

- [54] **COPPER BASE ALLOYS**
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75/159, 148/12.7, 148/32, 148/160
- [51] Int. Cl. **C22c 9/06, C22f 1/08**
- [58] Field of Search. **75/153, 157.5, 159;**
148/12.7, 32, 32.5, 160

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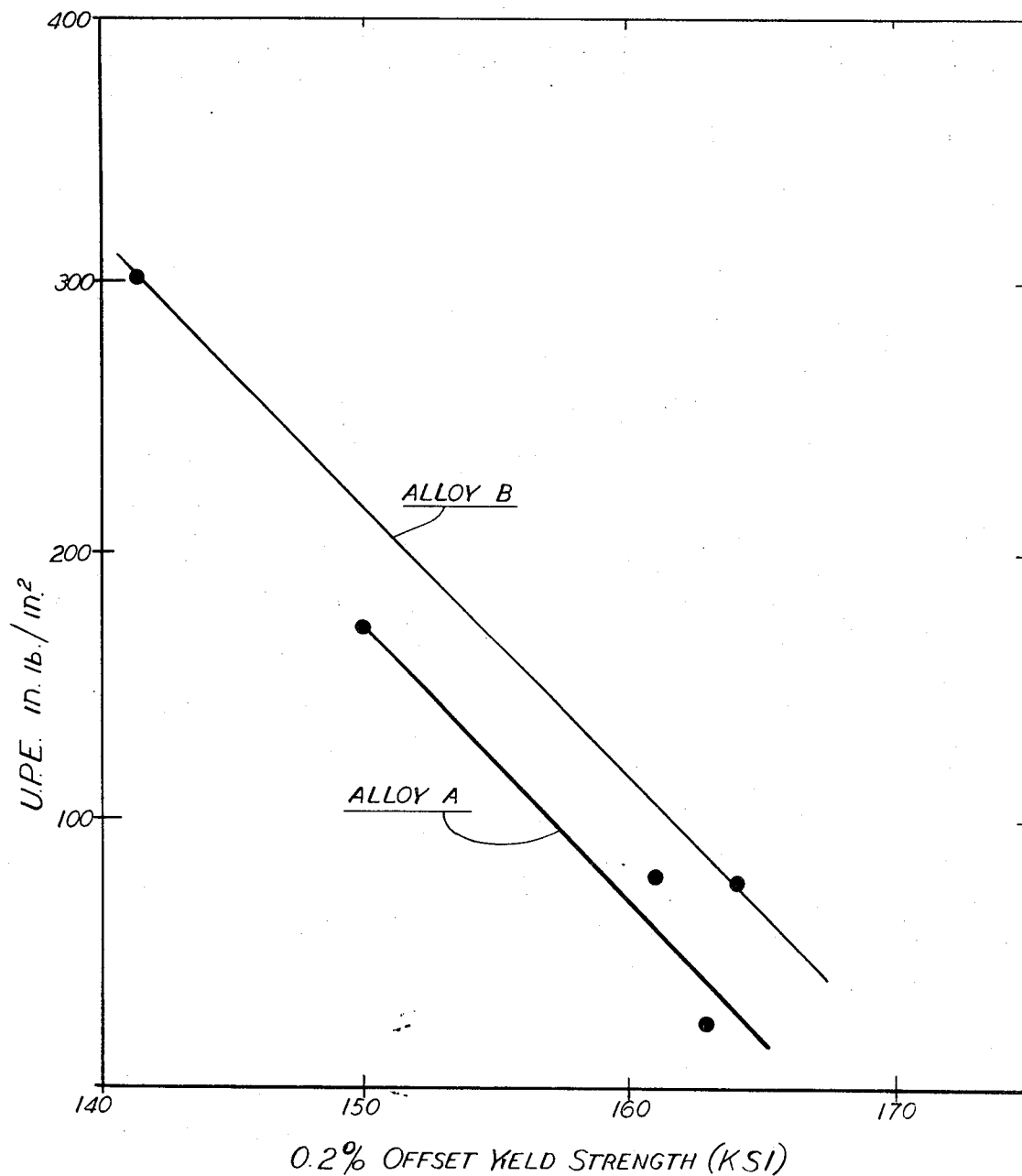
[57] **ABSTRACT**

The disclosure teaches novel copper base alloys having improved toughness and stress corrosion resistance. The copper alloys contain from 12.5 to 30 percent nickel, from 12.5 to 30 percent manganese, a material selected from the group consisting of aluminum from 0.01 to 5 percent, boron from 0.001 to 0.1 percent, magnesium from 0.01 to 5 percent and mixtures thereof and a material selected from the group consisting of zirconium, from 0.01 to 2.0 percent, titanium, from 0.01 to 2 percent, and mixtures thereof.

8 Claims, 1 Drawing Figure

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COPPER BASE ALLOYS

BACKGROUND OF THE INVENTION

Copper base alloys are known which contain relatively large amounts of nickel and manganese. Alloys of this type are highly desirable since they are capable of obtaining yield strengths in excess of 200 ksi upon aging. In addition, these alloys appear to have reasonable processing and in particular are not quench sensitive.

The presence of a marked aging response to obtain high strengths in copper-nickel-manganese alloys is known. It has been found that different types of precipitation reactions may occur in this alloy system, depending on the aging temperature. For example, aging at a low temperature, such as 350°C., yields a cellular precipitate which nucleates at the grain boundaries and with time grows throughout the entire grain. The cellular precipitate consists of adjacent lamellae of a manganese-nickel rich phase and the copper-rich solid solution. Aging at higher temperatures, such as 450°C., yields mainly finely dispersed, spherical precipitates of the manganese-nickel rich phase within the grains and only a small amount of the cellular precipitate at the grain boundaries.

However, in any event, the presence of a cellular precipitate at grain boundaries is generally found to have deleterious effects on alloy properties, such as fracture toughness and stress corrosion resistance. This is indeed found to be the case in these alloys and is a significant factor in the limited commercial success which these alloys have enjoyed.

It would be highly desirable to develop an alloy within the copper-manganese-nickel alloy system which has increased fracture toughness. It would also be highly desirable to improve the stress corrosion resistance of such alloys.

Accordingly, it is a principal object of the present invention to develop a copper base alloy containing relatively large amounts of nickel and manganese.

It is an additional object of the present invention to develop an alloy as aforesaid which is capable of obtaining yield strengths in excess of 200 ksi upon aging.

It is a still further object of the present invention to develop an alloy as aforesaid which is readily processed commercially and which is characterized by improved fracture toughness.

It is a still further object of the present invention to provide a copper base alloy with good stress corrosion resistance, good ductility, toughness and excellent yield strength characteristics.

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

SUMMARY OF THE INVENTION

In accordance with the present invention, it has now been found that the foregoing objects and advantages may be readily obtained.

The alloy of the present invention consists essentially of from 12.5 to 30 percent nickel, from 12.5 to 30 percent manganese, a material selected from the group consisting of zirconium from 0.01 to 2 percent, titanium from 0.01 to 2 percent and mixtures thereof, and a material selected from the group consisting of aluminum from 0.01 to 5 percent, magnesium from 0.01 to 5 percent, boron from 0.001 to 0.1 percent and mixtures thereof, balance essentially copper, wherein the

nickel to manganese ratio is at least 0.75 and preferably 1.0 or higher.

BRIEF DESCRIPTION OF DRAWINGS

The drawing which forms a part of the present specification is a graph plotting the fracture toughness as a function of yield strength for the alloy of the present invention (Alloy B) and a comparative alloy (Alloy A).

DETAILED DESCRIPTION

In accordance with the present invention, the foregoing alloy has been found to obtain surprisingly improved fracture toughness while retaining the excellent strength characteristics of this alloy system.

This enables the attainment of several significant advantages. The alloy of the present invention is an excellent lower priced replacement for beryllium-copper, with increased fracture toughness. The alloy of the present invention achieves levels of fracture toughness approaching high alloy steels which are limited in applicability by poor corrosion resistance. The alloys of the present invention are superior to maraging steels in marine environments since the alloys of the present invention are not susceptible to hydrogen embrittlement. In addition, the alloys of the present invention are characterized by excellent stress corrosion resistance.

In accordance with the present invention, the instant alloys contain from 12.5 to 30 percent nickel, and from 12.5 to 30 percent manganese. Preferably, both the nickel and manganese contents should range from 15 to 25 percent. The nickel to manganese ratio must be at least 0.75 and preferably 1.0 or higher.

The nickel and manganese contents have an affect on aging response, yield strength and workability of the alloys. The lower the manganese and nickel content, the slower the aging response and lower the maximum yield strength obtainable upon aging, especially below 12.5 percent nickel and manganese. On the other hand, increasing the amount of nickel and manganese has deleterious effects on the workability of the alloys during processing especially over 30 percent each of nickel and manganese.

As indicated hereinabove, the preferred nickel to manganese ratio is 1.0 or higher. The maximum aging response is obtained for a given amount of nickel and manganese when the nickel to manganese ratio is about 1.0. If the ratio is less than 1.0, an excess of manganese exists which can have adverse effects on the stress corrosion resistance of the alloy. A ratio greater than about 1.5 does not give improved results over a ratio of about 1.0 and is more expensive due to the high cost of the nickel.

In addition to the foregoing, the alloy of the present invention contains a material selected from the group consisting of aluminum in an amount from 0.01 to 5.0 percent, magnesium from 0.01 to 5.0 percent, boron from 0.001 to 0.1 percent and mixtures thereof. Each of these elements act as deoxidizers and assist in the melting of the alloys. Aluminum is the preferred addition since it tends to form a protective oxide coating during melting. When aluminum is used as a deoxidant only, the aluminum should be added in an amount from 0.01 to 0.75 percent. Similarly, magnesium should be used in an amount from 0.01 to 0.75 percent as a deoxidant. In addition, the aluminum and magnesium may be used as advantageous alloying additions in amounts greater than 0.6 percent for increased corrosion resis-

tance and fracture toughness. The aluminum when used at the higher levels, also tends to modify the cellular precipitate at the grain boundaries.

The zirconium and/or titanium are particularly important alloying additions in amounts 0.01 to 2.0 percent each, and preferably from 0.15 to 0.30 percent each. These materials tend to desirably change morphology and chemistry of inclusions and desirably change morphology of cellular precipitate at grain boundaries.

In addition to the foregoing, several additives are particularly advantageous. A zinc component may be present in an amount from 0.1 to 3.5 percent and preferably 1 to 3 percent. Increased amounts of zinc give rise to a decrease in the stress corrosion resistance and fracture toughness.

The zinc addition controls the grain size, reduces the cellular precipitate at the grain boundaries, changes the morphology of the inclusions, promotes sound castings and increases the aging response of the alloy.

Tin is a particularly desirable additive in an amount from 0.1 to 2 percent and preferably from 0.5 to 1.0 percent. Tin tends to alter the morphology of the cellular precipitate at the grain boundary.

In addition, chromium is a desirable addition in an amount from 0.01 to 1.0 percent, and preferably from 0.15 to 0.30 percent. Chromium tends to control the grain size and change the morphology and chemistry of inclusions.

Additional desirable alloying additions are cobalt and/or iron in amounts from 0.05 to 1.0 percent each, and preferably from 0.2 to 0.5 percent each. These materials also tend to control the grain size.

Naturally, other additives may be desirable in order to achieve or accentuate a particular property and conventional impurities may be tolerated.

The casting of the alloy of the present invention is not particularly significant. Any convenient method of casting may be employed. Pouring temperatures in the range of about 1000° to 1200°C. are preferably employed with an optimum pouring temperature in the range of 1050° to 1100°C.

Generally, the alloy of the present invention is processed by breakdown of ingot into strip using a hot rolling operation followed by cold rolling and annealing cycles to reach final gage. Preferred properties are obtained using an aging treatment.

It is preferred that the starting hot rolling temperature be in the range of 700° to 900°C., and preferably 780° to 900°C. The cooling rate from hot rolling should preferably be in excess of 25°C. per hour down to 300°C. in order to avoid precipitation of manganese-nickel rich phases. The alloy is capable of cold rolling reductions in excess of 90 percent, but the cold rolling reduction should preferably be between 30 and 80 percent in order to control the grain size.

It has been found that an average grain size less than 0.015 mm gives the optimum fracture toughness. An average grain size of this order can be obtained by control of the cold rolling reduction, annealing times and annealing temperatures. In general, annealing temperatures in the range of 550° to 900°C. for times from one minute to 10 hours can give the required grain size.

After annealing, the material is cooled in excess of 25°C. per hour down to 300°C., as indicated above, and the cold rolling and annealing cycles repeated as desired depending on gage requirements.

The alloy of the present invention, as previously stated, may be aged in the range of 250° to 475°C., with temperatures of 380° to 460°C. being preferred. Aging times of 30 minutes to 10 hours, with preferred times of one to six hours, are used to obtain the desired properties. In addition, it has been found that controlling the amount of cold work prior to aging has an effect on fracture toughness and aging response. In particular, it has been observed that the cold work gives rise to increased nucleation sites for the intragranular precipitation of the discrete manganese-nickel rich particles. Hence, cold working of the alloys prior to aging at the higher temperatures of the aging range increases the aging response and decreases the amount of cellular precipitate. The amount of cold rolling can vary from 10 to 50 percent, with from 15 to 45 percent yielding the optimum fracture toughness.

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

EXAMPLE I

The Durville method was used to cast the two alloys listed in Table I. The copper and nickel were melted under a charcoal cover. Aluminum was added to deoxidize the melt. Following the removal of the charcoal cover, the zirconium and manganese additions were made. The slag was removed and the melt was poured from approximately 1080°C.

TABLE I

Composition — Weight %

Alloy	Nickel	Manganese	Aluminum	Zirconium	Copper
A	19.72	19.92	0.36	—	Substantially balance
B	20.00	20.00	0.50	0.25	Substantially balance

EXAMPLE II

The alloys prepared in Example I were processed in the following manner. Both alloys were homogenized at 840°C. for about two hours. The alloys were hot rolled from 1.500 inches to 0.418 inches and water quenched. The alloys were cold rolled 60 percent to 0.167 inches. Both alloys were annealed at 600°C. for about 30 minutes. After a water quench, the alloys were cold rolled 60 percent to 0.067 inches and annealed. Subsequent to the water quench, the alloys were cold rolled 25 percent to 0.050 inches and aged at 450°C. for various times. The resultant properties were determined after various aging times. The properties transverse to the rolling direction are presented in Table II. The term "UPE" is a relative value of the fracture toughness determined by the Kahn Tear Test. The average grain diameter of the alloys tested was 0.005 to 0.010 mm.

TABLE II

Transverse Properties

Alloy	Aging Time at 450° C., Hours	Yield Strength 0.2% Offset ksi	UPE in.lb./in. ³
A	2.5	150	172
A	3.0	161	80
A	3.5	163	25
B	2.0	141.5	302
B	3.0	164.0	77

The zirconium addition shifts the unit propagation versus yield strength relation to higher values without

significantly changing the slope. FIG. 1 clearly shows the improved properties of Alloy B, the alloy of the present invention. This permits an increase in the yield strength at which the alloy can be used.

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 wrought copper base alloy having improved toughness and stress corrosion resistance consisting essentially of from 12.5 to 30 percent nickel, from 12.5 to 30 percent manganese, a material selected from the group consisting of zirconium from 0.01 to 2 percent, titanium from 0.01 to 2 percent and mixtures thereof, and a material selected from the group consisting of aluminum from 0.01 to 5 percent, magnesium from 0.1 to 5 percent, boron from 0.001 to 0.1 percent and mixtures thereof, balance essentially copper, wherein the nickel to manganese ratio is from 0.75 to 1.5, said alloy

having an average grain size less than 0.015 mm. and an intragranular precipitation of discrete manganese-nickel rich particles.

2. An alloy according to claim 1 wherein the nickel content is from 15 to 25 percent and the manganese content is from 15 to 25 percent.

3. An alloy according to claim 1 wherein said material is aluminum in an amount from 0.6 to 5 percent.

4. An alloy according to claim 1 wherein said material is magnesium in an amount from 0.6 to 5 percent.

5. An alloy according to claim 1 wherein said material is aluminum in an amount from 0.01 to 0.75 percent.

6. An alloy according to claim 1 wherein said material is magnesium in an amount from 0.01 to 0.75 percent.

7. An alloy according to claim 1 wherein the zirconium and titanium contents are from 0.15 to 0.30 percent.

8. An alloy according to claim 1 containing a material selected from the group consisting of iron from 0.05 to 1 percent, cobalt from 0.05 to 1 percent and mixtures thereof.

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,772,094

Dated November 13, 1973

Inventor(s) Stanley Shapiro et al.

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

In Column 1, line 40, correct the spelling of the word "manganese";

In Column 1, lines 64 and 65, correct the spelling of the word "aluminum".

In Column 5, line 21, Claim 1, "0.1" should read "0.01".

Signed and sealed this 11th day of June 1974.

(SEAL)

Attest:

EDWARD M. FLETCHER, JR.
Attesting Officer

C. MARSHALL DANN
Commissioner of Patents