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MANGANESE-BASE ALLOYS

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2 Claims. (Cl. 75—134)

The invention relates to alloys containing a large proportion of manganese, and has for one of its principal objects the provision of manganese alloys which may be cold-worked. Another object is to provide a method of making and treating such alloys to improve their amenability to cold-working.

It is known that electrolytically refined gamma manganese remains in that state for several weeks, and that during such time it may be cold-worked. But in time the gamma manganese alters to the brittle alpha form, and it has heretofore been impossible to obtain by thermal treatment forms of manganese or high-manganese alloys that are stably ductile at room temperatures.

I have observed that pure manganese obtained by distillation may be hot rolled at temperatures above the alpha-beta transformation point, the best results being obtained in the neighborhood of the gamma transformation point; but when quenched it passes over immediately to the brittle alpha state.

The present invention is based on the discovery that the above-described conversion of ductile manganese to the brittle form may be to a great extent prevented by means of certain alloying additions which act to inhibit such conversion, and that when suitable thermal treatment is employed, the resulting alloys may be kept in a ductile condition at room temperature.

The alloying addition producing the most favorable results is copper in a proportion of about 1% to 60%, preferably between 10% and 35%, of the alloy.

In order to obtain the maximum freedom from brittleness, it is important when making the alloys to protect the molten metal from the nitrogen and oxygen of the air. This may be done by the use of protective fluxes, e. g. slags containing manganese chloride, manganese oxide and alkaline earth metal halides; or by the use of a protective atmosphere, for instance hydrogen, methane, and the rare permanent gases such as argon or helium; or by the use of a partial vacuum, if it be not carried to such a point as to vaporize manganese too rapidly; or by a combination of two or three of these measures. Alumina crucibles may be used in preparing the alloy.

The hot rolling of the alloys of the invention must be conducted entirely above the beta-alpha transformation temperature, and preferably is commenced while the alloy is in the gamma form. Otherwise, the metal tends to be red-short or

cold-short. The beta-alpha point is about 740° C. in the case of the manganese-copper alloys. Further alloying additions may change the transformation point upwards or downwards.

Moreover, the cast ingots (particularly in heavy sections) should not be permitted to cool below the beta-alpha transformation temperature before rolling. While the brittle as-cast structure is still present, cooling to room temperature and reheating to rolling temperature will cause cracks and red-shortness.

According to the invention, the cast ingots, still hot, are hot rolled in the gamma-beta regions until the grain has been broken down. The thinner cross sections may then be rapidly cooled, thereby avoiding embrittlement. Thus, for example, ingots 50 mm.² of a manganese alloy containing 15% or more copper are rolled at 950° C. into sheets 2 mm. thick which may then be air cooled.

Cold working may be done within wide limits, intermediate anneals being effected by rapid heating to within the beta or gamma field, followed by quenching.

Although the manganese-copper alloys are relatively stable, they nevertheless tend to become brittle when heated to certain moderately elevated temperatures within the alpha field. For instance, the 5% copper, 95% manganese alloy becomes brittle after two hours heating at 200° C., whereas the 15% copper, 85% manganese alloy becomes brittle in the same time at 500° C. The 35% iron, 65% manganese alloy can stand up to 450° C. The transformation causing embrittlement requires a certain time at the critical temperature, therefore no brittleness appears when the alloy passes rapidly through the critical temperature range, and it is possible so to control the embrittlement as to exploit it for the purpose of increasing the hardness and strength of the alloy. Thus, a binary manganese-copper alloy containing 15% copper was rolled at 900° C. and quenched. The tensile strength of the rolled and quenched sheets, 0.75 mm. thick, was 40.3 kg./mm.² with an elongation of 34.5% and a Brinell hardness of 111. By reheating the sheets at 500° C. for five minutes the strength was increased to 50 kg./mm.² with an elongation of 6%. A 5% copper alloy after rolling and quenching from 1000° C. had a tensile strength of 55.2 kg./mm.², an elongation of 8% and a Brinell hardness of 124.

The stability of the manganese-copper alloys may be further increased by the addition of nickel in a proportion of 0.5% to 25%. With

suitable proportions of nickel and copper, preferably within the range of 0.5% to 10% nickel and 5% to 40% copper, the tendency to become embrittled at moderately elevated temperatures within the alpha field is suppressed or may be substantially eliminated. For example, an alloy containing 6.9% Ni, 5.1% Cu, rest Mn, is substantially entirely stable, and after working and quenching from 950° C. has a tensile strength of 39.9 kg./mm.² with 20% elongation and a Brinell hardness of 105. In general, the alloys containing the higher percentages of copper tolerate the higher nickel additions.

Aluminum, suitably in an amount between 0.1% and 10%, serves to deoxidize the alloys of the invention, thereby improving their workability. Furthermore, aluminum protects the alloy against oxidation at high temperatures and during melting and casting it forms a superficial film of oxide which hinders oxidation and nitrogen pick-up. It promotes the existence of a surface favorable for rolling. The aluminum-containing alloys may advantageously be made from manganese produced by aluminothermic reduction.

Zinc may also be added in a proportion up to 20%, the copper preferably being correspondingly reduced. A more narrowly circumscribed limit for such alloys is between 5% and 35% copper and 1% to 8% zinc. For instance, an alloy containing 10% Cu, 5% Zn, rest Mn, after rolling and quenching from 1050° C. and subsequent cold working, had a tensile strength of 47.7 kg./mm.² with 13.1% elongation and a Brinell hardness of 131.

Other metals may be present, as one or more of iron, cobalt, tungsten, or chromium, in a total percentage up to 5% but preferably not over about 2%. In general, the elements Si, Sn, Ti, Ta, Mo, Ag, Ce, Mg, and Be appear to be injurious and should ordinarily not exceed 0.5% Si, 1% Sn, 2% Ti, 5% Ta, 2% Mo, 2% Ag, 2% Ce, 1% Mg, or 0.5% Be. Calcium, lithium, or thorium may be used in a proportion of 1% or more as a deoxidizer. The alloys containing the higher percentages of copper or of copper and nickel will tolerate the higher amounts of such other metals. It is preferred that the silicon content be less than 0.15%.

The alloys of the invention preferably contain less than 0.2% carbon and should usually contain less than 0.05% of this element, although somewhat higher carbon contents will on occasion be permissible. It is also preferred that the manganese content be at least 50%, although on occasion it may be as low as 40%.

The resistance of the alloys of the invention to corrosion by moist air is about the same as that of pure copper. Scaling accompanied by peeling is noticeable only above 600° C. in the case of the lower copper alloys and only about 700° C. in the case of the higher copper alloys.

The alloys containing over 30% copper may easily be soldered with either soft or hard solder. Those with less than 30% copper are soldered with some difficulty.

The alloys of the invention have a particularly high electrical resistivity, generally between about 1.2 and 2 ohm/m./mm.². For instance, the binary manganese-copper alloy containing 40% copper has a resistivity slightly more than 2 ohm/m./mm.². The binary alloys harden by quenching and annealing with at first a decrease

in electrical resistivity; upon continued annealing, the resistivity again rises. The stable manganese-copper-nickel alloys, are particularly useful as resistance alloys. For example, an alloy containing about 37% copper, 8% nickel, rest manganese, has an electrical resistivity of about 1.8 ohm/m./mm.², three times that of commercial resistance-wires of copper-base alloys; while an alloy containing 5% copper, 8% nickel, rest manganese, has a resistivity of 1.35 ohm/m./mm.².

The highest resistivities are obtained in the range of 30% to 55% copper, and the addition of 6% to 8% nickel is sufficient to stabilize the alloy.

If the alloy is to be used at temperatures below 100° C., the nickel content may be as low as 0.5% or be eliminated entirely. If desired, the nickel content may be raised as high as 20%. Nickel only slightly affects the resistivity, the latter being determined chiefly by the solid solution of manganese and copper.

Within the range of 25% to 55% copper, 0% to 15% nickel, rest manganese, the temperature coefficient of electrical resistivity is low, e. g. $\alpha = 0.0003$ for an alloy containing 50% manganese and 50% copper. The higher-manganese alloys have a relatively high temperature coefficient, for instance, $\alpha = 0.03$ for an alloy containing 95% manganese and 5% copper. Nickel does not have any pronounced effect on the temperature coefficient of electrical resistivity.

The alloys of the invention also have an unusually high coefficient of expansion, and are accordingly useful as thermoregulator elements. If such elements are to be used at elevated temperatures, the stable ternary manganese-copper-nickel alloys containing about 4% to 20%, preferably 5% to 12%, nickel are most suitable.

An alloy containing 5% copper and 8% nickel, rest manganese, has an average coefficient of expansion of $\alpha = 390 \times 10^{-7}$, an electrical resistance of about 1.3 ohm/m./mm.², a Brinell hardness of about 150, and a melting point at about 1100° C. The temperature-expansion curve is almost straight, is without breaks, and is reproducible as often as desired.

An alloy containing 37% copper and 8% nickel, rest manganese has a coefficient of expansion of $\alpha = 290 \times 10^{-7}$ and an electrical resistance of more than 1.8 ohm/m./mm.².

Bimetallic elements may be formed by fastening a strip of metal having a low thermal expansion, e. g. an iron-nickel alloy of the "Invar" type, or an iron-nickel-cobalt alloy of the "Kovar" type, of the alloy of the invention, as by casting, soldering, or welding.

It is to be understood that the several specific compositions described herein are examples illustrative of the invention, and that the invention is not limited to or by such examples. This application is a division of my application Serial Number 314,229, filed January 17, 1940.

I claim:

1. Alloy composed of manganese, copper, nickel and aluminum, the aluminum being between 0.1% and 10%, the nickel being between 0.5% and 10%, and the copper being between 1% and 35%, the remainder being manganese, the manganese percentage being at least 50%.

2. Alloy composed of between 0.1% and 10% aluminum, between 5% and 25% copper, more than 0.5% but less than 10% nickel, remainder substantially all manganese.

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