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3,202,530

METHOD OF FORMING A COMPOSITE
METAL ARTICLE

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The present invention relates to a method of improv-
ing the surface properties of metals.

As is well known, most alloy compositions have com-
binations of properties which render them most useful
for specific applications. Improvements have been made
in properties of metals for special uses by cladding or
coating the surfaces to retain the bulk properties of a base
metal while adding the surface properties of the metal
deposited on the surface. In order to form the most use-
ful surface deposits some form of energy is customarily
applied to the deposit in forming it or after it is formed.
Where surface alloying is to be produced a high tempera-
ture heat is usually used. However, heating of a sub-
strate to a high temperature can lead to undesirable
changes in the base metal.

An object of the present invention is the production of
metal articles having at least partially alloyed surface de-
posits produced without heat damage to the metal base.

Another object is to provide a highly efficient method
of forming alloyed surface deposits on base metal.

A further object of the invention is to provide articles
having alloyed surface coatings of character which is dis-
tinctive from those previously formed.

Still another object is to provide a means for precisely
controlling the degree and/or rate of alloying of a sur-
face deposit on a metal surface.

Other objects and advantages of the invention will be
in part apparent and in part pointed out in the descrip-
tion which follows.

In one of its broader aspects the objects of the inven-
tion are achieved by treating a metal surface to impart a
metastable vitreous layer to the surface of a metal article
and, without delay, depositing a layer of metal on said
surface adapted to be alloyed with said surface metal.

In practicing the method sequence of the essential steps
of producing the vitreous surface layer and the deposit
of an alloying element is not critical. A critical factor
in practice of the invention is that the formation of the
vitreous layer and the deposit of the layer of the alloy-
able element must not be separated by too great a length
of time. Thus, the alloying element may be added to the
surface before the vitreous layer is formed thereon, dur-
ing the process of forming the layer, or after it is formed.
However, when the alloying material is deposited after
vitreous surface layer formation, optimum results are ob-
tained only if the deposit is made within a short time after
the vitreous layer is formed.

With regard to the nature of the vitreous layer formed
in the metal surface in practicing this invention, this layer
is vitreous in that it has properties of a highly viscous
liquid. Thus, it is vitreous in that it is non-crystalline and
amorphous in structure and it is able to accept metal
layers deposited thereon as if by solution to form surface
alloys. Once the layer is formed, its treatment must be
restricted to avoid any deleterious effects to its alloying
properties. For example, use of heat energy is not suit-
able because it dissipates the capability of the surface layer
to alloy metals and can also cause other undesirable side
effects.

It has been found that the capability of a vitreous sur-
face layer, formed by working the surface, to alloy metals
deposited thereon, dissipates within a relatively short time
after being formed on a base metal surface, but that if a

layer of an alloying component is deposited on the sur-
face without delay, an alloying takes place and an article
having a surface deposit alloyed with the base metal is
formed.

The method of this invention will be made additionally
clear from the following examples, although it will be
understood that these examples are given for illustrative
purposes only and that the scope of the invention is not
limited to the methods illustrated.

Examples

Surfaces of 70-30 brass have been prepared by work-
ing the surface by machine buffing followed by a clean-
ing step such as vapor degreasing to remove buffing com-
pounds. When such surfaces were coated with aluminum
by condensation of aluminum vapors in vacuum within
four hours after buffing, the resultant surfaces were found
to be brass-like in appearance and uniform in color in-
dicating that alloying of brass and aluminum had oc-
curred. The resultant surfaces were also found to be
uniformly and significantly more resistant to oxidation by
air at elevated temperatures as high as 1100° F. than the
original brass surface. Furthermore, such surfaces were
found to have improved tarnishing resistance to atmos-
pheres containing sulfur compounds such as sulfur dioxide
or hydrogen sulfide. Alloy layers produced by aluminum
deposits as thin as 100 to 300 Å. were found to be effec-
tive in preventing rapid tarnishing and oxidation.

On the other hand, when buffed surfaces of brass were
not coated with aluminum by these techniques but al-
lowed to stand for several hours, subsequent deposits of
aluminum were found to be mottled in color, and resistance
to oxidation and tarnishing was non-uniform and un-
predictable. A particular surface of brass was buffed,
vapor degreased using trichloroethylene, and stored in a
desiccator for 24 hours to prevent excessive air oxidation
at room temperatures. This specimen was then coated in
vacuum with a 300 Å. deposit of aluminum resulting in a
surface of mottled appearance and one which tarnished
in a non-uniform manner.

Such elements as chromium, nickel, silicon, and titani-
um have been vapor deposited onto freshly buffed sur-
faces of copper and of brass and surface alloying was
found to occur.

Working of the base metal surface to be alloyed may
be carried out by any of several conventional techniques.
For example, the surface may be shot peened or it may
be burnished by high velocity frictional contact with a
rapidly moving object. It may be wire brushed as de-
scribed in the above examples or by other known brush-
ing techniques.

Other methods of working metal surfaces which im-
part a vitreous form to the surface metal to produce a
vitreous surface layer may similarly be employed in carry-
ing out the method of this invention.

A most important factor in obtaining high efficiency in
carrying out the surface alloying is the depositing of metal
soon after the vitreous layer is formed on the surface and
before the alloying capability has attenuated appreciably.

Also, in order to improve the efficiency of the surface
alloying process, steps can be employed to accelerate the
alloying. For this purpose a mild heating of the bulk or
of the surface only of the buffed base material with its
layer of element to be alloyed may be employed to advan-
tage. Such heating increases the rate of alloying of de-
posited metal.

This heating should be mild whether through the en-
tire metal base or at the surface only, because a high tem-
perature heating causes a dissipation of the alloying
capability of the vitreous surface layer before appreci-
able alloying takes place. By contrast, mild heating ac-

celerates alloying. Control of temperature accordingly permits control of alloying progress and rate.

Cooling of the vitreous surface layer extends the period during which the vitreous layer retains a capability for alloying with metals deposited in intimate contact therewith.

One of the unique advantages of this invention is that it may be practiced in connection with conventional metal finishing steps. Thus, where the appearance of a surface is to be improved as by burnishing or polishing in a manner which imparts a vitreous layer to the surface, it is possible to gain greater improvement in the surface properties by the deposit of a light layer of an alloying element to the freshly burnished surface and to develop a surface alloy therein in this manner. Increased stain resistance and similar improved properties can be developed from this combination of steps.

Further improvements in surface properties and appearance can be obtained by reworking the surface after an initial alloying operation as described above to introduce the same or additional alloying components therein.

In general the surface should be clean and free of alloy inhibiting foreign matter when the step of forming the vitreous layer is carried out. Methods of surface cleaning are described in the patent literature, as for example in U.S. Patent 2,880,115 and others.

The amount of metal which is deposited on the surface is determined by the extent and depth of alloying which is to be produced. Where an amount of alloying is sought which changes the metal surface properties but does not appreciably change the appearance or color of the surface, light working of the surface to develop a vitreous layer of shallow depth thereon may be employed, followed by the deposit of a light layer of a metal element for alloying.

Where deeper surface metal working is employed, deeper alloying will occur. Similarly, the amount of alloying, i.e. the amount of metal which will alloy, in a surface increases with the amount of work done on the surface in forming the vitreous layer. Thus, where a greater amount of work is done in a given surface layer, greater degree of alloying can be developed by deposit of heavier surface layers of alloying elements.

Surface deposits must be in intimate contact with the metal surface for alloying. For this reason vapor deposition methods of and other methods which produce intimate contact of surface layers, such as gas plating and the like, are particularly effective.

The surface deposit of the component to be alloyed can also be prepared by one of the many known techniques such as those described in the patent and technical literature. Vapor or inert atmosphere deposition is preferred for many purposes where the metal surfaces are highly reactive, as with oxygen of the atmosphere, to form alloy inhibiting surface reaction products. Metal surfaces can be rendered less subject to reaction with atmospheric gases and contaminants by surface alloying with the more noble metal alloying elements in accordance with this invention.

Among the metals from which surface alloys can be

formed successfully are the following: silicon, titanium, aluminum, chromium, nickel, zinc, tin, lead, and gold.

Among the base metals on which surface alloys can be formed advantageously by the practice of this method are the following: copper, brass, mild steel, lead, gold, and aluminum.

Since many examples of the foregoing procedures and apparatus may be carried out and made and since many modifications can be made therein without departing from the scope of the subject invention, the foregoing is to be interpreted as illustrative only and not as defining or limiting the scope of the invention.

What is claimed is as follows:

1. A method of surface alloying a metal sheet comprising:

- (A) providing a copper sheet,
- (B) cold working a surface layer of said sheet to impart a metastable formation thereto capable of forming surface alloys with metals deposited thereon,
- (C) depositing an alloying element consisting essentially of a metal selected from the group consisting of silicon, titanium, aluminum, chromium, nickel, zinc, tin, lead and gold to said sheet while said surface layer thereof is in said metastable state within four hours of said cold working,
- (D) maintaining intimate contact between said sheet and said alloying element while simultaneously continuing said deposition of said alloying element until said element has alloyed with said sheet to the desired depth.

2. The method of claim 1 wherein said alloying element deposition comprises the step of condensing vapors of said alloying element on said surface layer in a vacuum.

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