

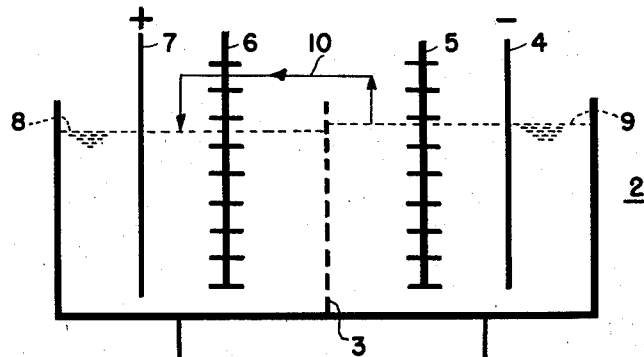
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METHOD OF MAKING ELECTROLYTIC CHROMIUM

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Anolyte containing iron and chromium

Extract iron with organic solvent

Heat chromium solution to volatilize organic solvent

Purified chromium solution

Treat with electrolytic chromium

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METHOD OF MAKING ELECTROLYTIC CHROMIUM

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5 Claims. (Cl. 204—105)

This invention relates to the production of electrolytic chromium and more particularly to methods of producing electrolytic chromium, which include as the first step the production of an alloy of iron, chromium and carbon by smelting chromite ores or concentrates with carbonaceous material.

In my copending application filed jointly with Holbert E. Dunn on June 27, 1951, Serial No. 233,786, we have disclosed a method of anodically dissolving iron-chromium-carbon alloys in solutions of sulphuric acid and ammonium sulphate. That method and others known in the art require crystallization of iron ammonium sulphate to purify the solution. Further, the method of anodic solution of the alloy disclosed in that application requires special procedures to maintain the iron in the ferrous state so that it can be removed subsequently by crystallization of iron ammonium sulphate.

In my present invention I substitute chloride solutions for sulphate solutions in both the anodic solution of the iron-chromium-carbon alloy and in the electrolytic deposition of chromium. This procedure has definite advantages, as will appear in the further description of the invention.

A principal feature of my invention is the anodic solution of iron-chromium-carbon alloy in a solution containing hydrochloric acid and one or more salts such as alkali-metal chloride, alkaline earth metal chloride or ammonium chloride. This electrolyte is advantageous over the sulphate from the standpoint of anodic solution because the anodic voltage drop is less for a given current density, i. e., there is less passivity of the alloy anode. The iron is separated from the product of anodic solution of the alloy by extraction of ferric chloride with an organic liquid, and therefore it is not necessary to add SO₂ or other reducing agent for maintaining the iron in the ferrous state as in the case of sulphate electrolyte.

Another important feature of my invention is the cathodic deposition of the chromium from the solution from which the iron has been removed, while the iron-chromium-carbon alloy is being dissolved in another compartment of the same cell. The use of the soluble anode in the chloride solutions solves the anode problem arising in the deposition of chromium from the chloride electrolyte in a separate cell.

In a way then my invention may be considered as an electrolytic refining process in a two-compartment cell in which the anolyte is removed from the cell and iron is removed from it by extraction with an organic solvent, and the purified anolyte is passed to the catholyte compartment of the cell for deposition of chromium after the spent catholyte is passed to the anolyte compartment for replenishing the chromium content.

The accompanying drawing is a flow sheet illustrating my process.

The extraction of ferric chloride from aqueous solutions by the use of organic liquids is well known. This extraction, however, by known means requires a high acidity

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which renders the chromium solution after extracting the iron unsuitable for chromium deposition. I have overcome this difficulty by adding substantial amounts of alkali-metal chloride or alkaline earth metal chloride or ammonium chloride. The iron may be extracted from such a solution at pH=1-3 by several organic solvents which are at least partially immiscible with such a solution but which are miscible with dilute salt solutions and therefore incapable of practical use with dilute salt solutions. A preferred solvent is a mixture of 90% acetone with 10% ethyl ether. Isopropyl ether may be used in place of ethyl ether but in either case the solvent should contain at least 80% acetone. Such solvents will extract sufficient ferric chloride to permit the use of the purified solution for chromium deposition. The dissolving of the solvent in the chromium solution is such, however, that the solvent must be distilled and recovered from the solution before electrolysis of the chromium solution. The solvent also is recovered from the ferric chloride solution by distillation.

The principal steps which characterize my invention are:

1. Anodic solution in a two-compartment cell of an iron-chromium-carbon alloy in an electrolyte containing hydrochloric acid and at least one chloride selected from the group consisting of alkali-metal chlorides, ammonium chloride and alkaline earth metal chlorides, to form a solution containing chromic chloride and ferric chloride.

2. Removal of the ferric chloride from such solution by extraction with an organic liquid which is at least partially immiscible with the solution at relatively low acidity and which contains at least one ketone.

3. Heating the chromium solution from which the iron has been extracted to volatilize and remove the organic solvent dissolved in the solution.

4. Electrolysis of the chromium solution in the cathode compartment of the cell used for step 1.

5. Passing the spent catholyte solution to the anode compartment of the cell for replenishing its chromium content.

Having described the general features of my invention, I will illustrate it with a specific example, reference being made to the accompanying flow sheet.

Example 1

I used anodes of iron-chromium-carbon alloy having the following analysis:

65.10	Cr
24.76	Fe
3.38	Si
6.76	C

These were in the form of castings 4" x 8" x 1".

The electrolytic cell, designated generally by the reference numeral 2, contained a porous alumina diaphragm 3 and a stainless steel cathode 4. The cell was equipped with stirrers 5 and 6 for circulation of both anolyte and catholyte and the level of the catholyte was maintained slightly above that of the anolyte so that any flow would be from catholyte to anolyte. The iron-chromium-carbon alloy anode is designated by the reference numeral 7. The anolyte 8 was a hydrochloric acid solution containing 70 grams per liter ammonium chloride and 35 grams per liter of sodium chloride although the amount of ammonium chloride may vary from 70 to 100 grams per liter. The pH of the anolyte was maintained at 1.2 by the addition of hydrochloric acid.

The catholyte 9 was the same as the anolyte except that it contained 30 grams per liter of chromium at the start of the process. A direct current was passed through the electrolytes in the cell. This caused solution of the anode

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7 in the anolyte forming a solution containing iron and chromium. Chromium was deposited on the cathode 4 from the catholyte, thereby depleting the chromium content of the catholyte. The process was stopped when the chromium content of the catholyte was 10 grams per liter, at which time the chromium concentration in the anolyte had been built up to about 30 grams per liter. The catholyte pH was maintained at 1-2.

The current efficiency for the deposition of chromium was about 60% and as the anode efficiency was also about 60% for chromium dissolution, the two circuits remained fairly balanced. The anode current density and the cathode current density were each about 70 amperes per square foot.

The anolyte in which the concentration of chromium had been built up to about 30 grams per liter was drawn off from the cell and the spent catholyte was passed to the anolyte chamber as indicated by reference numeral 10. The anolyte containing ferric chloride and chromic chloride was extracted with a mixture of 90% acetone and 10% ethyl ether to extract ferric chloride. Six stages of extraction were used. In each stage the solvent was shaken with the anolyte solution, the mixture allowed to separate into layers, and the layers separated from each other. The total iron extracted was:

Stage:	Total iron extracted, percent
1	85
2	91
3	96
4	96.5
5	97
6	97.1

For each liter of anolyte the final volume of chromium solution was 1437 ccs. and the acetone-ether extract was 1075 ccs. Distillation of these two products gave 850 ccs. of chromium solution and 145 ccs. of ferric chloride solution and substantially quantitative recovery of the acetone and ether.

The chromium solution contained 28.0 grams per liter chromium and 0.28 grams per liter iron. This solution was treated with powdered electrolytic chromium to precipitate any more noble metals and reduce the remaining iron to the ferrous condition. This solution was used in the catholyte compartment of the cell to deposit chromium.

In the example given the chlorides other than chromium chloride were ammonium and sodium chlorides. I have found that potassium chloride, lithium chloride, calcium chloride and magnesium chloride may be used as constituents of the electrolyte. The relative proportions of the chlorides are not critical. They must be present in a total amount sufficient to provide a good conducting solution and to "salt out," i. e., render the organic solvent used to extract the ferric chloride at least partially immiscible. When acetone with only a small proportion of ether is used as the solvent, at least 100 grams per liter of total chlorides must be present. Less concentrations of chlorides may be used, however, if dibutyl ketone or other ketone which is less miscible with the chromium solution is used as the extractant. It will be understood that extraction with ethers such as diethyl ether and isopropyl ether may be used to remove the iron without regard to the salt concentration, but such extraction must be carried out at high acidity, preferably 6 to 8 normal. The extraction at low acidity according to the present invention with solvents such as acetone which must be "salted out" is, therefore, an important feature of my invention.

The invention can be utilized in carrying out either a batch or a continuous process.

The invention is not limited to the preferred embodiment but may be otherwise embodied or practiced within the scope of the following claims.

I claim:

1. The method of making electrolytic chromium from

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an iron-chromium-carbon alloy, which comprises making such alloy an anode in the anode compartment of a compartment cell separated by an ion-permeable diaphragm and having an insoluble cathode in the cathode compartment, said anode compartment having an electrolyte containing hydrochloric acid and at least one chloride selected from the class consisting of alkali metal chlorides, ammonium chloride, and alkaline earth metal chlorides, said cathode compartment having an electrolyte containing hydrochloric acid, chromium chloride and at least one of the aforesaid chlorides, passing a unidirectional current through said cell from said anode to said cathode whereby to dissolve the alloy at the anode and deposit electrolytic chromium at the cathode, withdrawing from the cell the anolyte containing the metals, including iron, dissolved from the anode, extracting the iron from said withdrawn anolyte at a pH of 1-3 by a volatile organic solvent containing at least 80% ketone, said withdrawn anolyte containing chloride from said class in an amount sufficient to render said organic solvent at least partially immiscible with said withdrawn anolyte, removing dissolved solvent from the solution by evaporation and using the so treated solution as the electrolyte in the cathode compartment for the deposition of chromium, and then using the solution so depleted of chromium for the electrolyte in the anode compartment whereby to replenish the chromium content thereof.

2. The method of claim 1 further characterized by the electrolyte containing at least 100 grams per liter of salts selected from the group consisting of alkali metal chlorides, alkaline earth metal chlorides and ammonium chloride.

3. The method of claim 1 further characterized by the organic solvent for extracting the iron being a mixture of acetone and a solvent selected from the class consisting of ethyl ether and isopropyl ether, the acetone amounting to at least 80% of the organic solvent.

4. The method of claim 1 further characterized by the anolyte containing from 70-100 grams per liter of ammonium chloride and 35-80 grams per liter of sodium chloride.

5. The method of making electrolytic chromium from an iron-chromium-carbon alloy, which comprises making such alloy an anode in the anode compartment of a compartment cell separated by an ion-permeable diaphragm and having an insoluble cathode in the cathode compartment, said anode compartment having an electrolyte containing hydrochloric acid and at least one chloride selected from the class consisting of alkali metal chlorides, ammonium chloride, and alkaline earth metal chlorides, said cathode compartment having an electrolyte which is substantially free from iron and containing hydrochloric acid, chromium chloride and at least one of the aforesaid chlorides, passing a unidirectional current through said cell from said anode to said cathode to effect in said anode compartment dissolving of chromium and iron from said anode and to effect simultaneously in said cathode compartment electrodeposition at the cathode of chromium which is substantially free from iron, preventing flow of electrolyte from said anode compartment to said cathode compartment during flow of said current through said cell, withdrawing from the cell the anolyte containing the metals, including iron, dissolved from the anode, as well as the salts of said class, extracting the iron from said withdrawn anolyte at a pH of 1-3 by a volatile organic solvent containing at least 80% ketone, said withdrawn anolyte containing chloride from said class in an amount sufficient to render said organic solvent at least partially immiscible with said withdrawn anolyte, removing dissolved solvent from the solution by evaporation, and using the so treated solution as the electrolyte in the cathode compartment for the deposition of chromium, and then using the solution so depleted of chromium

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for the electrolyte in the anode compartment whereby to replenish the chromium content thereof.

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