The present invention relates to a method of improving the surface properties of metals. As is well known, most alloy compositions have combinations 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 useful 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 temperature heat is usually used. However, heating of a substrate 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 deposits 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 distinct from those previously formed.

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

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

In one of its broader aspects the objects of the invention 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 the practice of the invention is that the formation of the vitreous layer and the deposit of the layer of the alloying 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, during 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 obtained 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 thus formed, its treatment must be restricted to avoid any deleterious effects to its alloying properties. For example, use of heat energy is not suitable 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 surface 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 surface 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 working the surface by machine buffing followed by a cleaning step such as vapor degreasing to remove buffering compounds. When such surfaces were coated with aluminum by condensation of aluminum vapor in vacuum within four hours after buffing, the resultant surfaces were found to be brass-like in appearance and uniform in color, indicating that alloying of brass and aluminum had occurred. 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 atmospheres containing sulfur compounds such as sulfur dioxide or hydrogen sulfide. Alloy layers produced by aluminum deposits as thin as 100 to 300 A. were found to be effective in preventing rapid tarnishing and oxidation.

On the other hand, when buffed surfaces of brass were not coated with aluminum by these techniques but allowed 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 unpredictable. 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 A. 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 titanium have been vapor deposited onto freshly buffed surfaces 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 described in the above examples or by other known brushing techniques.

Other methods of working metal surfaces which impart a vitreous form to the surface metal to produce a vitreous surface layer may similarly be employed in carrying 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 advantage. Such heating increases the rate of alloying of deposited metal.

This heating should be mild unless the entire metal is formed or at the surface only, because a high temperature heating causes a dissipation of the alloying capability of the vitreous surface layer before appreciable alloying takes place. By contrast, mild heating ac-
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3. accelerates 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 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, 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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