

Corrosion-resistant layered composite comprising a metal substrate and an outer layer of a different material, in particular a noble material.

The invention relates to a layered composite comprising a metal substrate and an outer layer of a different material, in particular a noble material, such as a precious metal (gold, platinum or the like), Chinese lacquer or the like. The invention relates more particularly to a layered composite of this type in which the substrate is capable of resisting corrosion under difficult and prolonged conditions.

Such use conditions apply, in particular, to wristwatch cases, which remain in direct contact with the skin for long periods and are consequently subjected to the corrosive action of perspiration. It is therefore appropriate, when making backs of watch cases, even for deluxe watches, to use so-called "stainless" steel, because it is rendered stainless, under the normal use conditions, by passivation of its outer surface, that is to say by the formation of an impermeable film of oxides on this surface, which is thereby protected.

Of course, it is possible to make backs of watch cases out of gold, since this metal is perfectly resistant to the usual types of attack and corrosion. However, the cost of such cases is such that they cannot be used for just any type of watch, even a deluxe watch, but can only be used for watches of very great value.

Attempts have of course been made to gold-plate backs of watch cases, but all the experiments carried out

in this direction have proved unsuccessful.

In fact, when a thin layer of metal is deposited on another metal or alloy by an electrolytic or other method, this layer always possesses micropores or microcracks, regardless of the care taken to produce it, and the same applies when a metal is covered with a layer of varnish or the like.

If the substrate is not stainless, the micropores and microcracks cause local oxidation, which ultimately separate the outer layer from the substrate.

If in (sic) substrate of stainless steel alloy is used, this presents the problem of the stability of the passivating film in the presence of the constituents of perspiration, in particular chlorides and organic acids.

The passivating film, which consists of oxides, can only form in an oxygen-containing environment and therefore requires substantial aeration to re-form in the event of attack. Now, if traces of chlorides, for example, deposit in the micropores and microcracks, the surface of the stainless steel in contact with these chlorides is inadequately aerated for the passivating film to re-form, with the result that the steel corrodes locally, the long-term consequence of which is detachment of the outer layer.

It has also been proposed to replace the conventional stainless steel by special steels. However, this came up against the same phenomena of local attack in the regions of the micropores and microcracks in the outer layer.

The object of the present invention is to propose a layered composite in which the metal substrate is capable of resisting any attack by human perspiration, even in the regions of micropores and microcracks in the outer
5. layer.

According to the invention, this metal substrate consists of a nickel alloy containing, in % by weight, a minimum of 45% of nickel, 7% of chromium and 7% of molybdenum, any additives present representing at most 15%.

10 Preferably, the amount of chromium will be approximately equal to the amount of molybdenum and will represent about a quarter of the amount of nickel. More preferably, the substrate will comprise, in % by weight, about 54% of nickel, 16% of chromium and 16% of molybde-
15 num.

The fact that the composite according to the invention is perfectly resistant to prolonged exposure to the action of human perspiration is all the more surprising because systematic experiments carried out before-
20 hand by the Applicant Company with composites comprising substrates of materials recognised for their corrosion resistance under normal conditions had shown that these substrates corroded very rapidly in contact with perspiration.

25 These experiments had been conducted by bringing samples into contact with an atmosphere of air at 40°C, saturated with a mixture of chemical compounds capable of reproducing the effects of human perspiration, and by noting the period of time after which either corrosion of

the substrate or in (sic) detachment of the outer layer appeared on these samples.

The composition of the mixture was that recommended by the German Institute Bundes Anstalt für Material-
prüfung, namely, in grams per litre of aqueous solution:

- sodium chloride : 20.0 g,
- ammonium chloride : 17.5 g,
- urea : 5.0 g,
- acetic acid : 2.5 g,
- pyruvic (sic) acid : 2.5 g,
- butyric acid : 5.0 g,
- lactic acid : 15.0 g,
- sodium hydroxide :

amount required to bring the pH to 4.7.

Using an atomiser, this mixture was spread in the form of a fine mist over the whole surface of the samples tested, and the samples were then suspended above the same mixture, in a hermetically sealed container, placed in an oven at 40°C.

The samples tested were in the shape of discs having a diameter of two centimetres and a thickness of two to three millimetres. They were coated either with a 20 micron thick layer of gold or with Chinese lacquer.

As indicated above, the experiments were conducted with samples of known materials recognised for their corrosion resistance in the widest variety of environments such as those encountered in the chemical industry, the food packing industry or the field of human or animal

prostheses. The results of these experiments are collated in the table which follows, in which:

- column 1 gives the name and composition of the alloy tested;
- 5 - column 2 indicates the number of days after which traces of corrosion were observed on the gold-plated samples; and
- column 3 indicates the number of days after which detachment of lacquer was observed on the lacquered
- 10 samples.

TABLE

1	2	3
Brass (Cu:60.0% Zn:40.0%)	1	4
"A" Nickel* (Ni:99.5% other elements: 0.5%)	2	10
Inconel 600* (Ni:76.0% Cr:16.0% Fe: 7.0% other elements: 1.0%)	2	13
Stainless steel 18-10 (Fe:78.5% Cr:18.0% Ni:10.0% other elements: 3.5%)	2	15
Stainless steel 18-10-3 (Fe:75.5% Cr:18.0% Ni:10.0% Mo: 3.0% other elements: 3.5%)	3	12
"K" Monel* (Ni:66.0% Cu:29.0% Al: 3.0% other elements: 2.0%)	4	15
Hastelloy B* (Ni:62.0% Mo:28.0% other elements:10.0%)	0.5	40
* Registered Trademark		

By way of comparison, the Applicant Company tested bare (that is to say uncoated) pieces of these same alloys under the same atmospheric conditions, and the table which follows gives the classification of these alloys in decreasing order of degree of corrosion:

	After 5 hours	After 8 hours	After 24 hours
	1 Brass	1 Brass	1 Brass
	2 Monel	2 Stainless Steel 18-10	2 Stainless Steel 18-10
10	3 Stainless Steel 18-10	3 Monel	3 Monel
	4 Nickel	4 Nickel	4 Hastelloy B
	5 Hastelloy B	5 Inconel	5 Nickel
	Inconel	6 Hastelloy B	6 Stainless Steel 18-10-3
15	6 Stainless Steel 18-10-3	7 Stainless Steel 18-10-3	7 Inconel

The tables above show the deceptive aspect of the experiments carried out and the random nature of the results obtained. In fact, first of all, significant differences in the stability of these alloys are observed, depending on whether they are used by themselves or as substrates.

In the cases where nickel alloys are used as substrates, it will also be noted that Inconel 600, containing 76% of nickel and 16% of chromium, proves inferior to "K" Monel, containing 66% of nickel and 29% of copper, and to Hastelloy B, containing 62% of nickel and 28% of molybdenum: such a result seems surprising when

chromium is known to protect against corrosion.

The same comment can be made as regards the stainless steels: the addition of 3% of molybdenum, which is nevertheless very significant as regards the resistance to corrosion by organic acids, does not substantially modify the results of the tests.

If reference is now made to the uses of the alloys tested, it is again impossible to establish, amongst the results obtained, a correlation capable of directing the search for a satisfactory substrate.

It is found, for example, that alloys such as "Inconel", "A" nickel and "K" Monel, which are recommended for their stability to organic acids and their stability to chlorides, do not resist corrosion when they are used as substrates under the conditions defined above.

It is also found that the stainless steels used in the field of human and animal prostheses do not resisting (sic) as a substrate in an environment reproducing the physico-chemical characteristics of human perspiration.

It is therefore particularly surprising that the metal substrate of the composite according to the invention remains insensitive to the effects of human perspiration when this composite stays in contact with the human skin for long periods, whereas the corrosion resistance of this substrate under normal use conditions is in every respect comparable to that of the alloys mentioned in the above table.

The Applicant Company thus successfully tested

two types of substrate falling within the scope of the present invention by subjecting them to the experimental conditions referred to above. These two substrates are nickel alloys marketed under the registered trademark Hastelloy C.

5 The composition of the first substrate was as follows, in % by weight:

	- Ni :	54.0%
	- Mo :	15.5%
	- Cr :	15.5%
10	- Others :	15%

and that of the second substrate was:

	- Ni :	62.0%
	- Mo :	16.0%
	- Cr :	16.0%
15	- Others :	6.0%

After an experiment lasting more than 140 days without interruption, no trace of oxidation had appeared on discs of these substrates coated with a 20 micron thick layer of gold.

20 Experiments continued for a longer period starting with the same substrate but this time coated with Chinese lacquer made it possible to observe that no trace of detachment of the layer of lacquer appeared after a period of 500 days.

25 Additional experiments carried out by the Applicant Company enabled it to establish who (sic) the nickel content of an alloy capable of forming the substrate of a composite according to the invention must represent at least 45% by weight of this alloy, whereas the chromium

and molybdenum contents must be respectively equal to at least 7% by weight. Moreover, the other constituents of the alloy, such as tungsten, iron, cobalt, manganese and silicon, taken together, must not exceed about 15% of the total weight of the substrate, again in % by weight.

Claims

1. Corrosion-resistant layered composite comprising a metal substrate and an outer layer of a noble material, characterised in that the said substrate consists of an alloy comprising, in % by weight, at least 45% of nickel, at least 7% of chromium and at least 7% of molybdenum, the other constituents of the substrate together representing at most 15% by weight of the alloy.
2. Layered composite according to Claim 1, characterised in that the chromium content is substantially equal to the molybdenum content and represents at most 25% of the nickel content.
3. Layered composite according to Claim 1, characterised in that it comprises, in % by weight, about 54% of nickel, 16% of chromium and 16% of molybdenum.
4. Application of a layered composite according to one of Claims 1 to 3 to the production of articles required to be in contact with the human skin for long periods of time, in particular the backs of watch cases.

Claims (as printed)

1. A stratified corrosion-resistant complex comprising a metal substrate and an external layer of a noble material, characterized in that said substrate is formed by an alloy comprising, in % by weight, at least 40%



and molybdenum contents must be respectively equal to at least 7% by weight. Moreover, the other constituents of the alloy, such as tungsten, iron, cobalt, manganese and silicon, taken together, must not exceed about 15% of the total weight of the substrate, again in % by weight.

Claims

1. Corrosion-resistant layered composite comprising a metal substrate and an outer layer of a noble material, characterised in that the said substrate consists of an alloy comprising, in % by weight, at least 45% of nickel, at least 7% of chromium and at least 7% of molybdenum, the other constituents of the substrate together representing at most 15% by weight of the alloy.
2. Layered composite according to Claim 1, characterised in that the chromium content is substantially equal to the molybdenum content and represents at most 25% of the nickel content.
3. Layered composite according to Claim 1, characterised in that it comprises, in % by weight, about 54% of nickel, 16% of chromium and 16% of molybdenum.
4. Application of a layered composite according to one of Claims 1 to 3 to the production of articles required to be in contact with the human skin for long periods of time, in particular the backs of watch cases.

Claims (as printed)

1. A stratified corrosion-resistant complex comprising a metal substrate and an external layer of a noble material, characterized in that said substrate is formed by an alloy comprising, in % by weight, at least 40%



70

of nickel, at least 7% of chromium and at least 7% of molybdenum, the whole of the other constituents of the substrate representing at most 16% by weight of the alloy.

5 2. The stratified complex according to claim 1, characterized in that the chromium content is substantially equal to that of molybdenum and represents at most 25% of that of the nickel.

3. The stratified complex as claimed in claim 1,
10 characterized in that it comprises, in % by weight, about 50% nickel, 16% chromium and 16% molybdenum.

4. The application of a stratified complex according to one of claims 1 to 3 to the construction of objects required to be in contact for long periods of time with
15 the human skin, particularly the backs of watch cases.

Revendications

1. Complexe stratifié résistant à la corrosion comprenant un substrat métallique et une couche externe en un matériau noble, caractérisé en ce que ledit substrat
20 est constitué par un alliage comprenant, en % en poids, au moins 45% de nickel, au moins 7% de chrome et au moins 7% de molybdène, l'ensemble des autres constituants du substrat représentant au plus 15% en poids de l'alliage.

2. Complexe stratifié selon la revendication 1, caractérisé en ce que la teneur en chrome est sensiblement
25 égale à celle du molybdène et représente au plus 25% de celle du nickel.

3. Complexe stratifié selon la revendication 1, caractérisé en ce qu'il comprend, en % en poids, environ



54% de nickel, 16% de chrome et 16% de molybdène.

4. Application d'un complexe stratifié selon l'une des revendications 1 à 3 à la réalisation d'objets appelés à être en contact pendant de longues durées avec la
- 5 peau humaine, notamment des fonds de boîtiers de montres.

Patentansprüche

1. Korrosionsbeständiger Verbundwerkstoff, enthaltend ein metallisches Substrat und eine Aussenschicht aus einem Edelmetall, dadurch gekennzeichnet, dass das Substrat aus einer Legierung besteht, die (in Gewichtsprozent) mindestens 45% Nickel, mindestens 7% Chrom und mindestens 7% Molybdän enthält, wobei alle anderen Bestandteile des Substrats höchstens 15 Gewichtsprozent der Legierung ausmachen.
- 10
2. Verbundwerkstoff nach Anspruch 1, dadurch gekennzeichnet, dass die Menge des Chroms praktisch gleich der des Molybdäns ist und höchstens 25% der Menge, des Nickels ausmacht.
- 15
3. Verbundwerkstoff nach Anspruch 1, dadurch gekennzeichnet, dass er (in Gewichtsprozent) etwa 54% Nickel, 16% Chrom und 16% Molybdän enthält.
- 20
4. Verwendung eines Verbundwerkstoffs nach einem der Ansprüche 1 bis 3 zur Herstellung von Gegenständen, die über einen längeren Zeitraum mit der menschlichen Haut in
- 25 Berührung stehen sollen, insbesondere von Bodenplatten für Uhrengehäuse.