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(54) Layered structures for metallic articles

(57) A method for forming an article comprises the steps of providing a metallic substrate (4), applying a layer of copper or copper-based alloy (6) to the metallic substrate and then diffusing aluminium into the copper or copper-based alloy layer (6). The method may be used, for example, as a convenient and low cost alternative to existing techniques for the manufacture of coins having an aesthetically pleasing and highly durable "aluminium bronze" finish.

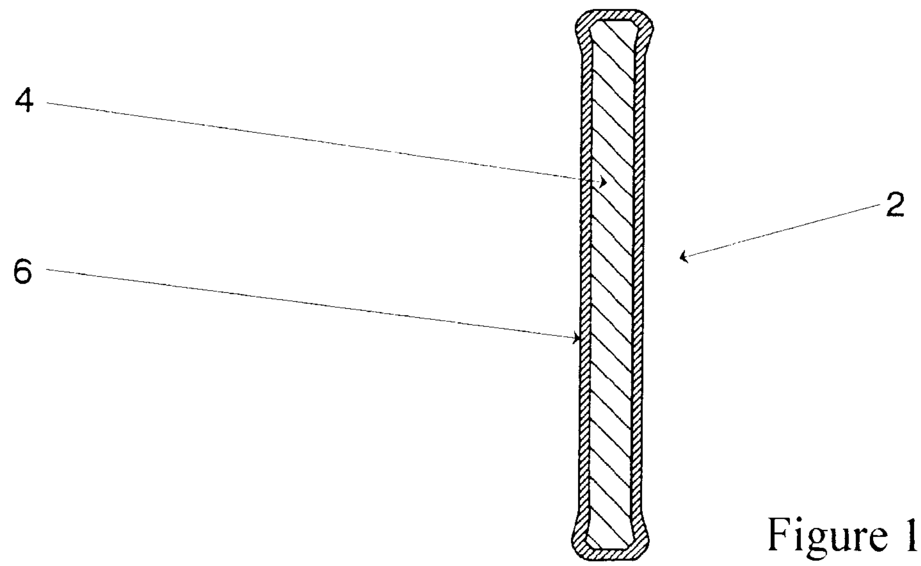

Figure 1

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Description

[0001] The present invention relates to methods for forming metallic articles, and in particular to methods for forming articles having a pleasing yellow finish and good tarnish resistance.

[0002] In the past twenty years many coins made of copper-based alloys have been replaced by coinage made of mild steel electroplated with a protective coating similar in colour to the original alloy. This change has been brought about primarily for reasons of economy, steel being substantially cheaper than the non-ferrous alloys. Thus, copper-plated steel has been substituted for so-called copper coins, nickel-plated steel has often replaced coinage made from cupro-nickel and other alloys, and brass-plated steel has often replaced various brass alloys.

[0003] Many countries, however, have continued to issue coins made from copper-aluminium alloys (aluminium bronze). These have a pleasing yellow colour and a good resistance to tarnish and discolouration. These alloys typically contain 6-9% of aluminium and there is sometimes also a small quantity of nickel. The formulation Cu-6%Al-2%Ni is in widespread use.

[0004] Because aluminium cannot be electrodeposited from an aqueous solution, there has been no practicable method of producing steel coins electroplated with a copper-aluminium alloy. Substitute coinage analogous to those described above are therefore not available for this alloy.

[0005] A possibility exists for making coinage from steel strip precoated (by some physical technique) with aluminium bronze. This method is wasteful of metal and leaves an exposed edge after the blanking operation. Other methods of applying coatings in aluminium bronze (e.g. by hot spraying) are not suitable for small articles produced in large volumes, as are coins.

[0006] We have now devised a low-cost method for forming coins or other articles with a coating of yellow-coloured copper-aluminium alloy.

[0007] In accordance with the present invention, there is provided a method for forming an article, the method comprising the steps of providing a metallic substrate, applying a layer of copper or copper-based alloy to the metallic substrate and then diffusing aluminium into said layer.

[0008] Coins or other articles may thus be made with coatings of aluminium bronze on a metallic substrate.

[0009] Preferably the layer of copper is electroplated onto the metallic substrate.

[0010] Preferably the step of diffusing aluminium into the copper layer comprises the step of depositing aluminium from a gaseous precursor onto the surface of the copper layer, the deposition step being carried out at high temperature so that a net diffusion of aluminium into the copper layer occurs.

[0011] Preferably the gaseous precursor comprises a monohalide of aluminium (AlX) which is preferably formed by the reaction, at high temperature, of an aluminium halide (AlX_3) with hydrogen and/or aluminium.

[0012] Whilst it is known to diffusion coat a copper substrate with aluminium deposited from a gaseous precursor, existing methods result in relatively high surface concentrations (over ten percent) of diffused aluminium. Articles having such high surface concentrations of diffused aluminium do not provide a finish having the pleasing yellow colour and tarnish resistance associated with existing 'aluminium-bronze' coins. It is therefore desirable to regulate the amount of aluminium deposited onto the surface of the copper layer.

[0013] In order to regulate the resulting concentration of aluminium adjacent the surface of the copper layer, preferably a monohalide of aluminium (AlX) is used which exhibits a low vapour pressure at high temperature. Most preferably the monohalide of aluminium comprises aluminium fluoride (AlF).

[0014] Where the monohalide is formed by the reaction of an aluminium halide (AlX_3) with aluminium, the amount of aluminium deposited onto the surface of the copper layer may instead or also be regulated by alloying the aluminium with a material that makes it less available for reaction with the aluminium halide (AlX_3). Whilst the alloy containing aluminium may, for example, comprise a nickel-aluminium or cobalt-aluminium alloy, it preferably comprises a chromium-aluminium alloy.

[0015] Preferably the copper-aluminium coating is formed by heating the copper-coated metallic substrate, in the presence of the monohalide of aluminium (AlX), for a period of between one and fifteen hours at a temperature of between seven hundred and fifty and one thousand and thirty seven degrees centigrade. Most preferably heating is for between two and eight hours. A preferred heating period is three hours at a temperature of eight hundred and twenty five degrees centigrade.

[0016] In a preferred embodiment of the present invention, the copper-aluminium coating is formed by heating the copper-coated metallic substrate, together with an aluminising material comprising aluminium fluoride (AlF_3) and chromium-aluminium alloy as solid reactants, in an atmosphere comprising hydrogen gas.

[0017] Preferably the aluminising material comprises between one and thirty percent aluminium fluoride (AlF_3) and between one half and fifteen percent chromium-aluminium alloy, the remainder of the material comprising a bulking material, perferably calcined alumina.

[0018] More preferably the aluminising material comprises between one and twenty percent aluminium fluoride (AlF_3) and between one half and ten percent chromium-aluminium alloy.

[0019] More preferably still the aluminising material comprises between two and fifteen percent aluminium fluoride (AlF_3) and between one and eight percent chromium-aluminium alloy.

[0020] Most preferably the aluminising material comprises between two and eight percent aluminium fluoride (AlF_3) and between one and five percent chromium-aluminium alloy.

[0021] A first preferred aluminising material comprises five percent aluminium fluoride (AlF_3) and two percent chromium-aluminium alloy.

[0022] A second preferred aluminising material comprises twelve and one half percent aluminium fluoride (AlF_3) and five percent chromium aluminium alloy.

[0023] Preferably the hydrogen gas is carried by an inert gas. Most preferably the aluminising compound is heated in an atmosphere comprising five percent hydrogen in argon.

[0024] Preferably the substrate comprises mild steel. However, in some circumstances, it may be desirable for the substrate to be formed from nickel or to have a layer of nickel applied to it, so that the step of diffusing aluminium into the copper layer forms a copper-aluminium-nickel alloy coating on the substrate. Furthermore, it is well known that coins having nickel cores offer greater security in automatic coin validators, and a nickel substrate may be preferred for this reason.

[0025] Also in accordance with the present invention, there is provided an article comprising a metallic substrate having a coating of copper or copper-based alloy into which is diffused a quantity of aluminium to form a copper-aluminium alloy.

[0026] Preferably the metallic substrate is formed from a relatively inexpensive material such as mild steel.

[0027] Preferably the copper coating is electroplated onto the metallic substrate.

[0028] Preferably the copper-aluminium alloy comprises less than ten percent aluminium. Most preferably the copper-aluminium alloy comprises approximately six percent aluminium.

[0029] The copper-aluminium alloy may comprise a copper-aluminium-nickel alloy, in which case, the copper-aluminium-nickel alloy would preferably comprise approximately two percent nickel.

[0030] An embodiment of the present invention will now be described by way of an example only and with reference to the accompanying drawings, in which:

Figure 1 is a sectional view of a coin blank;
Figure 2 is a sectional view of a plurality of copper plated coin blanks arranged within a retort; and

[0031] Referring to Figure 1 of the drawings, a coin blank 2 is shown comprising a circular disc 4 of mild steel, electroplated with a thirty micrometer thick layer 6 of copper.

[0032] The blank 2 is packed, as shown in Figure 2, together with a plurality of other blanks, in a tray 8 containing an aluminising material 10 in powder form. When packing the tray, care is taken to ensure that the blanks are sufficiently spaced apart to allow gaseous substances to pass freely between them. The aluminising material comprises a mixture of five percent aluminium fluoride (AlF_3), two percent chromium-aluminium alloy (70% Cr - 30% Al) and ninety three percent calcined alumina (Al_2O_3): all percentages are given by weight.

[0033] The tray is placed in a retort 12 which is purged via an inlet 14 and exhaust 16 with a gaseous mixture of five percent hydrogen (H_2) in argon (Ar) and heated to a temperature of eight hundred and twenty five degrees centigrade. The retort 12 is maintained at this temperature for 3 hours and then allowed to cool, during which time a continuous flow of hydrogen in argon to the retort is maintained.

[0034] The effect of heating the retort 12 is to form a monohalide of aluminium fluoride (AlF) by the reaction of the aluminium fluoride (AlF_3) with the chromium-aluminium alloy and with the hydrogen within the retort.

[0035] At high temperature, aluminium is deposited from the monohalide of aluminium fluoride (AlF) onto the surface of the blank and diffuses into its copper layer 6 to form a copper-aluminium alloy coating.

[0036] The method thus described provides a low cost means for forming coins or other articles with a finish having a pleasing yellow colour and good tarnish resistance.

Claims

1. A method for forming an article, the method comprising the steps of providing a metallic substrate (4), applying a layer (6) of copper or copper-based alloy to the metallic substrate and then diffusing aluminium into said layer.

2. A method as claimed in Claim 1, wherein the layer (6) of copper is electroplated onto the metallic substrate (4).

3. A method as claimed in Claim 1 or Claim 2, wherein the step of diffusing aluminium into the copper layer (6)comprises the step of depositing aluminium from a gaseous precursor onto the surface of the copper layer, the deposition step being carried out at high temperature so that a net diffusion of aluminium into the copper layer occurs.

4. A method as claimed in Claim 3, wherein the gaseous precursor comprises a monohalide of aluminium (AlX).

5. A method as claimed in Claim 4, wherein the copper-coated metallic substrate (2) is heated, in the presence of the monohalide of aluminium (AlX), for a period of between one and fifteen hours at a temperature of between seven hundred and fifty and one thousand and thirty seven degrees centigrade.

6. A method as claimed in Claim 5, wherein heating is for a period between two and eight hours.

7. A method as claimed in Claim 6, wherein heating is for a period three hours at a temperature of eight hundred and twenty five degrees centigrade.

8. A method as claimed in any of Claims 4 to 7, wherein the gaseous precursor is formed by the reaction, at high temperature, of an aluminium halide (AlX_3) with hydrogen.

9. A method as claimed in any of Claims 4 to 8, wherein the monohalide of aluminium (AlX) exhibits a low vapour pressure at high temperature.

10. A method as claimed in Claim 9, wherein the monohalide of aluminium comprises aluminium fluoride (AlF).

11. A method as claimed in any of Claims 4 to 10, wherein the gaseous precursor is formed by the reaction, at high temperature, of an aluminium halide (AlX_3) with aluminium.

12. A method as claimed in Claim 11, wherein the amount of aluminium deposited onto the surface of the copper layer (6) is regulated by alloying the aluminium with a material that makes it less available for reaction with the aluminium halide (AlX_3).

13. A method as claimed in Claim 12, wherein the alloy containing aluminium comprises a nickel-aluminium alloy.

14. A method as claimed in Claim 12, wherein the alloy containing aluminium comprises a cobalt-aluminium alloy.

15. A method as claimed in Claim 12, wherein the alloy containing aluminium comprises a chromium-aluminium alloy.

16. A method as claimed in Claim 15, wherein the copper-coated metallic substrate (2) is heated, together with an aluminising material (10) comprising aluminium fluoride (AlF_3) and chromium-aluminium alloy as solid reactants, in an atmosphere comprising hydrogen gas.

17. A method as claimed in Claim 16, wherein the aluminising material (10) comprises between one and thirty percent aluminium fluoride (AlF_3) and between one half and fifteen percent chromium-aluminium alloy, the remainder of the material comprising a bulking material

18. A method as claimed in Claim 17, wherein the bulking material comprises calcined alumina.

19. A method as claimed in Claim 17 or Claim 18, wherein the aluminising material (10) comprises between two and fifteen percent aluminium fluoride (AlF_3) and between one and eight percent chromium-aluminium alloy.

20. A method as claimed in Claim 19, wherein the aluminising material (10) comprises twelve and one half percent aluminium fluoride (AlF_3) and five percent chromium-aluminium alloy.

21. A method as claimed in any of Claims 16 to 20, wherein the hydrogen gas is carried by an inert gas.

22. A method as claimed in Claim 21, wherein the atmosphere comprises five percent hydrogen in argon.

23. A method as claimed in any preceding claim, wherein the substrate (4) is formed from mild steel.

24. A method as claimed in any preceding claim, wherein the substrate (4) is formed from nickel or has a layer of nickel applied to it, so that the step of diffusing aluminium into the copper layer forms a copper-aluminium-nickel alloy coating on the substrate.

25. A method substantially as herein described with reference to the accompanying drawings.

26. An article comprising a metallic substrate (4) having a coating (6) of copper or copper-based alloy into which is diffused a quantity of aluminium to form a copper-aluminium alloy.

27. An article as claimed in Claim 26, wherein the metallic substrate (4) is formed from mild steel.

28. An article as claimed in Claim 26 or Claim 27, wherein the copper coating (6) is electroplated onto the metallic substrate (4).

29. An article as claimed in any of Claims 26 to 28, wherein the copper-aluminium alloy comprises less than ten percent aluminium.

30. An article as claimed in Claim 29, wherein the copper-aluminium alloy comprises approximately six percent aluminium.

31. An article as claimed in any of Claims 26 to 30, wherein the copper-aluminium alloy comprises a copper-aluminium-nickel alloy.

32. An article as claimed in Claim 31, wherein the copper-aluminium-nickel alloy comprises approximately two percent nickel.

33. An article substantially as herein described with reference to the accompanying drawings.

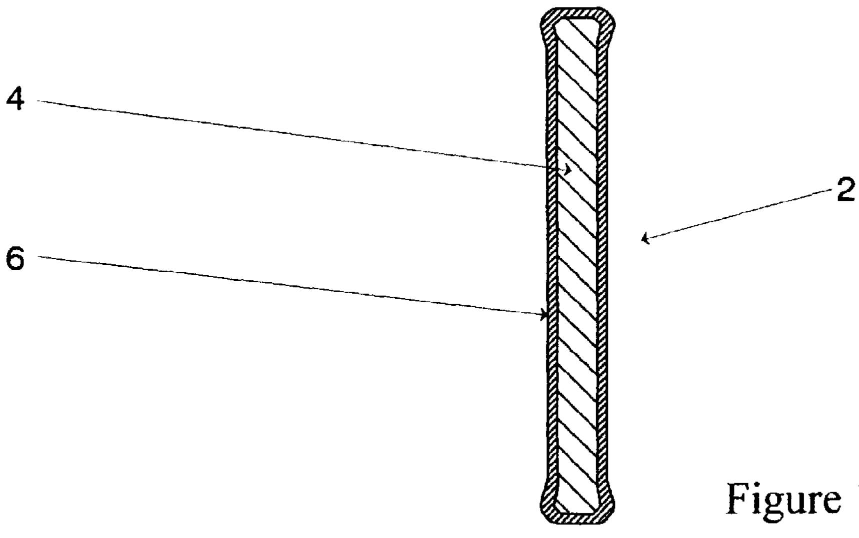

Figure 1

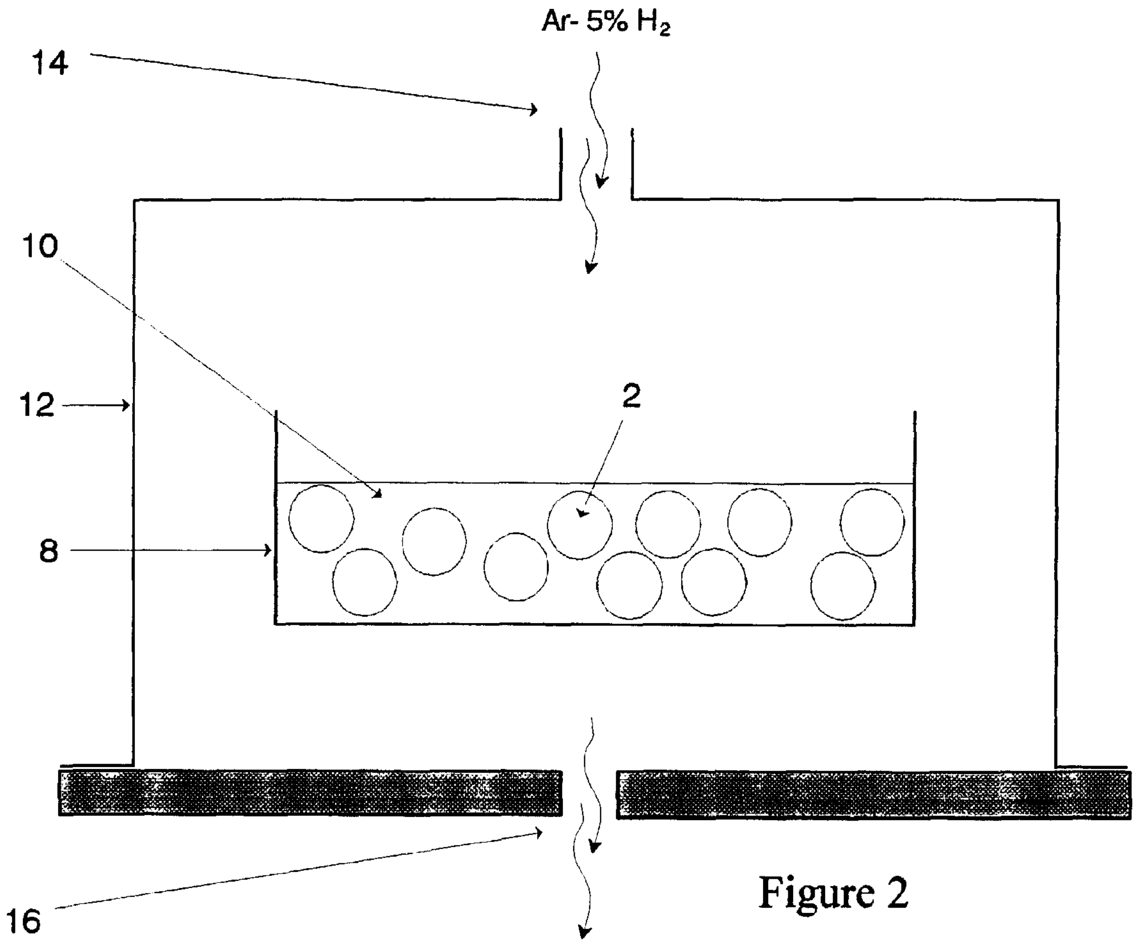

Figure 2

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EUROPEAN SEARCH REPORT

Application Number
EP 99 30 3808

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
A	US 2 819 208 A (GALMICHE; ONERA) 7 January 1958 (1958-01-07) * the whole document * ---	1-25	C23C10/02 B32B15/01
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			TECHNICAL FIELDS SEARCHED (Int.Cl.6)
			C23C B32B G07F

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	23 August 1999	Lippens, M

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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