

## TITANIUM PLATING ON COPPER SURFACES USING TITANIUM HYDRIDE

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The authors use the principle of decomposition of  $TiH_2$  and elevated temperature to plate titanium on the surface of metallic copper. A similar procedure has the purpose of preparing materials with the internal properties of pure copper but with increased surface hardness. The authors describe the procedure studied and used to obtain a compact and adherent titanium plating on metallic copper and report the micrographic results, recommending more appropriate tests to show the solid solutions formed. They report microhardness measurements made to determine the properties of the titanium layer and attempt to use the hardness of the Cu-Ti bond to obtain maximum increase in hardness of the surface layer prepared. (Au)

## INTRODUCTION

Some applications, especially those of an electrotechnical nature, require copper with optimum electrical conductivity and considerable surface hardness that pure copper cannot give. On the other hand, a hard metal added to the copper would take away the essential electrical properties. Since such hardness is needed on the surface layer of the copper so that it will resist attrition, erosion, etc., it was proposed to study depositing on the copper a minimum surface layer of an element that would immediately bind to the copper and harden the surface.

The first proposal was to use beryllium because of its hardening capacity for copper, but the difficulty of obtaining sufficient amounts of this material resulted in its being discarded a priori.

Our studies were therefore based on titanium metal because of its capacity for hardening and the possibility of making solid Cu-Ti solutions which, with heat treatment, ages and offers a considerable hardness to the bond.

Titanium element is preferred because in small percentages in the copper it does not seriously decrease the conductivity of the metal base.

The effect of titanium on copper is similar to that of beryllium, being only much less efficient.

Figure 1 shows the Cu-Ti diagram, preliminary from our experiments.

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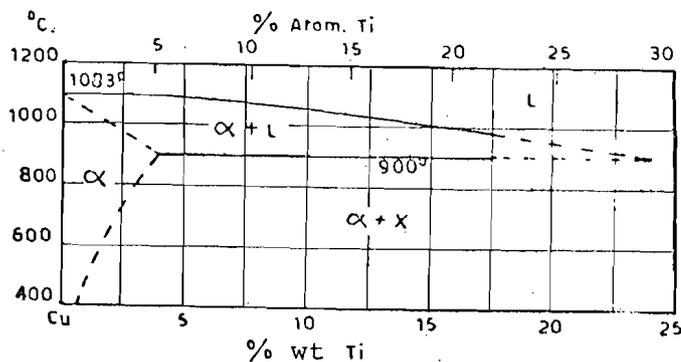
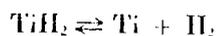


Fig. 1. Cu-Ti diagram.

Our experiments were based on the following principle: titanium hydride,  $TiH_2$ , like other hydrides of groups IV and V, such as  $ZrH_2$ ,  $HfH_2$ ,  $TaH_2$ ,  $NbH_2$ , and  $TaH_2$ , is stable at ambient temperatures and can be preserved for an indefinite time. When heated in the atmosphere, it decomposes at  $150^\circ C$ , being converted to  $TiO_2$ , but if heated in a non-oxidizing atmosphere or in a vacuum above  $150^\circ C$  it gradually dissociates to hydrogen and pure metal:



This property allows producing a Cu-Ti bond when powdered  $TiH_2$  is placed on metallic copper and the system heated under vacuum or in a reducing atmosphere to a temperature that decomposes the  $TiH_2$ .

The atomic state of the Ti formed at the decomposition temperature allows immediate solution of this metal in the copper solvent.

In the literature there are procedures recommended for production of titanium hydride. Arach and Alexander prepared  $TiH_2$  by heating granular Mg with  $TiO_2$  in a current of hydrogen in the reaction zone. Clauber obtained  $TiH_2$  by electrolysis of 0.1 to 0.2 N  $H_2SO_4$  solutions with Ti electrodes.

This material is available commercially and we used that supplied by Metal Hydrides, Inc., Beverly, Mass., U.S.A. and that produced in our own laboratory.

#### APPARATUS USED FOR TITANIUM PLATING ON COPPER SURFACE

A copper plate is covered with a layer of titanium hydride to the thickness desired, depending on the thickness of the titanium coating desired. It is then put into a suitable furnace in which the temperature can vary from  $700$  to  $900^\circ C$  in vacuum or in an inert gas atmosphere.

One can understand the difficulty of the preparation which should reach and maintain the high temperature in vacuum. The apparatus comprised a reaction tube, vacuum equipment, heating furnace, and means for temperature control.

### Reaction Tube

This is a drawn steel tube, 23 mm i.d., 1 mm thick, and 600 mm long, closed at the end with an autogenous weld. On the other end it is welded to a pipe which allows <sup>for</sup> connection with the vacuum pump.

This connection requires special precautions because in operation a significant pressure develops in the reaction tube because of the hydrogen formed in titanium hydride decomposition.

### Vacuum Equipment

In the circuit which connects the reaction tube with the vacuum pump there is a U-shaped manometer, with mercury, supplied with a 3-way valve which allows disconnecting the pump when the desired vacuum has been reached and using the manometer as a safety valve while following, instant by instant, all pressure variations which show in the reaction tube.

Between the U manometer and the vacuum pump, connected with a T connector, is a MacLeod vacuumeter for a precise indication of the degree of vacuum reached.

### Heating Furnace and Temperature Control

A furnace is used with a 60-cm-long Pt ribbon mounted in series with an ammeter and a variable rheostat. In reaching and maintaining the desired temperature of 900°C, a disadvantage is the significant time required to take the ambient temperature of the furnace to the temperature required for the work. At first it was fed with a 5-A current which was increased to 30 A in 0.5 hr by successively removing resistances.

Temperature control was with a Pt-Pt/Rh thermocouple with a millivoltmeter.

The couple was placed in the space between the external wall of the tube and the internal wall of the furnace.

Figure 2 shows schematically the components mounted in our laboratory.

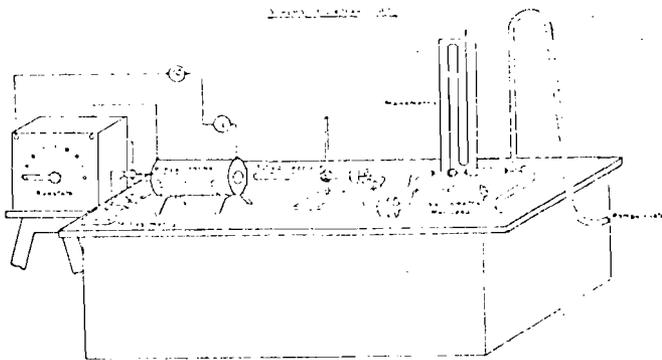


Fig. 2. Schematic diagram of apparatus.

### Sample Preparation

Small bars of electrolytic copper, 99.9%, size 25 by 12 by 4 mm were used. They were polished on one face with emery paper. On this face was placed a layer of powdered  $TiH_2$ , made adherent and compacted by different means. Practically, a suspension of powdered  $TiH_2$  was made in a wetting medium and applied with a brush, like a varnish, on the copper surface and allowed to dry.

For making the suspension, as a means of dispersing the  $TiH_2$  were used ethyl and methyl alcohol, which gave irregular and incomplete deposits but had the advantage of allowing easy drying of the suspension on the area.

Thus a means was sought for dispersing the  $TiH_2$  in a viscous state with drying in the reaction furnace and which allows obtaining on the sample a much more homogeneous and compact layer.

Good results were obtained with the use of glycerine, which gave a compact, heavy deposit of the powder on the copper. Similar results were obtained with bidistilled lubricating mineral oil. But the Ti surface was definitely irregular and stratified with this dispersing medium.

The problem was overcome by using a transparent nitrocellulose varnish in which powdered  $TiH_2$  was suspended like an ordinary pigment, and the viscosity of the medium could be varied at will with the use of the appropriate diluent. An advantage is that the varnish applied with a brush or spray gun dries in air in a few minutes, remaining smooth, adhesive, resistant, and transparent and allowing us to observe and handle the sample immediately after the titanium-plating treatment without any special precautions.

### TITANIUM-PLATING PROCEDURE

The sample was prepared and placed in a small porcelain boat with about 1 g of  $TiH_2$  in order to create a reducing atmosphere in the furnace during the decomposition. Then the boat is placed in the reaction tube and the tube is placed in the furnace when the temperature has reached around 400°C.

The vacuum pump, at around 15', evacuates the tube to about 0.05 Hg [sic] which is required for the work. The progress of the reaction is followed by observing the pressure variation (level of Hg in the manometer). Hydrogen starts to form at 500°C (at 400°C, for safety, the pump tube is disconnected), and with an initial vacuum of 0.05 mm Hg the pressure reaches 300-400 mm Hg when the temperature reaches 900-950°C. At this temperature the  $TiH_2$  is practically all dissociated and there is no further increase in pressure with the temperature kept constant.

After about 20 min at this temperature, the tube is removed from the furnace, hermetically sealed, and allowed to cool rapidly in air. During the cooling any re-formed  $TiH_2$  will deposit on the bottom of the boat and can be used for subsequent operations. However, the reaction for re-forming  $TiH_2$  does not occur with the part of the titanium which has been deposited on the copper surface and dissolved in the copper.

This phenomenon explains the fact that, after cooling, the tube does not go back to the initial vacuum and the pressure remains around 20 mm Hg rather than going to the value of 0.05 which it was initially, a pressure which we think is due to free hydrogen because part of the Ti is bound to the copper.

It should be noted that, while the decomposition of  $TiH_2$  takes place at  $500^\circ C$ , to obtain solution of the metal on the copper surface it is necessary to raise the temperature to  $900^\circ C$  (see Fig. 1) so that the solid solution of Ti in Cu will form.

In this condition, numerous tests are made on titanium plating on thin sheets and wires of copper.

Especially interesting are the results of the test on titanium plating on thin copper strips, 0.3 mm thick. The  $TiH_2$  layer was applied on both sides of the strip, and the titanium layer completely lost the properties of semi-finished copper, becoming hard and elastic, and having laminations (cold-rolling) of 0.1 mm. In this case the titanium penetrated almost all the laminated section and lost all semi-worked properties and became more like pure copper.

It should be noted that the titanium plating operation carried out by this procedure can be done only on pure copper (electrolytic), which has been de-oxidized, because the presence of hydrogen at high temperatures would immediately make brittle any copper containing oxygen (hydrogen disease).

A precaution to be observed:  $TiH_2$  dispersed on the bottom of the boat and serving to produce hydrogen should be removed from the copper sample by means of an iron rod. Without this precaution, direct contact of the copper with excess powdered  $TiH_2$  would cause melting of a Cu-Ti bond. In fact, in pushing the temperature to around  $900^\circ C$ , we risk reaching the temperature at which a eutectic Cu-Ti, containing about 25% Ti, would form between the fused phase ( $950^\circ C$ ) and the Cu-Ti bond, rich in fine Ti and offering a eutectic composition, only if the Cu comes in contact with the excess Ti that deposits on the bottom of the boat.

The temperature limits between which we should remain for a sufficiently long time for the titanium plating to occur are restricted and make the experiment difficult. The treatment is maintained for 15-20 min at a temperature of 980°C with the precaution that 100°C above or below this either Ti plating does not occur or the copper burns and fuses.

#### RESULTS OF TESTS

##### Micrographic Analysis

The Ti samples were examined microscopically in sections prepared on a resin base. The specific reagents were:

1. For fluoride attack: 1 part (by vol) HFl [sic], 38%; 1 part by vol glycerine. The glycerine acts as a moderator of the attack. This is reactive and specific for Ti, leaving the Cu unaltered.
2. For Nitric attack: 1 part by vol. conc. HNO<sub>3</sub>; 1 part by vol. glycerine. The glycerine moderates the attack. This is reactive and specific for Cu, leaving the Ti unaltered.
3. Nitric-fluoride attack: 1 part by vol. conc. HNO<sub>3</sub>; 1 part by vol. HF, 38%; 2 parts by vol. glycerine. The reaction clearly shows the solid solutions formed whether rich in Cu or rich in Ti.
4. Cuproammonico attack: 10 g CuCO<sub>3</sub>, 5 g Na<sub>2</sub>CO<sub>3</sub>, 10 cc NH<sub>3</sub>. The reaction shows, with dark gray coloration, the solid Cu-Ti solution containing a large amount of copper.

The micrographs (X740) are shown of samples of titanated copper:

Fig. 3. Fluoride attack: the clear phase contains mostly copper and the dark, mostly Ti.

Fig. 4. Nitric attack: the clear phase contains mostly Ti, the dark, mostly Cu.

Fig. 5. Nitric-fluoride attack: the dark phase is rich in Ti, the light in Cu.

Fig. 6. Cuprammonium attack: the light phase contains mostly Ti, the dark, mostly Cu.

The microscopic examination of this last sample of the Cu-Ti surface bond, without attack, shows the two distinct phases with various Ti concentrations colored differently---one rose and the other gray, but almost of the same intensity so that in the micrograph, even made with orthochromatic film and

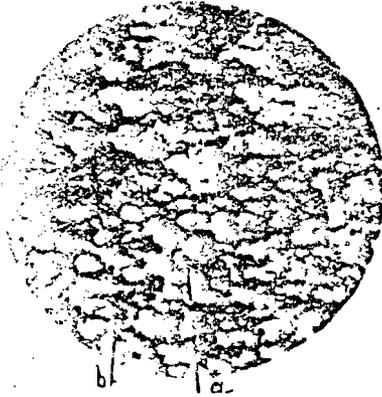


Fig. 3



Fig. 4



Fig. 5

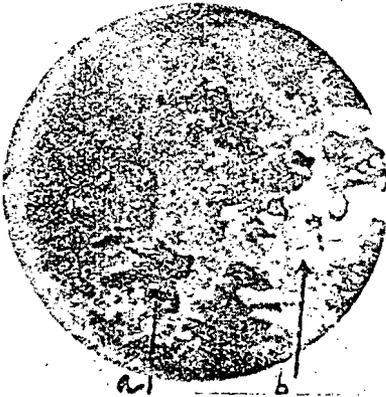


Fig. 6

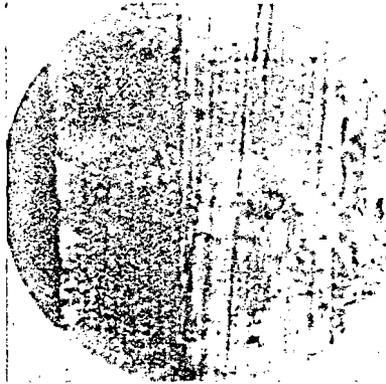


Fig. 7



Fig. 8

with long exposure time, they are not resolvable.

To be able to distinguish them, the samples were immersed in a solution of ammoniacal  $\text{CuCO}_3$ . The reaction produced on one of the two phases---the one colored rose---a dark gray coloration, leaving the other phase practically unaltered.

It should be noted that the cuprammoniacal solution has the same effect as on brass but not on pure copper, and not even on pieces of copper and zinc placed in close contact with each other. The action confirms only the solid solution of copper. The dark coloration produced in the presence of the cuprammoniacal reagent is due to the solid Cu-Ti solution which is richer in Cu.

The possibility of distinguishing the various solid solutions and the copper phase of the solid solution phase allows also making measurements of the

depth of the Ti plating, deduced from the micrographic analysis. The depth is, of course, regulatable by adjusting either the Ti-plating temperature or the amount of  $TiH_2$  deposited on the Ti plates.

Figure 7 shows a micrographic section (X90) of a piece of copper treated with  $TiH_2$ .

Figure 8 shows, at higher magnification (X700) the limiting zone of diffusion of the solid Cu-Ti solution and copper base in the sample of Fig. 7.

The micrographs allow confirming the best conditions for making a homogeneous, adherent, compact, and uniformly dispersed Ti plating on the whole surface of the sample.

#### Debyegrams

The Debyeogram made on a titanated Cu wire shows, by comparison with literature data, the presence of Cu (the base) but the absence of Ti. This indicates that the bond has its own lattice.

#### Microhardness

Given the minimum thickness of the Cu-Ti bond, a hardness test can be made only with the microdetermination system.

We cannot report absolute data on hardness but with the measurements we made we can state that the surface bond has a hardness that is about double that of the base copper.

#### CONCLUSIONS

The most important consideration is the fact that the Cu-Ti bond can undergo thermal treatment with a significant increase in its mechanical properties, which possibility can be applied on the Ti-plated copper to give a metal base with an outside layer that is very hard. The same possibility can be better developed by submitting the Ti-plated metal first to plastic deformation and then to thermal treatment to improve the hardness of the surface bond.

Preliminary tests readily show the possibility of obtaining by such a procedure a surface layer of Ti on Cu with a hardness 2 to 3 times that of the metal base. We intend to continue the studies on applicability of this procedure and the principles shown to be realizable in our experiments.

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