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Suzuki et al.

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[54] PROCESS FOR PRODUCING AN INGOT OF CHROMIUM METAL OR CHROMIUM-BASE ALLOY

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[52] **U.S. Cl.** .....**75/10 C**, 13/18, 75/176, 164/52, 164/252, 204/9, 204/23, 204/37 R

[51] **Int. Cl.**.....**C23b 7/02**, C23b 7/00, C23b 5/52

[58] **Field of Search** .....204/9, 23, 35, 37; 13/18; 164/52; 75/176, 10 C, 10 R

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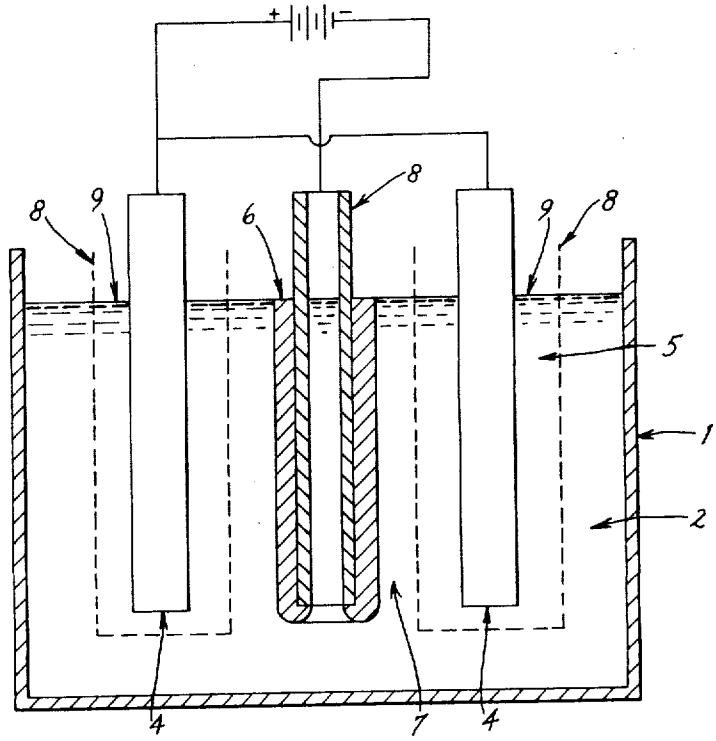
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[57] **ABSTRACT**

A process for producing an ingot of chromium metal or chromium-base alloy having a low content of impurities, such as hydrogen, nitrogen, oxygen, carbon, phosphorus, sulfur, and the like, in which an aqueous solution containing chromium salt is electrolyzed using as the cathode a metal material formed in a predetermined shape, such as circular, elliptical, rectangular or the like in horizontal cross section, to electrodeposit chromium on said metal material. The metal material, if desired, may be removed by chemical dissolution or heat melting after the electrolysis. The thus obtained chromium metal of the predetermined shape may be used as a consumable electrode. Additional materials are filled into the electrodeposited chromium metal which can be either free of the metal material used as the cathode or not free of the same. The chromium metal filled with the additional material is heated to sinter same under a reduced (vacuum) pressure or in a hydrogen atmosphere. A consumable electrode of chromium metal or chromium base alloy is thereby obtained. A high purity chromium metal ingot or chromium base alloy ingot is produced using the thus obtained consumable electrode by consumable-electrode-melting in a water-cooled metal crucible.

22 Claims, 13 Drawing Figures



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SHEET 1 OF 2

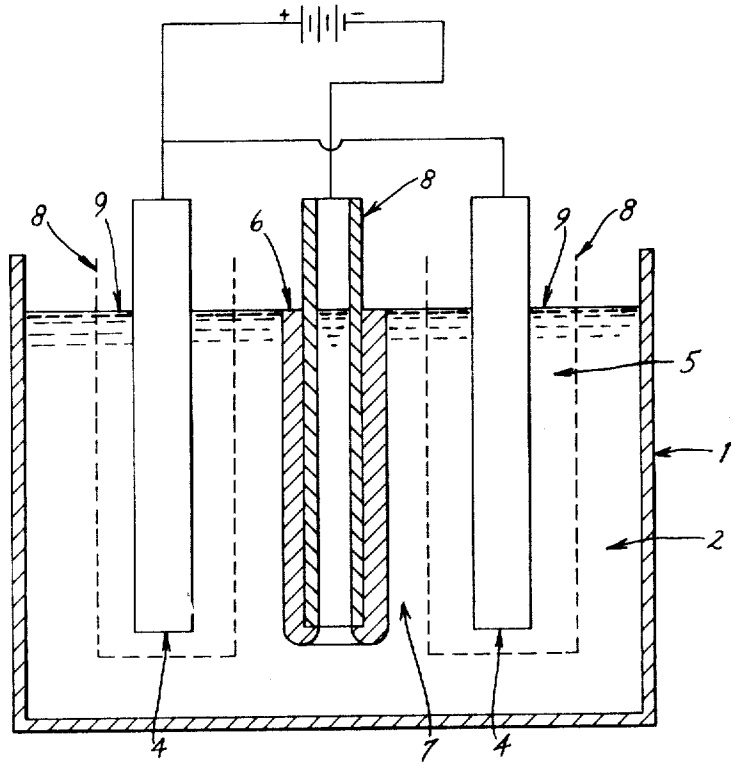


Fig. 1

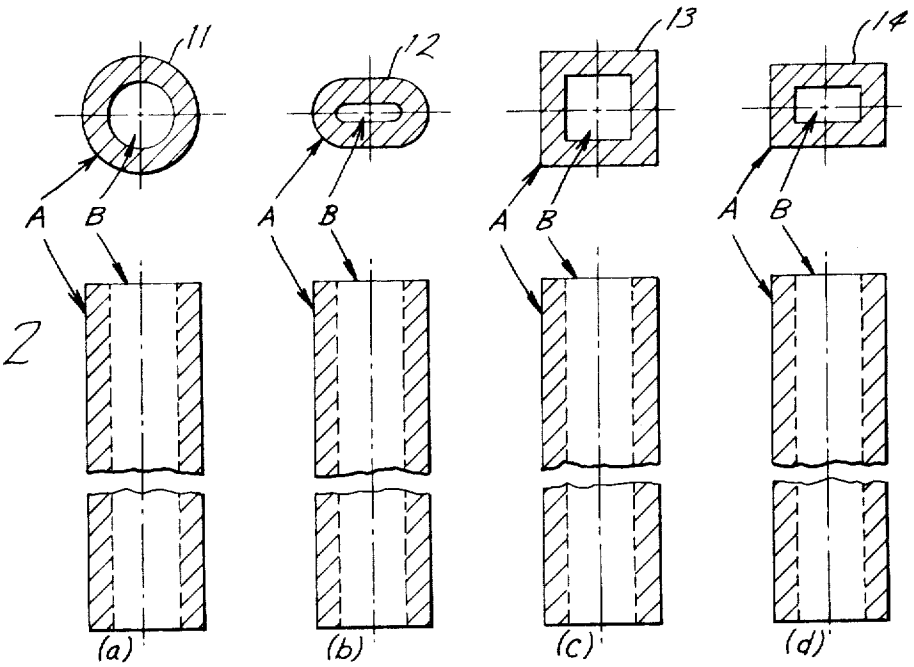


Fig. 2

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Fig. 3

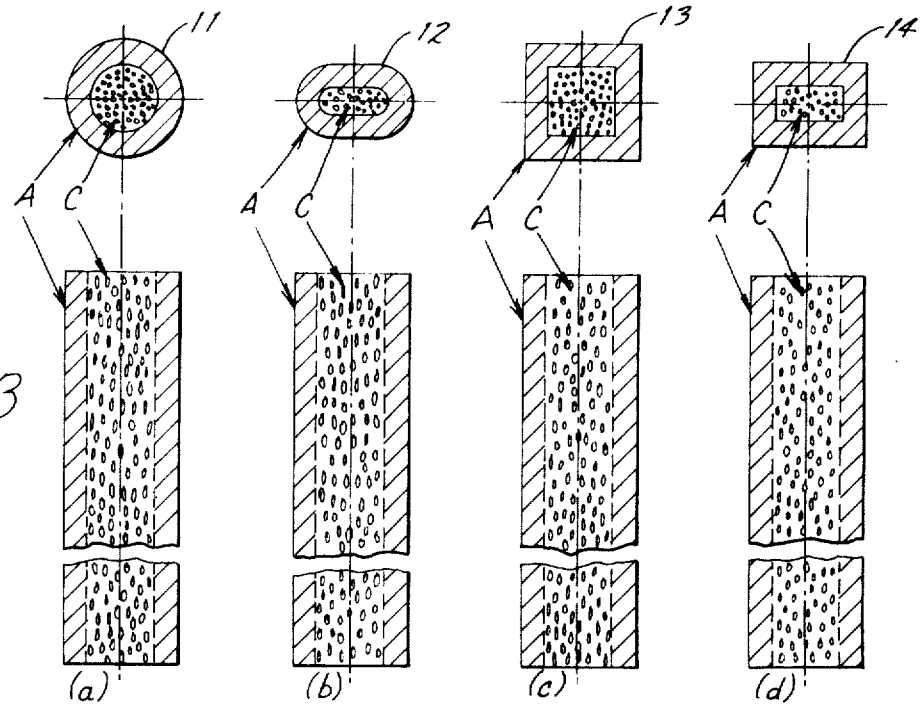
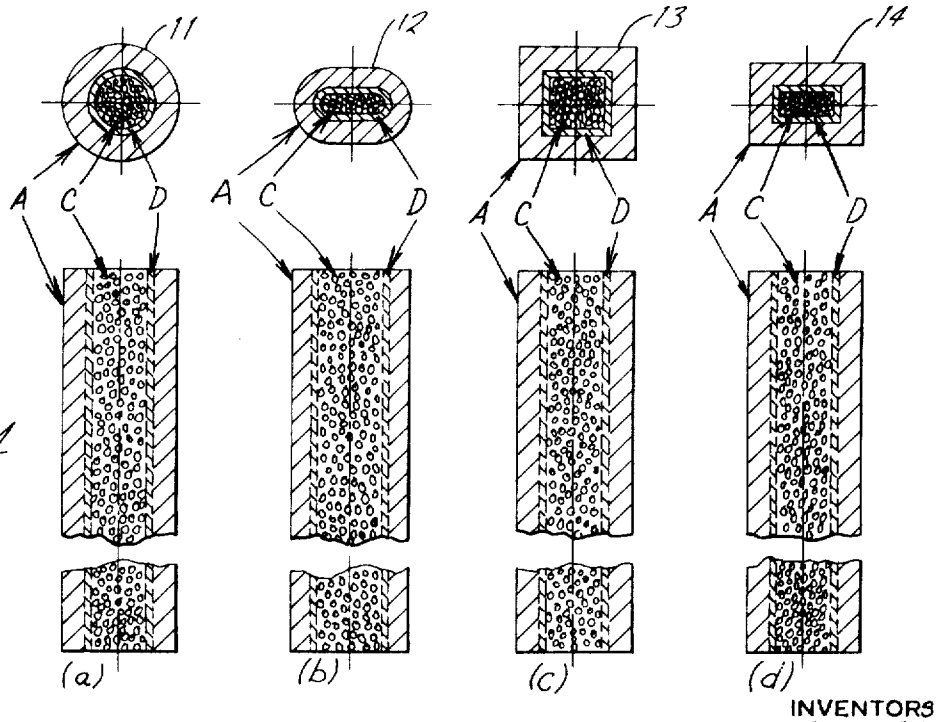


Fig. 4



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PROCESS FOR PRODUCING AN INGOT OF CHROMIUM METAL OR CHROMIUM-BASE ALLOY

BACKGROUND OF THE INVENTION

This invention relates to a process for producing an ingot of high purity chromium metal or chromium-base alloy.

DESCRIPTION OF THE PRIOR ART

Chromium metal and chromium-base alloys have high melting points and excellent properties including high resistivity to heat and to oxidation at high temperatures, high corrosion resistance against various acids, and stability in various atmospheres. Chromium metal is produced by electrolysis or the thermit process. The product obtained thereby contains substantial amounts of impurities which make it very brittle so that it is difficult to shape it directly to make a finished product. Thus, chromium obtained in this fashion is merely used as an additive component for alloy compositions, such as nickel-chromium alloy, stainless steel etc.

However, since chromium metal or chromium-base alloys have the excellent properties previously described, they may be widely used as heat resistive and corrosion resistive materials, if they are readily workable and also have improved mechanical properties.

In order to obtain a chromium metal or chromium-base alloy product, it has been proposed to mold a chromium metal or chromium-base alloy by powder metallurgy after powdering same and a process for machining or plastically working the ingot obtained by melting the metal or the alloy in a proper process.

The powder metallurgy process has the disadvantage that since the powdered material must be pressed under a high pressure, such as generally more than 5 tons/cm.^{2}, the weight of the resulting molded product is restricted to be less than several hundred grams because of the capacity of the pressure device. Thus, a heavier product can hardly be obtained. This is apparent from the fact that only relatively low-weight products of this type have been marketed.

In order to produce the ingots, there have been disclosed a process for heating the material directly in a crucible to melt same and a process for arc-melting the material in a water-cooled metal crucible by using a nonconsumable electrode or a consumable electrode. According to the process for melting the metal or the alloy in a crucible, a high-purity ingot cannot be obtained when the melting is carried out in a refractory crucible, because the melting point of the metal or the alloy is very high, for example, 1,905° C. for chromium metal, and because it is very active at that temperature so that it reacts vigorously with the crucible material and also any oxygen, nitrogen or the like that may be present so that the resulting ingot contains a substantial amount of impurities.

The process for arc-melting in a water-cooled metal crucible is described by Sully in his book entitled "Chromium." According to this description, in the case of a nonconsumable electrode system, a process for melting chromium metal powder using a tungsten electrode as the nonconsumable electrode is exemplified. This process has disadvantages, namely, that because the molten chromium has a high temperature, the metal will be contaminated by the tungsten electrode, while if less electric current is used in order to reduce such contamination, a segregation occurs, in the resulting ingot.

Although the process for melting chromium metal or chromium-base alloy using a consumable electrode has the advantage that lower amounts of impurities are contained in the product, it has not been possible to provide consumable electrodes on a large scale with the results that mass production of chromium or chromium alloy ingots cannot be accomplished so that the cost of the ingots is high.

Heretofore, the consumable electrodes have been obtained by a process similar to that of powder metallurgy in which the powdered material is pressure-molded and sintered or by a process in which the material is melted using the aforementioned nonconsumable electrode.

The powder metallurgy process has the disadvantages previously described so that larger-size consumable electrodes can hardly be obtained, while the latter arc-melting process requires a nonconsumable arc-melting step, in which particular care must be taken to avoid contamination, with the result that the cost of the ingot becomes very high.

SUMMARY OF THE INVENTION

A main object of this invention is to provide a process for making an ingot of chromium metal or chromium-base alloy which has a lower content of impurities such as hydrogen, nitrogen, oxygen, carbon, phosphorus and sulfur, than are present in ingots obtained by known methods and which also has improved mechanical properties.

Another object of this invention is to provide a process for producing an ingot of chromium metal or chromium-base alloy which is adapted for making ingots on a large scale, using a consumable electrode which is high in density and in mechanical strength and which may withstand a large current load.

We have discovered a process for producing a consumable electrode of chromium metal or chromium-base alloy which does not have the above-mentioned disadvantages. We have further discovered a process for producing an ingot of chromium metal or chromium-base alloy, which has a lower content of impurities and excellent mechanical properties, by consumable-electrode-melting using the consumable electrode obtained by the foregoing process. The discoveries are the results of studies on the physical and chemical properties of chromium metal and chromium-base alloys and on the electrolysis of chromium metal.

According to the present invention, an ingot of chromium or chromium-base alloy is produced by melting a consumable electrode which is obtained by a process comprising the steps of electrolyzing an aqueous solution containing chromium salt, using a cathode made of a metal material formed in a predetermined shape, electrodepositing chromium metal on said metal material to form a composite consisting of said metal material and the electrodeposited chromium metal and either removing or not removing said metal material from the composite. A modification of the process comprises electrolyzing an aqueous solution containing chromium salt, using a cathode made of a metal material formed in a predetermined shape, electrodepositing chromium metal on said material to form a composite consisting of said metal material and the electrodeposited chromium metal, either removing or not removing said metal material from the composite, either filling at least one of the components (which except for chromium are hereinafter referred to as alloying elements) of said chromium-base alloy or not filling the same into the composite which is either free or not free of said metal material, and then heating the same to degasify it and/or to sinter it under a reduced pressure or in a hydrogen atmosphere.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a sectional view of a cell used in a process for producing a consumable electrode of chromium or chromium-base alloy according to the invention.

FIGS. 2 (*a–d*) are sectional views of various shapes of consumable electrodes according to the invention, in which the cathode material has been removed.

FIGS. 3 (*a–d*) are corresponding sectional views of the consumable electrodes in which the cathode material has been removed and then the electrodes have been filled with chromium metal or alloying constituents.

FIGS. 4 (*a–d*) are corresponding sectional views of the consumable electrodes in which the cathode material is hollow and is filled with chromium metal or alloying constituents.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

Referring to FIG. 1, in a cell tank 1 which is filled with electrolyte 2, a cathode 3 of predetermined shape is positioned in

spaced relation to anodes 4 in the anode compartment 5. An electrodeposited chromium metal layer 6 is built up on the cathode 3 according to a conventional electrolysis procedure. The catholyte 7 passes through diaphragm 8 into the anode compartment 5 to form anolyte 9 and is then drained.

FIG. 2 illustrates four examples of tubular or hollow consumable electrodes obtained by removing only the cathode material from the composites consisting of the cathode material and electrodeposited chromium metal which were obtained as the results of electrolyses using various shapes of metal materials as cathodes. In this Figure the consumable electrode 11 is circular, the electrode 12 elliptical, the electrode 13 square, and the electrode 14 rectangular in their horizontal cross sections, respectively. A designates the chromium metal layer while B indicates the central openings in the electrodes.

FIG. 3 illustrates four examples of consumable electrodes obtained by filling chromium metal and/or alloying elements into the central openings in the tubular consumable electrodes illustrated in FIG. 2 and then heating them to sinter them under reduced pressure or in a hydrogen atmosphere. Said tubular consumable electrodes are prepared by removing only the cathode material from the composites consisting of cathode material and electrodeposited chromium metal which are obtained by electrolyzing aqueous solutions of chromium salt using various shapes of metal materials as cathodes. The electrode 11 is circular, the electrode 12 elliptical, the electrode 13 square and the electrode 14 rectangular in the horizontal cross section, respectively. A designates the chromium metal layer, while C designates the chromium metal and/or alloying elements filled into the central hollow portions.

FIG. 4 illustrates four examples of consumable electrodes obtained by filling chromium metal and/or alloying elements into the composites consisting of cathode material and electrodeposited chromium metal and then heating them to sinter them under reduced pressure or in a hydrogen atmosphere. Said composites are obtained by electrolyzing aqueous solutions of chromium salt using various shapes of metal materials as cathodes. The cathodes are hollow in this instance and the chromium metal and/or alloying elements fill the central openings in the cathodes. The electrode 11 is circular, the electrode 12 elliptical, the electrode 13 square and the electrode 14 rectangular in the horizontal cross section, respectively. A and D designate the chromium metal layers and cathode materials, respectively, while C designates the alloying elements and/or chromium metal filled into the hollow central openings in the cathodes.

The metal material used to make the cathode may be comprised of aluminum, aluminum alloy such as silumin, metals such as iron or their alloys, all of which are dissolvable in acid or alkali and/or have low melting points, if they are to be removed after electrolysis.

The metal material to be used as the cathode may be in the shape of a tube, rod or plate of circular, elliptical, polygonal, or any other suitable shape, in horizontal cross section. A tubular material is preferred because it is light in weight and it absorbs stresses in the electrodeposited substance to thereby reduce cracking of the electrodedeposited substance. Since little chromium metal is deposited on the inner wall of a tubular cathode material, the cathode material can be easily removed by melting it or by dissolving it. A cathode which is circular or nearly circular in shape, in horizontal cross section, may preferably be rotated during the electrolysis.

The electrolyte for electrodeposition of the chromium metal may be a conventional electrolyte used for electrowinning of chromium containing trivalent chromium sulfate and ammonium sulfate, or an aqueous solution containing hexavalent chromic acid.

The electrolysis is carried out under the conventional conditions for electrolytic deposition of chromium. One example is as follows:

Composition and pH of catholyte

Chromium ion	35 g./l.		
Ammonium ion	90 g./l.	Current density on cathode	7.0 A./dm.^{2}
pH	2.1–2.4		

The cathode material 3 can be removed from the electrodeposited layer 6 by the following steps after the electrolysis process is over. If the cathode material is made of aluminum or an aluminum alloy, the cathode material is removed from the electrodeposited substance by heating it to a temperature above the melting point of the cathode material so as to melt it, or by immersing it in an alkaline solution to dissolve only the cathode material.

If the cathode material 3 is, for example, made of iron, it may be immersed in an acid which does not dissolve chromium, such as nitric acid, so as to dissolve only the cathode material.

The alloying elements filled in the central openings (FIGS. 3 and 4) can be one or more of the substances required for forming a chromium-base alloy of the predetermined composition. The alloying elements can be of various shapes such as powder, grain, wire or strips. The amount and composition of the alloying elements is determined by the composition of the chromium-base alloy to be produced.

According to this invention, a consumable electrode may be directly obtained in the step of electrowinning of chromium metal. In this case, if the cathode material is formed to the desired shape and size, the consumable electrode produced will also be of the desired shape and size.

Accordingly, since this invention provides a less expensive and larger type of consumable electrode, a high-purity chromium metal ingot may be produced, with high productivity but at lower cost, by a consumable-electrode-melting process using the consumable electrode of this invention.

As previously described, the consumable electrode can be further filled with chromium metal and/or alloying elements as indicated in FIGS. 3 and 4, and no pressing process as in the conventional powder metallurgy procedure is required. Then, the resulting mixture is sintered under a reduced pressure or in a hydrogen atmosphere, whereby said consumable electrode is also sintered with the chromium metal and/or alloying elements. Accordingly, the thus obtained consumable electrode is of low cost, and since it has high-density electrodeposited chromium on its periphery, the weight per unit length is high and its electrical conductivity is very good. Thus, it can withstand a large current load during the consumable-electrode-melting and the latter can be easily carried out.

EXAMPLE I

A cathode was formed by blasting an aluminum pipe of 50 mm. in outer diameter and 750 mm. in length with metal grit, and then chromium metal was electrodeposited on the outer surface of the aluminum pipe to form a composite under the following conditions:

Composition and pH of catholyte

Trivalent chromium ion	13 g./l.
Divalent chromium ion	20 g./l.
Ammonium ion	100 g./l.
pH	2.2–2.4
Temperature	50° C.
Current density	7.0 A./dm.^{2}
Time of deposition	170 hours

The cathode was rotated about its longitudinal axis at a constant rate of one complete revolution per each 8 hours during the electrolyzing and the direction of rotation was reversed each 8 hours in order to obtain uniform electrodeposition of chromium. After the electrodeposition was over, the cathode was pulled from the cell and cleaned with water, then immersed in a 10 percent sodium hydroxide aqueous solution so as to dissolve the aluminum component of the cathode with the result that a chromium metal pipe or tube of approximately 5 mm. in thickness and approximately 4 kg. in weight was obtained. Into this pipe was filled chromium metal powder which passed through a 10-mesh sieve, then the pipe was

heated at a temperature of 1,400° C. for 4 hours in a hydrogen atmosphere having a dew point of −40° C. so as to degasify and to sinter the pipe and its contents. The weight of the chromium metal consumable electrode thereby obtained was 10.0 kg. and the chemical analysis thereof was as follows:

Element	Content in weight % in the chromium metal powder used as filler	Content in weight % in the obtained chromium metal consumable electrode
Hydrogen	0.007%	0.0006%
Nitrogen	0.025%	0.012%
Oxygen	0.35%	0.05%
Carbon	0.02%	0.012%
Sulfur	0.023%	0.012%
Aluminum		0.003%

Three of these pipes were welded together to form a long consumable electrode, then consumable-electrode-arc-melting was carried out in a water-cooled copper crucible with the result that a high-purity chromium metal ingot was obtained. The produced ingot was 100 mm. in diameter and 27 kg. in weight. The current was 10,000 A. at 30 volts.

The chemical analysis of the impurities in the obtained ingot was as follows:

Hydrogen	0.0005%
Nitrogen	0.011%
Oxygen	0.03%
Carbon	0.010%
Sulfur	0.011%
Aluminum	0.002%

The obtained ingot was machinable by cutting, grinding, turning or the like, the transition temperature between brittle and ductile was 230° C., and the hardness was 117 measured by a 10 kg. Vicker's tester.

EXAMPLE 2

A cathode was formed by blasting an iron pipe of 25 mm. in outer diameter and 500 mm. in length with metal grit, then chromium metal was electrodeposited on the outer surface of the iron pipe under the same conditions as in example 1 except the time of deposition was 200 hours. The cathode was rotated as described in example 1 during the electrolyzing. After the electrodeposition, the cathode was pulled from the cell and cleaned with water, then immersed in a 20 percent nitric acid aqueous solution so as to dissolve the iron component of the cathode with the result that a chromium metal pipe of 25 mm. in inner diameter, approximately 6 mm. in thickness and 500 mm. in length was obtained. This pipe was heated in a vacuum furnace at a temperature of 500° C. for 90 minutes to remove hydrogen. The chromium metal pipe obtained was 1.65 kg. in weight.

Three of the thus obtained chromium metal pipes were welded together to form a long consumable electrode, which was then subjected to consumable-electrode-arc-melting in a water-cooled copper crucible with the result that a high-purity metal ingot was obtained. The produced ingot was 50 mm. in diameter and 4.0 kg. in weight. The chemical analyses of the impurities in the consumable electrode and in the ingot thus obtained were as follows:

Element	Content in % by weight in the obtained consumable electrode	Content in % by in the obtained metal ingot
Hydrogen	0.004%	0.001%
Nitrogen	0.028%	0.023%
Oxygen	0.40%	0.22%
Carbon	0.018%	0.016%
Sulfur	0.020%	0.017%
Iron	0.10%	0.10%

EXAMPLE 3

A cathode was obtained by blasting with metal grit the outside of an aluminum alloy pipe of silumin containing silicon 11.0 percent, iron 0.5 percent and aluminum balance, having the shape of the electrode **12** shown in FIG. **2**, and being 36 mm. in major dimension and 10 mm. in minor dimension, respectively, of the horizontal cross section and 500 mm. in vertical length. The pipe was disposed in a cell in which the major dimension (in cross section) of the pipe was placed in confronting relationship to an anode. Chromium metal was deposited on the outer surface of the aluminum cathode by electrolysis under the same conditions as in example 1 except the time of deposition was 200 hours.

After the electrodeposition was completed, the cathode with the electrodeposited chromium thereon was pulled from the cell, washed by water, and then put into a vacuum furnace. Said cathode was heated at 800° C. for 60 minutes to melt the aluminum alloy component and the electrodeposited chromium metal was separated from the aluminum alloy component and was dehydrogenated concurrently. The thus obtained chromium metal tube was 5–7 mm. in thickness, 500 mm. in length and 1.6 kg. in weight.

Three of these chromium metal tubes were welded together to form a long consumable electrode, which is consumable-electrode-arc-melted in a water-cooled copper crucible in an argon atmosphere (0.3 atm. pressure). A high-purity chromium metal ingot was obtained and it was 50 mm. in diameter and 3.9 kg. in weight.

The chemical analyses of the impurities in the consumable electrode and in the ingot were as follows:

Element	Content in % by weight in the obtained consumable electrode	Content in % by weight in the obtained metal ingot
Hydrogen	0.003%	0.0008%
Nitrogen	0.030%	0.024%
Oxygen	0.40%	0.23%
Carbon	0.020%	0.018%
Sulfur	0.020%	0.019%
Aluminum	0.03%	0.02%

EXAMPLE 4

Three of the consumable electrodes obtained in example 1 were welded together to make one long consumable electrode, which was melted by an electro-slag-melting using a slag having a composition of 60 percent CaF_2 and 40 percent Ce_2O_3.

The chemical analysis of the impurities in the thus obtained ingot was as follows:

Hydrogen	0.0006%
Nitrogen	0.008%
Oxygen	0.014%
Carbon	0.011%
Sulfur	0.005%
Aluminum	0.002%

The obtained ingot was machinable by cutting, grinding, turning or the like. The transition temperature between brittle and ductile was 72° C., and the hardness was 104 measured by a 10 kg. Vicker's tester.

No appreciable corrosion on the test piece prepared from the ingot was observed when it was boiled with 60 percent nitric acid, 30 percent nitric acid or aqua regia.

EXAMPLE 5

An electrolysis was carried out under the same conditions as in example 1 to obtain a composite which was identical with that in said example, followed by removing the aluminum from the composite in the same way as in example 1.

A powder mixture of 2.2 kg. of chromium metal, 4.2 kg. of low-carbon ferromolybdenum (Mo content: 63 percent) hav-

ing particle sizes of less than 10 mesh and less than 40 mesh, respectively, was filled in the chromium metal tube, then this was heated in a hydrogen atmosphere showing a dew point of −40° C. at a temperature of 1,400° C. for 4 hours so as to degasify and to sinter the tube and its contents.

Three of the thus obtained tubes consisting of chromium metal and low-carbon ferromolybdenum were welded together to form a long consumable electrode, then it was subjected to consumable-electrode-arc-melting in a water-cooled copper crucible with the result that an ingot of a high-purity alloy of 60 percent chromium–15 percent iron–25 percent molybdenum was obtained. The chemical analysis was as follows:

Chromium	Balance
Molybdenum	24.8%
Iron	15.4%
Hydrogen	0.0005%
Nitrogen	0.008%
Oxygen	0.012%
Sulfur	0.017%

The produced ingot was 100 mm. in diameter and 28 kg. in weight. The consumable-electrode-arc-melting was carried out by a current of 10,000 A. at 30 volts. The creep rupture strength at 900° C. of a test piece prepared from the ingot was 28 kg./mm.^{2} for 100 hours.

EXAMPLE 6

A cathode was formed by blasting with metal grit a nickel rod of 70 mm. in major dimension and 14 mm. in minor dimension of the horizontal cross section, and 750 mm. in vertical length. The nickel rod was disposed in an electrolyte so that the major dimension (in cross section) of the rod confronted an anode. Chromium metal was electrodeposited on the surface of the nickel rod under the following conditions:

Composition and pH of catholyte

Trivalent chromium ion	13 g./l.
Divalent chromium ion	20 g./l.
Ammonium ion	100 g./l.
pH	2.2–2.4
Temperature	45° C.
Current density	7.0 A./dm.^{2}

The electrolysis was continued for 240 hours until the weight of the electrodeposited chromium corresponded to that of the nickel cathode in order to prepare a consumable electrode having a composition of 50 percent chromium–50 percent nickel. The thus obtained electrodeposited chromium was 6–8 mm. in thickness and 6.3 kg. in weight.

After the electrodeposition, the cathode and the chromium thereon was pulled from the cell, washed by water, and then heated at a temperature of 1,300° C. for 10 hours in a hydrogen atmosphere showing a dew point of −40° C. so as to remove gases such as oxygen, hydrogen, nitrogen and the like contained in the electrodeposited metal.

The obtained consumable electrode was 12 kg. by weight and had an overall composition as follows, which was substantially identical with the desired one:

Chromium	Balance
Nickel	48.9%
Iron	0.07%
Silicon	0.013%
Hydrogen	0.001%
Oxygen	0.15%
Nitrogen	0.014%
Carbon	0.013%
Sulfur	0.008%

Four of these consumable electrodes were welded together to form a longer consumable electrode, which was then subjected to consumable-electrode-arc-melting in a water-cooled copper crucible with the result that an ingot of a high purity nickel-chromium alloy was obtained. The chemical analysis of the ingot was as follows:

Chromium	Balance
Nickel	45.2%
Iron	0.07%
Silicon	0.013%
Hydrogen	0.0007%
Oxygen	0.01%
Nitrogen	0.012%
Carbon	0.012%
Sulfur	0.007%

The produced alloy was 100 mm. in diameter and 40 kg. in weight.

The thus-obtained alloy showed excellent mechanical properties, for example, 105 kg./mm.^{2} in tensile strength and 13 percent in elongation and also an excellent resistivity to heat and corrosion, for example, a corrosion of 0.0071 cm./year in boiling 65 percent nitric acid and 0.0024 cm./year in boiling 20 percent sulfuric acid.

EXAMPLE 7

A cathode was formed by blasting an iron pipe of 25 mm. in outer diameter, 3 mm. in thickness and 750 mm. in length with metal grit, then chromium metal was electrodeposited on the outer surface of the iron pipe under the following conditions:

Composition and pH of catholyte

Trivalent chromium ion	13 g./l.
Divalent chromium ion	20 g./l.
Ammonium ion	100 g./l.
pH	2.2–2.4
Temperature	45° C.
Current density	7.2 A./dm.^{2}
Time of deposition	160 hours

The cathode was rotated as described in example 1 during the electrolyzing. The electrodeposited chromium metal was approximately 5.5 mm. in thickness and approximately 2.3 kg. by weight. After the electrolysis, the cathode was pulled from the cell, washed by water, and then heated at 1,300° C. for 10 hours in a hydrogen atmosphere showing a dew point of −40° C. to degasify such gases as oxygen, hydrogen, nitrogen and the like contained in the electrodeposited chromium metal.

The obtained composite consumable electrode was 3.5 kg. in weight and its overall composition was as follows, which was substantially identical with the desired one:

Chromium	Balance
Iron	34.1%
Silicon	0.10%
Manganese	0.07%
Hydrogen	0.001%
Oxygen	0.1%
Nitrogen	0.01%
Carbon	0.012%
Sulfur	0.012%

Three of these composite consumable electrodes composed of chromium and iron were welded together to form a long tubular consumable electrode, which was subjected to consumable-electrode-arc-melting in a water-cooled copper crucible with the result that an ingot of a high-purity chromium-iron alloy was obtained. The composition of the ingot was as follows:

Chromium	Balance
Iron	33.8%
Silicon	0.10%
Manganese	0.06%
Hydrogen	0.0008%
Oxygen	0.03%
Nitrogen	0.008%
Sulfur	0.011%

The produced ingot, which was 60 mm. in diameter and 9 kg. in weight, possessed good mechanical properties so that it could be subjected to either hot or cold working. The mechanical properties of this alloy were as follows:

Tensile strength	92 kg./mm.^{2}
Elongation	7%

This alloy contained so much chromium that excellent corrosion and heat resistance, listed as follows, were obtained:

Weight increase by oxidation in air at 1,000° C.	0.11 mg./cm.² hour

EXAMPLE 8

A cathode was formed by blasting an iron pipe of 50 mm. in outer diameter, 3 mm. in thickness and 750 mm. in length with metal grit, then chromium metal was electrodeposited on the outer surface of the iron pipe under the same conditions as in example 7, except that the time of deposition was 176 hours.

The electrodeposited chromium metal was approximately 6 mm. in thickness and approximately 5 kg. in weight.

After the electrolysis, the cathode was pulled from the cell, washed by water and dried, and in this pipe a mixture consisting of 2.5 kg. of chromium metal powder which passed through a 10-mesh sieve, 1.5 kg. of iron-aluminum alloy (35 percent by weight aluminum) powder which passed through a 10-mesh sieve and 0.8 kg. of iron wires of 2 mm. in diameter was placed in the pipe, then this was heated in a vacuum furnace at 1,300° C. for 5 hours so as to degasify and to sinter the composite.

The thus-obtained consumable electrode was 12.3 kg. in weight and had an overall composition shown as follows, which composition was substantially identical with the desired one.

Chromium	Balance
Iron	35.6%
Aluminum	4.3%
Silicon	0.11%
Manganese	0.09%
Hydrogen	0.001%
Oxygen	0.2%
Nitrogen	0.02%
Carbon	0.013%
Sulfur	0.018%

Four of the thus-obtained consumable electrodes were welded together to form one consumable electrode, which was subjected to electro-slag-melting by using a slag having a composition of 80% of CaF_2 and 20% of Al_2O_3 in a water-cooled copper crucible with the result that an ingot of a high-purity chromium-iron-aluminum alloy was obtained. The composition of the ingot was as follows:

Chromium	Balance
Iron	35.9%
Aluminum	4.1%
Silicon	0.10%
Manganese	0.08%
Hydrogen	0.001%
Oxygen	0.011%
Nitrogen	0.006%
Carbon	0.012%
Sulfur	0.004%

The product was 100 mm. in diameter and 44 kg. in weight. The thus-obtained alloy could be subjected to rolling or drawing. The mechanical property and the oxidation-resisting property of this product were as follows:

Tensile strength	93 kg./mm.²
Elongation	9%
Weight increase by oxidation in air at 1,200° C.	0.05 mg./cm.² hour

EXAMPLE 9

A cathode was formed by blasting titanium pipe of 50 mm. in outer diameter, 0.5 mm. in thickness and 750 mm. in length with metal grit, then chromium metal was electrodeposited on the outer surface of the titanium pipe under the same conditions as in example 6, except that the time of deposition was 144 hours. The cathode was rotated as described in example 1 during the electrolyzing. The electrodeposited chromium metal was 5.5 mm. in thickness and 4.05 kg. in weight.

After the electrolysis, the cathode was pulled from the cell, washed with water and dried. In this titanium pipe surrounded by the electrodeposited chromium there was placed a powder mixture consisting of 2.2 kg. of chromium metal powder which passed through a 10-mesh sieve and 4.2 kg. of low-carbon ferromolybdenum (63 percent by weight of Mo) powder which passed through a 40-mesh sieve, then this was heated in a vacuum furnace at 1,400° C. for 2 hours so as to degasify and to sinter the composite. The thus-obtained consumable electrode was 10.6 kg. in weight and its overall composition was as follows, which composition was substantially identical with the desired one.

Chromium	Balance
Molybdenum	24.5%
Iron	14.1%
Titanium	2.5%
Silicon	0.39%
Hydrogen	0.001%
Oxygen	0.25%
Nitrogen	0.020%
Carbon	0.023%
Sulfur	0.030%

Four of the thus-obtained consumable electrodes were welded together to form a long consumable electrode, which was subjected to consumable-electrode-arc-melting in a water-cooled copper crucible with the result that high-purity chromium-molybdenum-iron-titanium alloy (58.5 percent chromium–25 percent molybdenum–14 percent iron–2.5 percent titanium) was obtained. The product was 80 mm. in diameter and 40 kg. by weight.

This consumable-electrode-arc-melting was carried out under the current condition of 3,500 A. at 40 volts.

The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

1. A process for producing a metal ingot containing at least a substantial amount of chromium comprising the steps of electrolyzing an aqueous solution containing chromium salt as an electrolyte using as a cathode a metal material formed in a predetermined shape, thereby to form a composite comprising the metal material and the electrodeposited chromium metal, and then carrying out consumable-electrode-melting using at least the electrodeposited chromium metal, as a consumable electrode.

2. A process according to claim 1, wherein the metal ingot is a chromium metal ingot, and including the further step of, after the electrolysis and prior to the consumable-electrode-melting, removing the metal material from the composite.

3. A process according to claim 1, wherein the metal ingot is a chromium metal ingot, and including the further steps of, after the electrolysis and prior to the consumable-electrode-melting, removing the metal material from the composite and heating the electrodeposited chromium metal under a reduced pressure or in a hydrogen atmosphere to degasify the same.

4. A process according to claim 3, wherein aluminum or aluminum alloy is used as the metal material.

5. A process according to claim 3, wherein aluminum or aluminum alloy is used as the metal material and the removing of the aluminum or the aluminum alloy is carried out by dissolving the same in an alkaline solution.

6. A process according to claim 3, wherein aluminum or aluminum alloy is used as the metal material and the removing of the aluminum or the aluminum alloy is carried out by heating the composite to melt said aluminum or the aluminum alloy.

7. A process according to claim 3, wherein iron is used as the metal material and the removing of the iron is carried out by dissolving the same in an acid.

8. A process according to claim 3, including the further step of, after the removing of the metal material from the composite and prior to the heating of the electrodeposited chromium metal under a reduced pressure or in a hydrogen atmosphere, filling chromium metal into the electrodeposited chromium metal.

9. A process according to claim 8, wherein aluminum or aluminum alloy is used as the metal material.

10. A process according to claim 8, wherein aluminum or aluminum alloy is used as the metal material and the removing of the aluminum or the aluminum alloy is carried out by immersing the composite in an alkaline solution to dissolve the aluminum or the aluminum alloy.

11. A process according to claim 8, wherein aluminum or aluminum alloy is used as the metal material and the removing of the aluminum or the aluminum alloy is carried out by heating the composite to melt the aluminum or the aluminum alloy.

12. A process according to claim 8, wherein iron is used as the metal material, and the removing of the iron is carried out by dissolving the same in an acid.

13. A process according to claim 1, wherein the metal ingot is a chromium-base alloy ingot, and including the further steps of, after the electrolysis and prior to the consumable-electrode-melting, removing the metal material from the composite and filling a member selected from the group consisting of alloying elements and a mixture of alloying elements and chromium metal into the electrodeposited chromium metal.

14. A process according to claim 1, wherein the metal ingot is a chromium-base alloy ingot, and including the further steps of, after the electrolysis and prior to the consumable-electrode-melting, removing the metal material from the composite, filling a member selected from the group consisting of alloying elements and a mixture of alloying elements and chromium metal into the electrodeposited chromium metal and heating the electrodeposited chromium metal under a reduced pressure or in a hydrogen atmosphere to degasify the same.

15. A process according to claim 14, wherein aluminum or aluminum alloy is used as the metal material.

16. A process according to claim 14, wherein aluminum or aluminum alloy is used as the metal material, and the removing of the aluminum or the aluminum alloy is carried out by immersing the composite in an alkaline solution to dissolve the aluminum or the aluminum alloy.

17. A process according to claim 14, wherein aluminum or aluminum alloy is used as the metal material, and the removing of the aluminum or the aluminum alloy is carried out by heating the composite to melt the aluminum or the aluminum alloy.

18. A process according to claim 14 wherein iron is used as the metal material, and the removing of the iron is carried out by dissolving the same in an acid.

19. A process according to claim 1, wherein the metal ingot is a chromium-base alloy ingot, and in which the entire composite is subjected to said consumable-electrode-melting so that the metal material comprises a component of said chromium-base alloy ingot.

20. A process according to claim 19, including the further step of, after the electrolysis and prior to the consumable-electrode-melting, heating the composite under a reduced pressure or in a hydrogen atmosphere to degasify the same.

21. A process according to claim 19, including the further step of, after the electrolysis and prior to the consumable-electrode-melting, filling chromium metal and/or alloying elements into the composite.

22. A process according to claim 19, including the further steps of, after the electrolysis and prior to the consumable-electrode-melting, filling chromium metal and/or alloying elements into the composite and heating the composite under a reduced pressure or in a hydrogen atmosphere to degasify the same.

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