ABSTRACT OF THE DISCLOSURE

A cold-shapable cobalt alloy, and composite welding electrode containing the same and a submerged arc welding process using the same. The cobalt alloy contains at least 93% by weight of cobalt, 0.5 to 6% by weight of iron, at least one of the metals of the group consisting of manganese, titanium and aluminum and also incidental impurities the amount of which is insufficient to have an effect upon the properties of the alloy, any manganese, titanium and aluminum content being in the ranges from traces to 4.5% by weight for manganese, 0.1 to 2% by weight for titanium and 0.1 to 2% by weight for aluminum, and the sum of the iron content of said alloy of 9% of its manganese content, of 6% of its iron content, of 2% of its titanium content and, at 20% of its aluminum content being below 9% of its total weight. In addition, the electrode may include other ingredients in specified ranges such as chromium, tungsten and carbon.

The present invention relates to an alloy comprising at least 93% of cobalt and iron, optionally at least one of the metal of the manganese, titanium and aluminum group, and also optionally impurities consisting of nickel, carbon, silicon, sulphur and phosphorus.

Cobalt alloys having a very high cobalt content are known, which have at ambient temperature a face-centered cubic lattice which renders them particularly cold-shapable. Alloys of this nature have been proposed which contain iron in a proportion of 6 to 11% of nickel in a proportion of 24 to 30% of both iron and nickel in minimum proportions conforming to the relation percent Fe+\%Ni=4.7, with the additional condition that each of these two alloy elements is present in a proportion of at least 1%. It has been asserted that, with such iron and nickel contents, the cobalt alloy retains at ambient temperature a face-centered cubic lattice which is essential for cold-forging.

These known alloys have the disadvantage that they contain too many elements which greatly lower their hot hardness when they are used as a solid core or as a tubular sheath in electrodes which contain chromium and tungsten in addition, and which serve for the deposition of hard surfacing alloys. In addition, the presence of at least one percent of nickel in these alloys renders them particularly sensitive to the action of sulphur which is often contained in the medium in contact with the alloy.

The present invention relates to a cobalt alloy which is not attended by these disadvantages and which, although consisting of hexagonal crystals or a mixture of hexagonal crystals and face-centered cubic crystals, nevertheless has sufficient malleability to undergo cold shaping and more particularly to undergo drawing to a diameter of less than two millimeters and rolling into a strip less than 0.3 millimeter thick. The alloy according to the invention is characterized in that its proportions of iron, manganese, titanium and aluminum are such that the sum of its iron content, of 9% of its optional manganese content, of 6% of its optional titanium content and of 20% of its optional aluminum content is lower than 6% of its total weight, and in that the maximum optional manganese, titanium and aluminum contents are equal to 4.5%, 2% and 2% respectively.

In this alloy, the malleability is ensured in principle in the absence of nickel, which exists only to the extent that it constitutes impurities of the constituents of the alloy and is introduced into the latter essentially as an impurity of the cobalt. In any case, the nickel content cannot reach 1%.

The malleability of the cobalt alloy may be ensured solely by means of iron provided that its iron content is lower than 6%, in order that the hot hardness may not be greatly reduced when this alloy serves for the deposition of a hard alloy in combination with chromium and tungsten.

It is known that manganese, titanium and aluminum favor the malleability of the alloy of high cobalt content and that any one or more than one of these metals may be employed simultaneously with iron. According to the invention, when one or more of these metals are employed, the sum of the percentage of iron and of the products of the real percentages of each of the other three metals times the respective coefficients %0.100, %60 and %20 must be lower than 6%, provided that the real percentages of the latter three constituents do not exceed 4.5%, 2% and 2% respectively.

An alloy according to the invention may consist of, for example, 3.5% of iron, 2% of manganese, 1% of titanium and 0.5% of aluminum, because 3.5% + 0.100 × 2% + 0.60 × 1% + 0.20 × 0.5% = 5.55% is lower than 6%.

The iron content is preferably maintained between 3% and 4%. The manganese content is maintained below 4.5% in order to reduce the cracking tendency of the deposit. Titanium and aluminum are advantageous in a proportion not exceeding 2% each, because when the ductile alloy of which they form part is used as a continuous element of a composite welding electrode containing in its coating or in its core hardening elements such as chromium, tungsten and carbon, they create in the welding bath a highly reducing medium which favors the passage of hardening elements into this bath.

However, silicon, which is also a reducing agent, must be used in a small proportion because it favors the hexagonal structure. It is advantageous for the cobalt alloy to contain not more than 0.5% thereof.

Sulphur and phosphorus are also undesirable and the upper limit of each of them is 0.03%.

Zirconium, niobium and tantalum may also be used in
place of iron, but it is preferred to use manganese, titanium and aluminum because they are less costly. In the alloy according to the invention, the carbon content is very low and is below 0.05%. Carbon must be regarded as an impurity of cobalt, for the same reason as nickel.

The following are a number of alloy compositions according to the invention.

<table>
<thead>
<tr>
<th>Percent of alloys</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Constituents</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cu</td>
<td>93.31</td>
<td>94.41</td>
<td>95.33</td>
<td>97.21</td>
<td>96.41</td>
</tr>
<tr>
<td>Fe</td>
<td>3.58</td>
<td>3.60</td>
<td>3.56</td>
<td>2.6</td>
<td>3.1</td>
</tr>
<tr>
<td>Mn</td>
<td>1.5</td>
<td>0.49</td>
<td>0.20</td>
<td>1.1</td>
<td>1.1</td>
</tr>
<tr>
<td>Ti</td>
<td>0.16</td>
<td>0.20</td>
<td>0.4</td>
<td>0.4</td>
<td>0.4</td>
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<tr>
<td>Al</td>
<td>0.30</td>
<td>0.30</td>
<td>0.30</td>
<td>0.30</td>
<td>0.30</td>
</tr>
<tr>
<td>C</td>
<td>0.049</td>
<td>0.085</td>
<td>0.16</td>
<td>0.20</td>
<td>0.30</td>
</tr>
<tr>
<td>Si</td>
<td>0.59</td>
<td>0.20</td>
<td>0.40</td>
<td>0.10</td>
<td>0.07</td>
</tr>
<tr>
<td>S</td>
<td>0.012</td>
<td>0.014</td>
<td>0.012</td>
<td>0.008</td>
<td>0.025</td>
</tr>
<tr>
<td>P</td>
<td>0.017</td>
<td>0.009</td>
<td>0.016</td>
<td>0.019</td>
<td>0.015</td>
</tr>
<tr>
<td>Ni</td>
<td>0.22</td>
<td>0.25</td>
<td>0.25</td>
<td>0.05</td>
<td>0.25</td>
</tr>
<tr>
<td>Total</td>
<td>99.99</td>
<td>99.80</td>
<td>99.95</td>
<td>99.95</td>
<td>99.95</td>
</tr>
</tbody>
</table>

These alloys are produced by powder metallurgy, melting in vacuo, under an atmosphere for protection against oxygen and nitrogen, under slag or by any other known means.

Alloys of this type may be hot rolled without difficulty or hot extruded to billets of a diameter of 10 mm. These billets are thereafter drawn in 15 to 20 passes to a diameter of 4 or 3.25 mm. and even less than 2 mm. In drawing from 10 mm. to 4 mm., two intermediate annealing operations are necessary at about 7 mm. and 5 mm.

After annealing at a minimum temperature of 900° C. for one hour, these alloys have a hardness of 45 to 60 kg./mm.² and an elongation of 45% to 20%. These alloys are particularly useful for the manufacture of coated electrodes, cored electrodes or bare wires employed under flux or under slag for obtaining hard surfaces of the stellite type comprising, in addition to a high cobalt content, a relatively high chromium, tungsten and carbon content.

A wire consisting of the alloy according to the invention may constitute the core of a coated electrode, of which the coating contains the main alloying elements of stellite, such as chromium, tungsten and carbon in the form of powder, alloys or carbides. Part of the alloying elements may be present in the form of chromium oxide and tungsten oxide provided that there is introduced into the wire or into the coating a sufficient quantity of reducing metals such as aluminum, manganese or silicon. Thus, a wire conforming to the composition of alloy 1 in the table, having a diameter of 4 mm. and weighing 50 g., coated with 50 g. of a paste containing 24 g. of metallic chromium, 4 g. of metallic tungsten, and 2.7 g. of graphite, the remainder consisting of matter forming a slag and giving an electrode having an output of about 150%, gives a deposit conforming to the following analysis: cobalt 60%, chromium 30%, tungsten 5.5%, carbon 1% and iron 2.5%, the remaining 1% consisting of manganese, silicon and traces of nickel.

In this electrode, the proportion of metallic chromium, in relation to the total weight of the wire, of the metallic chromium, of the metallic tungsten and of the carbon is 24/80.7 = 29.74%. Likewise, the proportions of metallic tungsten and of carbon in relation to this total weight are 4/80.7 = 4.95% and 2.7/80.7 = 3.42%, respectively.

In the electrode according to the invention, the proportions of these three constituents in relation to the total weight of the wire, the metallic chromium, the metallic tungsten and the carbon may vary between the following limits: from 25% to 35% in the case of chromium, from 35% to 55% in the case of tungsten and from 0.5% to 8% in the case of carbon.

Deposits of higher tungsten and carbon content are readily obtained by increasing the percentage of tungsten, graphite or tungsten carbide, such as WC or WoC in the coating.

Sometimes, additions of powdered cobalt may be made to the coating of the electrode in order to bring its output to 200% or 250%.

The cobalt alloy in strip form may be used to form a tubular or composite electrode, the strip constituting the sheath, and the chromium, the tungsten and the carbon, as also the other alloying elements and slag, where necessary, being introduced by the powder to the center of the composite electrode. Thus, starting with a folded strip conforming to the composition of alloy 5 in the table, which has a width of 30 mm. before folding and a thickness of 0.30 mm., there was produced by addition to 100 g. of this strip of 4 g. of mixtures of powders consisting of 78% of chromium, 19% of tungsten and 3% of carbon, a composite wire 4 mm. in diameter which gave rise to the following deposit: cobalt 61%, chromium 28%, tungsten 6.5%, carbon 1% and iron 3%, the remaining 0.5% consisting of manganese, silicon and traces of nickel.

In an electrode according to the invention of this type, the weight of metallic chromium in the powder mixture is

|  | g.
|---|---
| 25 | 60 x 78 = 46.8 g.
| 30 | 60 x 19 = 11.4 g.
| 35 | 60 x 3 = 1.8 g.

The proportions of these three constituents in relation to the total weight of the strip and of the powder mixture are, respectively, 46.8/160 = 29% in the case of chromium, 11.4/160 = 7.125% in the case of tungsten, and 1.8/160 = 1.125% in the case of carbon.

As in the case of the aforesaid electrode consisting of a wire of an alloy according to the invention covered with a coating layer, the aforesaid proportion may vary between 25% and 35% in the case of chromium, between 3% and 15% in the case of tungsten and between 0.5% and 8% in the case of carbon.

In these two types of electrodes, the proportions of chromium, cobalt and carbon in the coating around the continuous metallic portion consisting of the wire or in the powder core maintained by the continuous metallic portion consisting of the strip may be so increased as to bring the output of the electrode to 200% or even to 250%.

If the electrode according to the invention is employed as a filler metal for gas welding, the tungsten is preferably supplied in the form of a powdered alloy of chromium, tungsten and carbon having a melting point below 2500° C., because it is known that tungsten has a melting point of 3380° C., and tungsten carbide, WC a melting point of 2750° C. These temperatures are generally too high and it is likely that the alloy will not be completely melted during the flame surfacing. Therefore, there are preferably employed in this case an alloy of tungsten, chromium and carbon with or without an addition of boron, having the lowest possible melting point, that is to say, one below 2500° C.

A chromium-tungsten-carbon alloy of relatively low melting point is, for example, that comprising 55% of chromium, 38% of tungsten and 3% of carbon, the remainder consisting of aluminum, silicon and iron. The melting point of this alloy is about 1900° C.

Instead of being of circular tubular form, the composite electrode may be of flattened form, whereby the penetration into the parts to be surfaced, and therefore the dilution, are generally reduced.
The strip or wire of cobalt alloy may also be used as an electrode for hard surfacing under a flux. In this case, a powder mixture containing chromium, tungsten and carbon is disposed in a manner known per se on the article to be hard-surfaced, whereafter the hard-surfacing operation is performed. In another process, the flux may contain metallic additions of chromium, tungsten and carbon such that the desired alloy is produced in the melting. Thus, a flux containing about 6% of tungsten, 20% of chromium carbide, Cr₇C₃ and 6% of metallic chromium, the remainder consisting of slag-forming elements, gave, under a current of 600 amperes at 34 volts, with an electrode wire containing 95% of cobalt and 4% of iron, a deposit of high cobalt content containing about 5% of tungsten, 23% of chromium, 1.5% of carbon and 5% of iron.

What I claim is:

1. A cold-shapable cobalt alloy consisting of at least 93% by weight of cobalt, 0.5 to 6% by weight of iron, at least one of the metals of the group consisting of manganese, titanium, and aluminum, and also incidental impurities, the amount of which is insufficient to have an effect upon the properties of said alloy, any manganese, titanium and aluminum contents being in the ranges from traces to 4.5% by weight for manganese, 0.1 to 2% by weight for titanium, and 0.1 to 2% by weight for aluminum, the sum of the iron content of said alloy, of 3₀/₅₀₀ of its manganese content, of 4₀/₁₀₀ of its content, and of 2₀₀₀₀₀₀₀₀₀₀ of its total weight.

2. A composite welding electrode comprising, on the one hand, a continuous metallic tubular sheath and, on the other hand, a mixture including substances forming slag and the principal alloying ingredients of stellite consisting of chromium, tungsten and carbon, in which said continuous metallic portion consists of an alloy of at least 93% by weight of cobalt, 0.5 to 6% by weight of iron, at least one of the metals of the group consisting of manganese, titanium, and aluminum, and also incidental impurities, the amount of which is insufficient to have an effect upon the properties of said alloy, manganese, titanium and aluminum contents being in the ranges from traces to 4.5% by weight for manganese, 0.1 to 2% by weight for titanium, and 0.1 to 2% by weight for aluminum, and the sum of the iron content of said alloy of 3₀/₅₀₀ of its manganese content, of 4₀/₁₀₀ of its titanium content, and of 2₀₀₀₀₀₀₀₀₀₀ of its total weight and in which such core contains 35% of chromium, 38% of tungsten and 27% of iron, the balance being aluminum, silicon and carbon, and the core being formed by reducing the oxides, said coating containing in addition metallic cobalt in such an amount that the output of the electrode is above 100%.

5. A composite welding electrode comprising, on the one hand, a continuous metallic tubular sheath and, on the other hand, a core in said sheath, including substances forming slag and the principal alloying ingredients of stellite consisting of chromium, tungsten and carbon, in which said metallic tubular sheath consists of an alloy of at least 93% by weight of cobalt, 0.5 to 6% by weight of iron, at least one of the metals of the group consisting of manganese, titanium and aluminum, and also incidental impurities the amount of which is insufficient to have an effect upon the properties of said alloy, any manganese, titanium and aluminum contents being in the range from traces to 4.5% by weight for manganese, 0.1 to 2% by weight for titanium, and 0.1 to 2% by weight for aluminum, and the sum of the iron content of said alloy of 3₀/₅₀₀ of its manganese content, of 4₀/₁₀₀ of its titanium content, and of 2₀₀₀₀₀₀₀₀₀₀ of its total weight and in which such core contains 35% of chromium, 38% of tungsten and 27% of iron, the balance being aluminum, silicon and carbon, and the core being formed by reducing the oxides, said coating containing in addition metallic cobalt in such an amount that the output of the electrode is above 100%.

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