aluminum concentration in the intermediate "processing" alloy of about 20% or more. A 20% aluminum concentration produced alloys which were friable, and had chemical reactivities with the usual solvent acids, such as sulfuric or hydrochloric, which were from 10 to 100 times or more greater than prior to the addition of aluminum. Greater amounts of aluminum may be employed for instance, aluminum concentrations in the processing alloy of 60% or more may be used, but ordinarily no advantage in friability or reactivity is incurred through such use, and the addition of large amounts of aluminum therefor merely has the effect of adding to the cost of processing. Satisfactory results were obtained with aluminum concentrations in the range of 13–15%, but with concentrations much below this, the character of the original alloy is not changed sufficiently to produce a useful improvement in the ease of processing. This is not to say, however, that the addition of small amounts of aluminum was without effect.

In carrying out the invention, a melt is first prepared, ordinarily by heating a mixture of the alloy from which salts are to be derived and a requisite amount of aluminum. In some instances, especially when chips and/or turnings are being processed, it may be desirable to briquette a mixture of the metals prior to melting. This procedure may be particularly advantageous if arc or induction melting is performed under vacuum. After a melt has been prepared and the metal constituents have mixed with each other, the mass is cooled, with the production of a metal ingot partially comprised of aluminum. During cooling, it is not uncommon for the ingot to crack

into smaller pieces, by reason of the internal thermal stresses produced during cooling.

The cooled "processing" alloy so formed preferably is reduced to a comminuted form prior to reaction with acid, as this increases the surface area of the metal available for contact with acid and thus the reaction rate of the alloy with acid. Disintegration of the alloy may be done in any of a number of conventional units, such as the usual ball or hammer mill, pneumatic attrition mill, and the like.

After disintegration, the comminuted alloy product is reacted with acid, with the production of metal salts of the acid and the evolution of hydrogen. In general, these acids comprise the usual metal oxidizing acids used in hydrometallurgical recovery processes. The acids generally are water soluble (i.e., more than about 80%), have a relatively high ionization potential, and are substantially stable and resistant to decomposition at atmospheric boiling temperatures. The concentration of acid used will vary, depending upon the metal sought to be dissolved, the solubility of the metal salts, etc. Illustrative of the acids which may be employed in the metal salt formation are the inorganic or mineral acids such as sulfuric, hydrochloric, nitric, and hydrofluoric acids. From an economic standpoint, since sulphuric acid is readily available commercially, this acid lends itself to the practice of this invention.

The amount of acid used in reaction with the powdered alloy normally will vary from stoichiometric amounts to amounts in excess of this. Since aluminum stands above the metals of the iron group (iron, cobalt, and nickel) in the electromotive series, it is necessary to have sufficient acid completely to combine with the aluminum before expecting the formation of salts of the iron-group metals.

During reaction of the powdered alloy with acid, the temperature of the reaction mixture ordinarily is raised above room temperature, as this also has the effect of speeding up the acid reaction. Thus temperatures of from between 80° C. and 100° C. may be used if the reaction is carried out at atmospheric pressure. Room temperatures may be employed, however, with satisfactory results. So also may temperatures above 100° C. be used if the reaction is carried out at elevated pressures. Superatmospheric pressures, other than allowing higher temperatures, apparently have little effect on the rate of reaction of the alloy with acid.

Other means may be employed to hasten the reaction of the powdered alloy with acid, such as providing agitation for the reaction mixture, removing spent or partially spent acid, etc. Such procedures would be apparent to one skilled in the art.

As an example of the process of this invention, a melt was prepared by heating to the melting point a mixture of 100 parts of a high cobalt, refractory alloy containing 62% cobalt, 27% chromium, 6% molydenum, 2% nickel and 3% of a mixture of iron, manganese, silicon, and carbon (with each of the latter components not exceeding 1%) and 25 parts of aluminum. (Unless otherwise indicated, parts and percentages used herein refer to parts and percentage on a weight basis.) Scrap turnings of the alloy were used, and these were briquetted with chips of aluminum using 25 tons pressure prior to producing the melt. The melt was made in an electric arc furnace, under vacuum. The melt was cooled to room temperature, with the approximately 20% aluminum alloy ingot which was formed cracking during cooling into coarse pieces of approximately walnut size.

The aluminum alloy was very friable and easily crushed with a mortar and pestle into a powder which passed through a 20 mesh Tyler screen. Fifteen parts of this powder was placed in a reaction vessel, and reacted with 200 parts of a 50% aqueous sulfuric acid solution. The sulfuric acid was poured slowly over the alloy powder, and the alloy powder and acid solution mixture simmered for about ¾ of an hour. At the end of this time, the alloy powder was completely dissolved.

A similar sample of alloy powder was reacted with an excess (600 parts) of 10% sulfuric acid, using a similar procedure, with substantially complete dissolving of the powder. An excess of hydrochloric, nitric, and hydrofluoric acids (25% solutions in water) was also effective substantially to completely dissolve such alloy powder.

In another example, a melt of about 100 parts of the refractory alloy having the composition set forth above and about 17 parts of aluminum was prepared, to yield an aluminum alloy having an aluminum content of about 14.5%. This alloy was tougher than the aluminum alloy first prepared, and not as friable, although the alloy could be ground to powder form.

Fifteen parts of the alloy containing 14.5% aluminum, ground to a powder which passed through a 20 mesh Tyler screen, was reacted with 200 parts of 50% aqueous sulfuric acid, over a period of about two hours, while simmering the reaction mixture. At the end of this time interval, the powdered alloy had been substantially completely dissolved.

An aluminum alloy prepared from 100 parts of the refractory alloy having the composition set forth above and about 100 parts of aluminum was very friable and easily ground to powdered form. This alloy and the 20% aluminum alloy were about equally reactive with 50% aqueous sulfuric acid and hydrochloric acid solutions.

In another treatment, 100 parts of Monel metal (67% nickel, 28% copper, 1–2% manganese, and 1.9–2.5% iron) was alloyed with 25 parts of aluminum. An extremely friable aluminum alloy was formed, which was readily ground to comminuted form. Fifteen parts of the ground-up alloy was simmered with 200 parts of 50% aqueous sulfuric acid over a period of about one hour. At the end of this time, the alloy powder had been substantially all dissolved. Similar results were obtained with 50% hydrochloric acid solution.

A sample of 100 parts of Waspaloy was alloyed with 25 parts of aluminum. The result was a friable product readily ground to powdered form. A 15 part sample of this product was reacted with 200 parts of 50% aqueous sulfuric acid, over a period of about two hours and at a temperature of from 95–100° C. At the end of the two-hour period, substantially all the powder had dissolved.

In another treatment, 100 parts of an alloy composed of about 0.3% carbon, 1.1% manganese, 0.6% silicon, 19.0% chromium, 9.0% nickel, 1.2% molybdenum, 1.2% tungsten, 0.4% columbium, 0.3% titanium, and the remainder iron was alloyed with 20 parts of aluminum. A friable product resulted, and a 15 part sample of the product ground to a powder reacted readily with 200 parts 50% aqueous sulfuric acid, with dissolving of the sample.

Thus, to summarize the invention, a process is contemplated whereby alloys may be readily changed to a state which makes them susceptible to chemical breakdown, i.e., reaction with acid materials whereby salts of the metallic constituents of the alloys are formed. Increased chemical reactivity is produced in an alloy conjointly with a change in the physical characteristics of the alloy which results in turning the alloy into a material which is considerably more amenable to mechanical disintegration. The process thus has particular importance in connection with the recovery of iron-group metals, such as cobalt and nickel, from alloys which normally resist physical and chemical degradation.

It is claimed and desired to secure by Letters Patent:

1. In the recovery of iron-group metals from a starting alloy containing the same, the process of producing salts of the iron-group metals in the starting alloy by alloying the starting alloy with aluminum to produce a friable aluminum alloy product, and dissolving the aluminum alloy product in an oxidizing acid which is reactive

with the product to produce salts of the acid and iron-group metals.

2. In the recovery of iron-group metals from a starting alloy containing the same, the process of producing salts of the iron-group metals in the starting alloy by alloying the starting alloy with aluminum thus to produce a friable aluminum alloy product, mechanically breaking up the aluminum-alloy product to form a particulate mass, and reacting the particulate mass with an oxidizing acid which is reactive with the mass to produce salts of the acid and iron-group metals.

3. In the recovery of iron-group metals from a starting alloy containing the same, the steps of rendering the starting alloy amenable to acid reaction through (1) alloying the starting alloy with aluminum to produce a friable aluminum alloy product, and (2) mechanically disintegrating the aluminum alloy product so formed and reacting the disintegrated aluminum alloy product with an oxidizing acid which is reactive with the product to produce salts of the acid and iron-group metals.

4. In the hydrometallurgical recovery of iron-group metals from an alloy containing the same, the process of forming a processing alloy from the original alloy by melting into the original alloy sufficient aluminum to produce an aluminum alloy product containing more than about 15% aluminum, mechanically disintegrating the aluminum alloy product, and reacting the disintegrated product with mineral acids which are reactive with the aluminum alloy to produce salts of the acid and iron-group metals.

5. In the hydrometallurgical recovery of metals selected from the group consisting of nickel and cobalt from an alloy containing the same, the process of alloying the original alloy with aluminum to produce a friable processing alloy which contains more than about 15% aluminum, mechanically disintegrating the processing alloy to obtain a pulverant product, and reacting the pulverant product with a mineral acid selected from the group consisting of sulfuric, hydrochloric, nitric, and hydrofluoric acids and mixtures thereof.

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