

[54] **COMPOSITE COPPER ALLOY**

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[58] **Field of Search**.....**29/199**

[56] **References Cited**

**UNITED STATES PATENTS**

2,988,630 6/1961 Moore et al.....29/199 X

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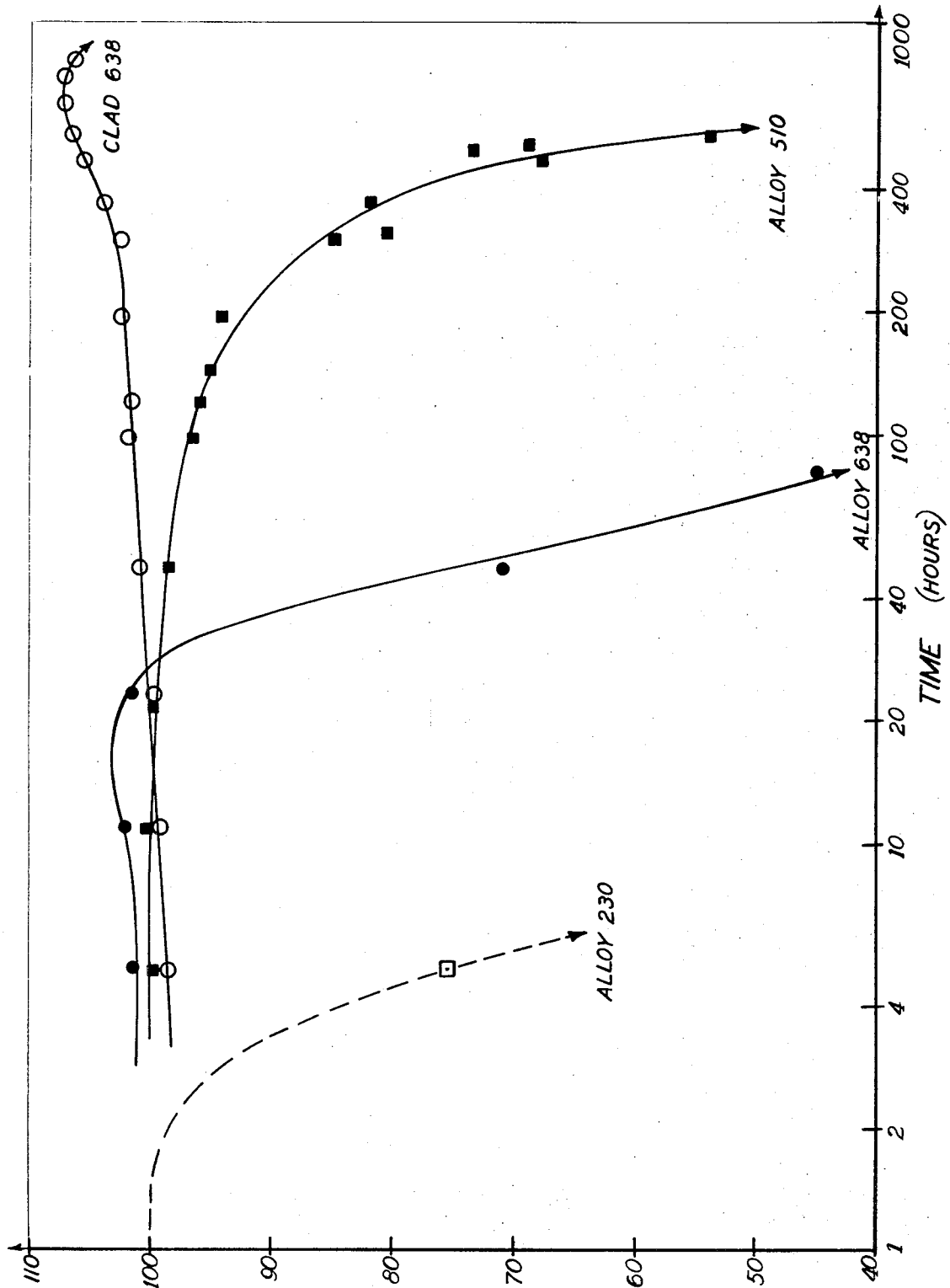
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[57] **ABSTRACT**

The disclosure teaches a novel, composite copper alloy having good stress corrosion resistance. The composite has a copper alloy core containing from 2 to 12 percent by weight aluminum, balance essentially copper, clad with copper or a high copper alloy containing at last 95 percent copper.

**6 Claims, 3 Drawing Figures**



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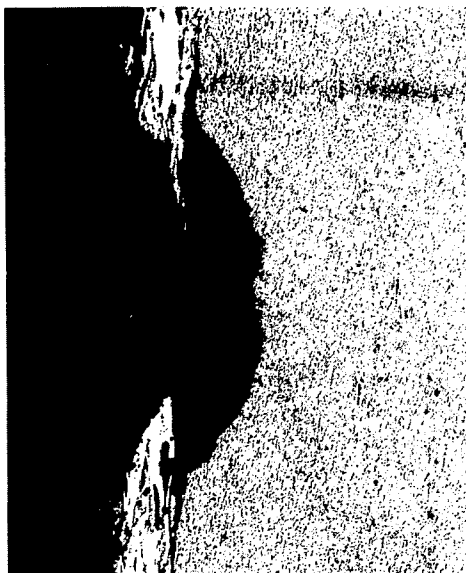


**FIG-3**

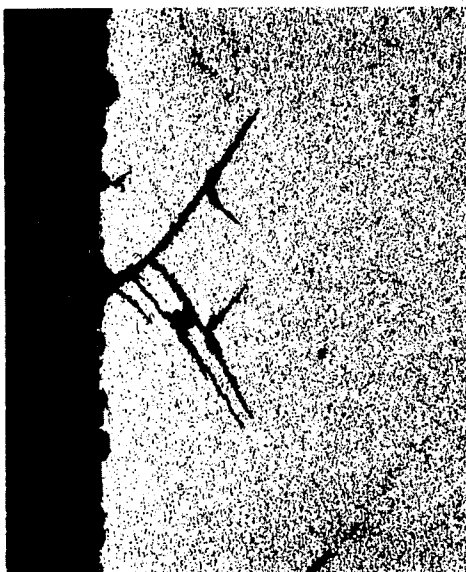


**FIG-2**

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## COMPOSITE COPPER ALLOY

### BACKGROUND OF THE INVENTION

Copper base alloys containing greater than about 2 percent by weight aluminum are characterized by moderate stress corrosion resistance.

Naturally, stress corrosion resistance is a highly desirable property and it is highly advantageous to improve the stress corrosion resistance of this class of materials.

By far the most commonly used and efficacious method of eliminating or reducing stress corrosion problems in copper base alloys consists of stress relief annealing. However, this procedure involves a further heat treatment of finished components and is, therefore, costly. In addition, of course, stress relief annealing is not effective in mitigating stress corrosion cracking resulting from the presence of applied, as opposed to residual, tensile stresses.

Accordingly, it is a principal object of the present invention to improve the stress corrosion resistance of aluminum-containing copper base alloys.

It is an additional object of the present invention to provide a novel composite based on aluminum-containing copper base alloys which has excellent stress corrosion resistance.

It is a further object of the present invention to provide a composite based on aluminum-containing copper base alloys which provides stress corrosion resistance without the necessity for stress relief annealing.

It is a still further object of the present invention to provide a composite having good stress corrosion resistance in the presence of both residual and applied tensile stresses.

Further objects and advantages of the present invention will appear from the ensuing specification.

### SUMMARY OF THE INVENTION

In accordance with the present invention the foregoing objects may be readily achieved.

The composite of the present invention consists essentially of a copper alloy core containing from 2 to 12 percent by weight aluminum, balance essentially copper, clad with a dissimilar high copper containing material containing at least 95 percent copper.

The composite of the present invention is characterized by many desirable advantages. The composite has excellent stress corrosion resistance in the presence of both residual and applied tensile stresses. In addition, the composite is characterized by good mechanical properties and electrical conductivity.

### BRIEF DESCRIPTION OF THE DRAWINGS

In the drawings which form a part of the present specification:

FIG. 1 is a graph showing the overall stress corrosion resistance of copper materials. The curve shows loss of springback of a U-bend specimen as a function of time of exposure to moist ammonia vapor. Fracture by stress corrosion cracking is complete when there is complete loss of springback;

FIG. 2 is a photomicrograph at a magnification of 250X showing the stress corrosion cracking of a copper-aluminum alloy; and

FIG. 3 is a photomicrograph at a magnification of 250X showing the composite of the present invention after extensive exposure to a highly stress corrosive atmosphere.

The drawings will be discussed in more detail in the examples which form a part of the present specification.

### DETAILED DESCRIPTION

As indicated hereinabove, the composite of the present invention is characterized by excellent stress corrosion resistance without the necessity of stress relief annealing, both in the presence of residual and applied tensile stresses. This is achieved at the cost of only a slight sacrifice in mechanical properties. The significant performance and improvement achieved by the composite of the present invention with respect to stress corrosion resistance is believed to be sufficient to eliminate completely most of the stress corrosion problems that are encountered in practice or service with copper-aluminum alloys.

The stress corrosion improvement of the composite of the present invention is due in part to the cladding with a relatively immune, aluminum-free copper or high copper alloy. Virtually all copper and copper base alloys can be made to show at least some degree of stress corrosion cracking susceptibility in ammoniacal environments. This is in large part due to an electrochemical process. It may be greatly accelerated by the application of anodic potentials and greatly retarded or even prevented by the application of cathodic potentials. Copper and high copper alloys are essentially equipotential with copper base alloys containing greater than about 2 percent aluminum. Despite this, it is a very surprising feature of the present invention that cladding a high copper alloy onto a copper-aluminum alloy results in improvement in the stress corrosion resistance of the composite. The pattern of attack at very long times of corrosion suggests that the high copper alloy is behaving as an anodic member of the galvanic couple in spite of the contrary information provided by potential measurements.

It should be noted that the composite specimens tested for stress corrosion resistance in the examples which form a part of the present specification were originally milled from clad sheet materials. Hence, the edges of the specimens were thus originally devoid of cladding.

The composite of the present invention has a core of a copper alloy containing 2 to 12 percent by weight aluminum, balance essentially copper, clad with a high copper containing material containing at least 95 percent.

Naturally, depending upon the particular application desired, the composite of the present invention may be clad on one or both sides. In the composite, each cladding layer represents from 2 to 20 percent of the total thickness of the composite, i.e., the cladding thickness is from 2 to 20 percent of the total composite thickness per side.

The core may contain from 2 to 12 percent by weight aluminum and preferably from 2.5 to 4 percent by weight aluminum. Naturally, the copper-aluminum alloy core may contain other materials depending upon the particular alloy which is used for the core. For ex-

ample, the alloy may contain one or more of the following: zinc in an amount up to 30 percent, cobalt up to 2 percent, iron up to 5 percent, manganese up to 15 percent, silicon up to 3 percent, nickel up to 10 percent, arsenic up to 0.5 percent plus conventional impurities. Zinc, cobalt and silicon are particularly preferred alloying additions. Naturally, amounts as low as 0.001 percent of any of the foregoing may be present.

The cladding may be any high copper containing material having at least 95 percent copper. For example, commercial purity copper, oxygen-free copper, electrolytic tough pitch copper, and high copper alloys containing one or more of the following materials, silver up to 1 percent, cadmium up to 1.5 percent, chromium up to 1.5 percent, iron up to 3 percent, zirconium up to 1 percent, and phosphorus up to 0.2 percent. Naturally, amounts as low as 0.001 percent of any of the foregoing may be present. Others should be present in total less than 1 percent.

The components of the composite may be clad together by any desired means known in the art. For example, the components may be rolled in accordance with the procedure described in U.S. Pat. No. 3,397,045. The only processing requirement is that a firm, metallurgical bond be present between the components.

As indicated hereinabove, the core is preferably clad on both sides. This is particularly advantageous from a standpoint of higher electrical and thermal conductivity.

The composite of the present invention is particularly suitable for many applications, for example, springs and terminals.

The present invention will be more readily apparent from a consideration of the following illustrative examples.

### EXAMPLE I

Two composites were metallurgically bonded by rolling together three sheets, with a copper-aluminum alloy being the core and with a high copper alloy being clad on both sides. In both cases the cladding material was copper alloy 110 which is electrolytic tough pitch copper containing about 99.9 percent copper. In one case the core material was copper alloy 638 which is a copper alloy containing 2.8 percent aluminum, 1.8 percent silicon, and 0.4 percent cobalt, balance essentially copper. In the second case the core material was copper alloy 688 which is a copper alloy containing 21.5 percent zinc, 3.4 percent aluminum and 0.5 percent cobalt, balance essentially copper. The thickness of both composites was 0.030 inch, with a ratio of 80 percent of the thickness being the core material clad on both sides with 10 percent of the cladding material on each side.

The stress corrosion resistance of these composites was compared to that of the following alloys.

- A. C.D.A. Alloy 230 — which is red brass containing about 85 percent copper, 0.05 percent lead, 0.05 percent iron, balance essentially zinc.
- B. C.D.A. Alloy 510 — which is phosphor bronze containing about 0.05 percent lead, 0.10 percent iron, 5 percent tin, 0.30 percent zinc, 0.3 percent phosphorus, balance copper.
- C. C.D.A. Alloy 638 — the composition of which is given hereinabove.

D. C.D.A. Alloy 688 — the composition of which is given hereinabove.

E. C.D.A. Alloy 260 — which is cartridge brass containing about 70 percent copper, about 0.07 percent lead, about 0.05 percent iron, balance zinc.

The longitudinal mechanical properties of the materials evaluated are shown in Table I below. All of the alloys and the composites were tested in the 50 percent cold rolled condition using triplicate 6 inch  $\times$  1/4 inch longitudinal U-bend specimens milled from 0.030 inch gage sheet materials. Moist ammonia vapor was used as the test environment. The springback of the U-bends was measured with time for each of the materials evaluated. Conventionally, the percentage loss of springback, corrected for creep relaxation, is used as a measure of stress corrosion crack propagation. Curves of percent corrected springback with time, during exposure to moist ammonia vapor, are shown in FIG. 1 for some of the materials evaluated. The stress corrosion life or mean time-to-failure,  $t_f$ , of U-bend specimens on exposure to moist ammonia vapor are shown in Table I.

The data shown in Table I and FIG. 1 show clearly that the composites of the present invention have greatly improved overall stress corrosion resistance, i.e., as regards both the crack growth rate and the total time to failure. Also, bare 50 percent cold rolled alloy 638 has mechanical properties somewhat superior to those of 50 percent cold rolled alloy 510; but has markedly inferior stress corrosion resistance. On the other hand, the composite of the present invention has mechanical properties directly competitive with those of 50 percent cold rolled alloy 510 and at the same time has significantly better stress corrosion resistance. Cladding of alloy 688 similarly results in a very significant improvement in stress corrosion resistance with only a slight concomitant decrease in mechanical properties. Improvement in resistance to pitting in saline environment was also observed for both composites.

TABLE I

#### Mechanical Properties

| Material  | Yield Strength (ksi) | Ultimate Tensile Strength (ksi) | Percent Elongation | Mean Stress Corrosion Life (Hrs.) |
|-----------|----------------------|---------------------------------|--------------------|-----------------------------------|
| Alloy 638 | 111                  | 121                             | 3.7                | 70                                |
| Clad 638  | 99.5                 | 110                             | 3.5                | >800                              |
| Alloy 688 | 93.0                 | 117                             | 2.0                | 2                                 |
| Clad 688  | 85.0                 | 104                             | 2.0                | 230                               |
| Alloy 510 | 101                  | 103                             | 3.4                | 650                               |
| Alloy 230 | 72.0                 | 75.4                            | 2.7                | 7                                 |
| Alloy 260 | 76.2                 | 96.2                            | 2.0                | 2                                 |

### EXAMPLE II

This example describes the photomicrographs which are FIGS. 2 and 3 of the present invention. FIG. 2 illustrates the stress corrosion cracks observed in a bare alloy 638 U-bend specimen after failure in moist ammonia vapor. The section is through the center of the apex of the U-bend, polished, etched in  $K_2Cr_2O_7/HCl$  and photographed at 250X. This particular material failed in about 95 hours.

FIG. 3 illustrates a section through the center of the apex of a composite of the present invention showing alloy 110 clad on alloy 638 as described in Example I. The material is shown after about 800 hours exposure

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to moist ammonia vapor. The material is shown in the center of the apex of the U-bend, polished and etched as FIG. 2 and photographed at 250X.

Note that in FIG. 3, although the protective alloy 110 cladding layer has been penetrated by the corrosive environment by a pitting mechanism, the underlying alloy 638 substrate is apparently galvanically protected and has not suffered stress corrosion cracking.

This invention may be embodied in other forms or carried out in other ways without departing from the spirit or essential characteristics thereof. The present embodiment is therefore to be considered as in all respects illustrative and not restrictive, the scope of the invention being indicated by the appended claims, and all changes which come within the meaning and range of equivalency are intended to be embraced therein.

What is claimed is:

1. A composite sheet having good stress corrosion resistance consisting essentially of a copper base alloy core containing 2 to 12 percent by weight aluminum, balance essentially copper, clad with a dissimilar high copper containing material containing at least 95 percent copper, wherein said cladding represents from 2 to 20 percent of the thickness of the composite.

2. A composite according to claim 1 wherein said

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cladding is clad on both sides of the core, with each cladding layer representing from 2 to 20 percent of the thickness of the composite.

3. A composite according to claim 1 wherein the core contains at least one material selected from the group consisting of zinc up to 30 percent, cobalt up to 2 percent, iron up to 5 percent, manganese up to 15 percent, silicon up to 3 percent, nickel up to 10 percent, and arsenic up to 0.5 percent.

4. A composite according to claim 1 wherein the cladding contains at least one material selected from the group consisting of silver up to 1 percent, cadmium up to 1.5 percent, chromium up to 1.5 percent, iron up to 3 percent, zirconium up to 1 percent and phosphorus up to 0.2 percent, others in total less than 1 percent.

5. A composite according to claim 4 wherein said cladding is clad on both sides of the core, with each cladding layer representing from 2 to 20 percent of the thickness of the composite and wherein said core contains at least one material selected from the group consisting of zinc up to 30 percent, cobalt up to 2 percent and silicon up to 3 percent.

6. A composite according to claim 2 wherein said cladding is electrolytic tough pitch copper.

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