

The present invention relates to the manufacture of an article comprising a substrate provided with a hard and corrosion-proof coating, and it relates especially to the manufacture of articles of this type constituting an item of jewellery, such as, for example, a bracelet or a watch casing.

It is known, especially in the field of watch casings, to coat a casing with a hard coating, which shields it from corrosion and scratching, or from wear and tear due to contact of the casing with external objects, or the clothes of the wearer of the watch. For instance, EP-A-0 038 294 and CH-A-631040 relate to hard titanium nitride based coatings, which display, in addition to their hardness, the advantage of displaying a colour very close to that of gold.

However, even though the coatings so obtained display very good resistance to wear and tear, their shock resistance, for instance against hard surfaces, is not entirely commensurate with this wear resistance. Indeed, because the coatings which are applied are relatively thin, of the order of several tens of microns, the hardness of the coated article is roughly that of the substrate, which can be brass or steel, and if a dent in the substrate occurs, such can lead to deterioration of the hard coating, and of the appearance of the article.

In order to remedy the above disadvantage, a substrate that is itself made from a hard material can be employed; however, the cost of such an item and the machining thereof prior to coating become prohibitive.

In an article in the journal "Thin Solid Films", 45(1977)397-406, J.A. Thornton and D.G. Cornog analyse a hard coating obtained using the plasma assisted deposition technique. In this case, the deposit is effected on a Hadfield type austenitic manganese steel. Depending on the deposition temperature the coatings obtained can display a dispersed cementite phase (Fe_3C). The result is a deposited layer, the hardness of which ranges between 350 and 750 kg mm^{-2} (Knoop Hardness).

Whilst this hardness value is already very considerable it has been found insufficient in certain cases. This applies notably in respect of watch casings.

It is thus an object of the invention to provide a process for the manufacture of an article provided with a coating, the hardness of which is markedly higher than that achieved by a coating using the previously known technique wherein the production method lends itself to mass production.

According to the present invention therefore there is provided a process for the manufacture of an article comprising a metallic substrate having a hard and corrosion resistant coating that consists in applying to the metallic substrate of this article a metal coating by means of plasma assisted deposition of an alloy, in a chamber having an inert gas atmosphere, characterized in that said alloy is a Stellite and that the process consists, in addition,

in maintaining the temperature of the substrate and the pressure of the inert gas atmosphere during deposition at values corresponding to a point in the T zone of the diagram proposed by J.A. Thornton in the journal Ann. Rev. Mater. Sci., 1977, page 242 in such a way as to impart to said coating an ultrafine distribution of hard particles in an alloy matrix and a compact structure.

In the present description a Stellite is understood to be an alloy based on cobalt, chromium, tungsten and carbon (see Ullman's Encyklopaedie der technischen Chemie, 1977, Vol. 14, page 283).

It has been found that by using an alloy so defined and in selecting a point in the T zone of the Thornton diagram, i.e. a well determined relationship between the temperature of the substrate and the pressure of the inert gas in the depositing chamber there is obtained a coating, the hardness of which reaches values between 1200 and 1500 HV 10p, whilst displaying excellent optical properties. Moreover the coating can be applied under temperature conditions that are not very critical, bearing in mind that the T zone for the alloy defined above is relatively large.

The above-mentioned article by J.A. Thornton published in the journal Ann. Rev. Mater. Sci. essentially deals with metal deposits obtained with the aid of a plasma and examines the physical properties of the growth and the structure of the coating layers obtained with the aid of these deposits.

For this purpose Thornton develops a technique for representing the microstructure of the layers basing himself on the "zone models" previously established. Thornton introduces another idea for describing these microstructures taking into consideration not only the temperature of the substrate, but also the pressure of the inert gas contained within the working chamber during depositing. In this way the author succeeds in determining a "T" zone in which the layer has a dense network of poorly defined fibrous grains. A structure of this type is particularly suitable for making articles that must present very great hardness provided that, according to the invention, one uses an alloy for the working material of the nature described above.

The invention will be better understood on reading the following description with reference to the enclosed drawings, in which:

- 45 - Figure 1 is a schematic sectional view of an article obtained according to the process of the invention;
- Figure 2 is a schematic view of an apparatus suitable for achieving the coating of the article
- 50 - in Figure 1;
- Figures 3 and 4 are microphotographs of hard layers according to the invention;
- Figure 5 is a view that is analogous to that of Figure 4 of a layer which does not display the
- 55 characteristics of the invention;

- Figure 6 is a perspective view showing the Thornton diagram used in the invention.

In Figure 1 a section of an article is schematically depicted which includes a substrate 1, and a hard coating which comprises an outer decorative layer 2 which resists wear and tear and corrosion and a metallic layer 3, of great hardness, which ensures for the entire article the required resistance against denting. The substrate 1 can also be made of a metallic material that is easy to machine, such as brass or steel. In the event that brass is used, an intermediate layer 4 which forms a diffusion barrier is interposed between the substrate 1 and the metallic layer 3, so as to prevent the zinc from the brass from migrating to the outer layers, which would impair the appearance of the article. Preferably the layer is of molybdenum, 0.1 to 0.5 μm thick. The outer layer 2 can be made of any wear and tear resistant material, but the use of a layer of titanium nitride having a thickness of 1 to 2 μm is especially recommended for jewellery applications. Finally, metallic layer 3 with a thickness of 2 to 100 μm , preferably between 5 and 15 μm and distinguished by an ultrafine distribution of hard materials is made from Stellite. Preferably an alloy composed of 2 to 3 % carbon, 40 to 55 % cobalt, 25 to 35 % chromium, 10 to 20 % tungsten, 15 % molybdenum and, optionally 4 % iron, nickel and titanium is used.

Experience has shown that when these alloys are deposited by methods of the plasma assisted deposition type, such as cathodic sputtering which is carried out with a flat magnetron or an ion beam, the layer that is made from a Stellite target included a stainless alloy matrix, in which ultrafine distribution of chromium or tungsten carbide results which imparts a very high degree of hardness to the article. By ultrafine distribution is meant that the fragments of hard materials which are distributed in the matrix display a size that is smaller than 0.01 μm and preferably lower than 0.005 μm . The hardness of the layer thus obtained equals about 1200 to 1500 HV 10p, whereas the hardness of the massive Stellite only equals 750 HV 10p. The depositing process, which is known per se, but applied to the cited material, destroys the platelet or dendritic structure of the chromium carbide, which is usually the cause of frailness in stainless alloys and that cannot be formed at the time of formation of the layer.

In Figure 2 is depicted schematically apparatus which makes it possible to obtain a metallic layer with an ultrafine distribution of hard materials according to the invention. For this purpose there is employed a vacuum chamber 10, in the upper section of which is a flat magnetron 11. The flat magnetron includes a cathode which is cooled by a water cooling circuit 12, 13 and permanent magnets 14 to 16 creating a magnetic field designed to confine a plasma in the immediate vicinity of a target 17 that is fixed on the cathode 11. A removable screen 18 can be inserted between the target 17 and the substrate 19

designed to be coated, which is deposited on a substrate electrode 20. The chamber 10 can be evacuated with a turbo-molecular pump (not shown) connected to an opening 21. A pressure of argon or of another inert gas can be established by means of a nozzle 22, equipped with a precision valve 23, and from a choke valve 24 mounted inside the opening 21. Electrically, a polarity select circuit 25 which is equipped with a switch 26 makes it possible to bring the substrate 19 to a negative potential in relation to that of the chamber when it is desired to clean it prior to depositing. Furthermore, a polarity select circuit 27 makes it possible to raise target 17 to a negative potential of about several hundred volts.

In order to form a layer which displays an ultrafine distribution of hard materials according to the invention, for instance on a steel substrate 19, the procedure is as follows. First of all, the substrate is placed on the substrate electrode 20, after having been polished. A target 17, which is formed for instance of a sintered or vacuum cast Stellite plate, is affixed to the flat magnetron cathode 11. Then the chamber 10 is evacuated and a pressure of argon is established there. The substrate is subjected to ion cleaning. Then the removable screen 18 is removed and polarization is applied to the target 17. The material is ejected from the target 17 by ion bombardment and projected onto the substrate 19. In view of the pressure of argon, the depositing speed of about 0.1 to 10 microns per minute, on which the substrate temperature depends, is determined so that those two latter parameters define a point which is included in the T zone in the diagram proposed by J.A. Thornton (Ann. Rev. Mater. Sci. 1977.7:239-260) (see Figure 6). In this T zone in the Thornton diagram, the deposits display a regular and compact structure, which leads to minimal surface toughness. With respect to a Stellite layer deposit, operating conditions are as follows: substrate polarization voltage: - 80 V; magnetron cathode polarization voltage: 420 V; argon pressure: 0.107 Pa. Preferably the target which is used in this latter instance is a Stellite plate obtained through vacuum casting, according to a conventional method.

The point in using Stellite to achieve the layer for ultrafine distribution of hard materials is that it displays very high hardness in the form of thin layers, of the order of about 1500 HV, and that the T zone for this alloy is especially large, which makes operating conditions less critical.

After the deposit of the ultrafine hard material distribution layer it can be coated with a decorative layer made of TiN for instance, according to the known process.

The microphotograph in Figure 3 shows through an 800 x enlargement an oblique section of a brass substrate which is coated with a Stellite layer of about 5 μ m in thickness that is deposited as stated above. This layer makes it possible to obtain a superficial hardness of $X_5 = 1736$ HV

10 p, whereas the substrate hardness is only $X_2 = 132$ HV 10 p. The various microdurometer imprints indicate that layer hardness increases as the distance from the interface increases in the way shown in the following table:

Imprint (from left to right) Real distance in relation to the interface Hardness

1	1.41 μm	515 HV 10p
2	2.38 μm	804 HV 10p
3	3.13 μm	1251 HV 10p
4	3.69 μm	1355 HV 10p

Figure 3 indicates that with the microscope enlargement, the Stellite layer seems perfectly homogenous, the size of the scattered hard material fragments being lower than $0.01 \mu\text{m}$. On the other hand, a massive Stellite alloy which is observed at the solidified state after being cast with the same enlargement discloses a structure of sharply separated phases, which leads to a less sound chemical resistance as a result of electro-chemical reactions which attack the grain joints.

Figure 4 is a photograph of a break in a coated substrate, observed under an electron microscope enlarged at 7000 x. This photograph indicates regular and compact morphology, the grain boundaries not being visible. This structure is characteristic of the T zone in the Thornton diagram and it leads to coatings with a perfect appearance as a result of minimal surface roughness.

As a comparison, Figure 5 is a view that is analogous to that of Figure 4 of a metallic layer which does not display the T zone structure in the Thornton diagram. This structure, which is characteristic of zone 1 in the same diagram, is distinguished by sharply separated columns; distributed in a non-compact fashion, and generating a relief at the surface which very greatly impairs the aesthetics of the coated article.



CLAIMS

1. A process for the manufacture of an article comprising a metallic substrate provided with a hard and corrosion-proof coating consisting in applying to this metal substrate (1) of this article a metal coating (3) by plasma assisted deposition of an alloy in a chamber containing an inert gas atmosphere, characterized in that said alloy is a Stellite and in that the process consists, in addition, of maintaining the temperature of the substrate and the pressure of the inert gas atmosphere during deposition at values corresponding to a point in the T zone of the diagram proposed by J.A. Thornton in the journal Ann. Rev. Mater Sci, 1977, page 242 in such a way as to confer to said coating an ultrafine distribution of hard particles in an alloy matrix and a compact structure.

2. A process according to claim 1, characterized in that said alloy is composed of 2 to 3 % carbon, 40 to 55 % cobalt, 25 to 35 % chromium, 10 to 20 % tungsten and 15 % molybdenum.

3. A process according to claim 2, characterized in that said alloy also includes 4 % iron, nickel and titanium.

4. A process according to any one of the preceding claims, characterized by depositing on the coating (3) of ultrafine distribution of hard materials a decorative layer (2) resistant to wear and tear.

5. A process according to claim 4, characterized in that said decorative layer is a layer of TiN.

6. A process according to any one of the preceding claims, characterized in that a substrate (1) of brass is used and in that an intermediate layer (4) forming a diffusion barrier is deposited on the substrate (1) before deposition of the coating (3) of ultrafine distribution of hard materials.

7. A process according to claim 6, characterized in that said intermediate layer (4) is a layer of molybdenum.

8. An article obtained by the process according to any one of claims 1 to 7, characterized in that the size of the hard particles forming the ultrafine distribution of said coating (3) is less than 0.01 μm .

9. An article according to claim 8, characterized in that said size is less than 0.005 μm .

10. An article according to either of claims 8 and 9, characterized in that the coating (3) of ultrafine distribution of hard particles displays a thickness of between 2 and 100 μm .

11. An article according to claim 10, characterized in that said thickness is between 5 and 15 μm .

12. An article obtained using the process according to either of claims 6 or 7, characterized in that the thickness of the intermediate layer (4) is between 0.1 and 0.5 μm .



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13. An article according to any one of claims 8 to 12, characterized in that it constitutes an article of jewellery.