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COPPER ALLOY AND PROCESS OF PRODUCING AND TREATING THE SAME.

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The invention relates to the production of hard and strong alloys containing high percentages of copper. It comprises the application of certain processes of heat-treatment to copper or copper alloys in which certain chemical elements are present in regulated and preferably small amount; and as applied to materials in which such elements are not already present in suitable quantity, it comprises their preliminary addition to impart the ability to assume a hard and strong condition upon suitable heat treatment. The primary object of the invention is to increase the strength and hardness of the material treated, but in some cases another important object is to preserve or improve certain other properties of the material. For example it may be desired to preserve the normal color of the material to be hardened, or to increase its resistance to corrosion, or to impair as little as possible its ductility or electrical conductivity. The description will be confined for the most part to a discussion of the effect of the invention on hardness, but it will be understood that the hardening will be accompanied in general by an increase in strength, and that in some cases such increase is more important than the hardening.

I have found that copper and copper alloys containing suitable quantities of silicon and one or more of a group of metals referred to herein as "hardening metals" will assume a remarkably hard and strong condition if subjected to the heat treatment presently to be described. Experimental evidence as well as theoretical considerations indicate that the actual hardening effect is due to silicides of definite composition. Furthermore it is indicated that the silicides which are most effective as hardening agents are present in the hardened material as discrete particles which are invisible under the microscope, from which it is concluded that they are present as ultramicroscopic crystals. The hardening effect is ascribed, in consonance with a theory recently advanced by others, to the action of these hypothetical ultramicroscopic crystals in preventing the breaking down of the grains of the copper or copper alloy, the crystals serving to key together or interlock adjacent planes and thus reduce their tendency to slip one upon the other under the influence of externally applied stress.

The silicides which I have found to be most effective as hardening agents are those of chromium, cobalt, and nickel. The principal effect appears to be largely due to silicides in which about six weights of chromium, or about four weights of either cobalt or nickel, combine with one weight of silicon, corresponding approximately to the formulæ Cr_2Si, Co_2Si, and Ni_2Si.

By adding the foregoing elements in suitable proportions, and by suitable heat treatment, copper can be prepared in which silicide exists either almost solely as microscopic crystals, or almost solely in the form which I have assumed to be ultramicroscopic crystals; or both varieties of silicide may be present in varying quantities. Upon examination of the silicide-containing products it is found that the microscopic crystals have only a slight hardening effect whereas the other form of the silicide has a very much greater hardening effect. Accordingly the invention in its preferred embodiment and where maximum hardening is desired contemplates that the quantity of silicide present in the copper shall be such, and the heat treatment shall be so controlled, that a maximum quantity of the variety of silicide which is the most effective hardening agent shall be produced. It is preferred in some cases to add only so much of the components of the desired silicide as corresponds to the quantity of the silicide which it is possible to bring into the more effective form, hypothetically the ultramicroscopic crystalline form, and then to apply a heat treatment adapted to bring substantially all the silicide present into this form.

It will be understood that the invention is not dependent upon the correctness of the hypothesis that the effective hardening agent in material treated according to my invention is a silicide present as crystals of ultramicroscopic dimensions, but as a matter of convenience in describing the invention such crystals will be referred to throughout the description as though their existence had been actually demonstrated.

My researches indicate that the maximum quantity of silicide which can be brought

into the ultramicroscopic crystalline form in the metal is about 0.9% for the chromium silicide; about 2.0% for cobalt silicide; and about 7.5% for the nickel compound. There are certain minimum quantities of the silicides which appear to be necessary before any ultramicroscopic crystals can be formed, quantities of silicide less than these minima evidently remaining in solid solution despite heat treatment designed to precipitate them. The minima referred to are about 0.2% for chromium silicide; about 0.3% for cobalt silicide: and about 1.2% for nickel silicide.

The incorporation into the metal to be hardened of silicides in quantities in excess of those which can be brought into the ultramicroscopic crystalline state by heat treatment is not precluded. Such excess quantities tend to form microscopic crystals and these have a hardening action through as mentioned above they are much less effective than the smaller crystals. The microscopic crystals have a much stronger effect than the ultramicroscopic in diminishing ductility, and it will therefore often be desirable to exclude them or to limit their quantity.

The chromium, cobalt or nickel and the silicon are not necessarily incorporated in the exact proportions which have been indicated as producing the most effective hardening silicides. An excess of either one of the components of the silicide can be used. Excess chromium, if present in sufficient quantity, appears in the hardened metal as spherical microscopic crystals, while excess cobalt and nickel are held by the copper in solid solution. The excess metal in each case exerts per se a slight hardening effect, but its most important effect is to alter the quantity of silicide which can be taken into solid solution and precipitated therefrom as ultramicroscopic crystals during the heat treatment. In the case of chromium the solubility of the silicide is not materially changed, but excess cobalt diminishes the solubility of the silicide while excess nickel strongly increases the solubility of nickel silicide. Due to this effect of nickel, copper-nickel alloys containing as high as 40% Ni can be hardened by appropriate heat treatment after a content of silicon has been incorporated.

Silicon may also be present in excess of the quantity which will combine with the hardening metal. The excess will occur in solid solution in the hardened metal and has the effect of diminishing somewhat the quantity of silicide which can be taken into solid solution as a preliminary to precipitating it as ultramicroscopic crystals. Excess silicon has per se a slight hardening effect. An excess of either silicon, cobalt or nickel in solid solution in the hardened metal diminishes its electrical conductivity. Excess nickel, because of the large quantity which can be held in solid solution, may diminish the conductivity enormously.

A suitable heat treatment for hardening the above-described compositions comprises holding the material at a high temperature until the hardening metal and silicon have been completely taken up by the copper, or until the copper approaches saturation with these elements, quenching the material, and then holding it at a lower temperature for a sufficient time for the silicide to precipitate in the desired form. The preferred range for the high-temperature homogenizing treatment is 750° to 975° C. Only a short period is required at these temperatures; the desired result will usually be brought about within two hours, and thirty minutes or less is often sufficient, especially at the higher temperatures of the range given. The quenching holds the bulk of the silicide in solid solution, and the quenched material is usually soft and suitable for any kind of cold work.

A second heat treatment wherein the silicide is caused to precipitate as ultramicroscopic crystals completes the hardening. The second heat treatment comprises heating the material to a temperature within the range of about 250° C. to 600° C. and holding it for a time. A few minutes suffice to produce the maximum hardening at 600° C. while many weeks may be required at 250° C. There is doubtless a tendency to hardening at still lower temperatures, but the action is too slow to be useful.

If the material is heated above 600° C. during this second heat treatment, the silicides precipitate as microscopically visible grainlets. As a general rule the ductility which accompanies a given hardness is greater the lower the hardening temperature. It has been observed, however, that when the hardening temperature is in the vicinity of 450° C. to 500° C., less ductility often accompanies a given hardness than when the hardening temperature is either higher or lower. To secure maximum ductility it is sometimes desirable to use the lower hardening temperatures even though the duration of the heat treatment is considerably prolonged by so doing.

If the hardening temperature does not exceed about 450° C., the material reaches its maximum hardness and then remains unchanged if the temperature is continued, but if the higher temperatures of the hardening range are employed an undue prolongation of the hardening temperature will result in the formation of silicide crystals of larger than optimum size, accompanied by a retrogression in hardness. This retrogression after the moment of maximum hardness is more pronounced the higher the hardening temperature.

Where it is desired to make wrought arti-

cles from material hardened according to my invention, for example an article shaped by drawing or forging, a variety of methods of procedure will suggest themselves and one can be chosen which is adapted to the particular conditions. Compositions according to the invention may be hot worked without difficulty. When the quantity of silicide present is relatively high, for example above about 4% of nickel silicide, the hot-working should be accompanied by sufficient holding at homogenizing temperatures to keep the material in a sufficiently homogeneous condition. At the end of the hot work the silicide should be brought into solid solution, if it is not already in that condition, by heating to 750° C.–975° C., and should be quenched from the temperature at which it is homogeneous whether this is incidental to the hot-working operation or is the result of reheating. The article is then in condition for cold-working or hardening in the manner already described. The hardened article may be subjected to a small amount of cold work, still further enhancing its strength, but where such cold work is contemplated the hardening step should usually be discontinued before the material has acquired its maximum hardness. Cold work increases the hardness of the material but little. Severe cold work may soften the material, bringing it into a condition wherein it resembles the annealed material.

I have produced copper hardened with chromium silicide having a Brinell hardness (500 kg. load, 10 mm. ball) higher than 100, and a tensile strength of 54,000 pounds per square inch which can be increased to 85,000 pounds per square inch by cold work. Using cobalt silicide the corresponding figures are 150 Brinell for hardness, 85,000 pounds per square inch for tensile strength as hardened, and 98,000 pounds per square inch as cold drawn. Copper hardened with nickel silicide has recorded over 250 Brinell, over 110,000 pounds per square inch tensile strength as hardened, and around 125,000 pounds per square inch when cold drawn. The hardening effect of one per cent of silicide is greatest for the chromium compound and least for the nickel, but since nickel silicide is more soluble in copper than is cobalt silicide, and the latter is more soluble than chromium silicide, copper can be made harder with nickel silicide than with the cobalt compound, and harder with cobalt silicide than with chromium silicide as indicated by the figures given above.

The invention can be applied in general to the alpha alloys of copper as these have the ability to take chromium, cobalt, or nickel silicides into solution at temperatures at which the alloys remain solid. Thus copper alloys containing for example 7% aluminum, or 8% tin, or 20% manganese, or 30% zinc, can be hardened with silicides, as these alloys are of the alpha type. The solubility of the silicides in the solid alloy diminishes with increasing content of zinc or other alloying metal, and less hardening is therefore possible where the content of zinc or the like is higher. Also the melting point of a brass or bronze is considerably less than that of copper, which further diminishes the quantity of silicide which can be caused to go into solid solution.

Manganese is a useful addition to materials to which my invention is applied, as it acts as a deoxidizer and tends to prevent oxidation and loss of silicon. Under some conditions manganese and iron appear to form silicides which act as hardening agents, perhaps in a manner similar to that which has been described in connection with chromium, cobalt, and nickel. Iron and manganese, however, are very much less effective as hardeners than the other metals referred to. The silicides of a plurality of the hardening metals may of course be used jointly in practising the invention.

It is well known that cobalt, nickel and silicon greatly increase the resistivity of copper if separately alloyed with it. As some of the compositions of my invention contain considerable quantities of cobalt or nickel or both, together with silicon, it might be expected that these compositions would exhibit rather high resistivities, but the resistivities are in fact much lower than might be predicted from the quantities of silicon and hardening metal present. The total increase in resistivity brought about by an addition of silicon accompanied by an addition of cobalt or nickel is not only less than the sum of the effects of the silicon and metal when added to separate lots of copper, but in some cases is actually much less than the effect of either the silicon or metal if added alone. This is true even when the copper containing both silicon and hardening metal is in the quenched condition and the additions are in solid solution,—the state in which they increase resistivity most strongly. If the additions are precipitated from the solid solution, as in the hardening heat treatment, the conductivity is still further greatly increased.

The following example will illustrate this phenomenon. Copper containing 1.5% Si and no hardening metal has a resistivity of the order of 16 microhms per centimeter cube. Copper containing 6% Ni and no silicon has a resistivity of about 21, measured in the same unit. But copper containing 6% Ni and 1.5% Si has a resistivity of only 9 or 10 microhms per centimeter cube as quenched, and this value may be reduced to 4.9–5.2 microhms per centimeter cube by the described hardening treatment. For a given total content of silicon and hardening metal,

the conductivity reaches a maximum when the silicon and hardening metal are present in about the proportions corresponding to the silicides for which formulæ have been given. The unexpectedly low increase in resistivity which accompanies the simultaneous addition of silicon and nickel may perhaps be explained by the theory that these elements tend to deform the crystal lattice of copper in opposite directions, the atomic volume of copper being intermediate those of nickel and silicon.

Copper hardened according to the invention with cobalt and silicon in amounts equivalent to about 3% Co_2Si may have a resistivity as low as 2.9 to 3.2, while if the hardening additions correspond to about 1% Cr_2Si, the resistivity may be as low as 2.0, pure copper being 1.75.

By the practice of the invention there may be produced a class of useful materials which to the best of my knowledge have not heretofore been prepared. This class of materials may be defined as those containing at least 93% copper, having good workability, and a conductivity of at least 35%; and in a condition free from cold-working strains having a hardness of at least 150 Brinell and a tensile strength of at least 95,000 pounds per square inch. A more restricted class of new and useful materials contain at least 97% copper, are readily workable, have a conductivity of at least 55%, and, without cold work, are above 135 Brinell in hardness and above 80,000 pounds per square inch in tensile strength. Finally, for use where nearly pure copper of high conductivity is required and considerable hardness and strength are desired, the invention is capable of producing a class of materials of good workability with copper at least about 98.5%, and conductivity at least 75%, testing without previous cold work at least 110 Brinell and at least 50,000 pounds per square inch.

I claim:

1. A process which comprises subjecting a material consisting predominantly of copper and containing silicon and a metal having the hereindescribed hardening effect of chromium, cobalt and nickel to an homogenizing treatment at high temperature, thereby bringing substantial quantities of silicon and hardening metal into solid solution; quenching; and then heating the material at a temperature between about 250° C. and about 600° C. for a sufficient period to develop a substantial proportion of the hardness attainable at such temperature; and finally cooling the material.

2. A process which comprises bringing a material consisting predominantly of copper, and containing silicon and a metal having the hereindescribed hardening effect of chromium, cobalt and nickel, to a temperature below 600° C. and into a condition wherein it contains substantial quantities of silicon and hardening metal in solid solution; heating the material at a temperature between about 250° C. and about 600° C. for a sufficient period to develop a substantial proportion of the hardness attainable at such temperature; and finally cooling the material.

3. A process which comprises bringing a material consisting predominantly of copper, and containing silicon and a metal having the hereindescribed hardening effect of chromium, cobalt and nickel, to a temperature below 600° C. and into a condition wherein it contains substantial quantities of silicon and hardening metal in solid solution by the steps of heating the material at a temperature between 750° C. and 975° C. and then quenching it; heating the material at a temperature between about 250° C. and about 600° C. for a sufficient period to develop a substantial proportion of the hardness attainable at such temperature; and finally cooling the material.

4. A process which comprises adding silicon and a metal having the hereindescribed hardening effect of chromium, cobalt and nickel, to a material consisting predominantly of copper; bringing the material so prepared to a temperature below 600° C. and into a condition wherein it contains substantial quantities of silicon and hardening metal in solid solution; heating the material at a temperature between about 250° C. and about 600° C. for a sufficient period to develop a substantial proportion of the hardness attainable at such temperature; and finally cooling the material.

5. A process which comprises adding silicon and a metal having the hereindescribed hardening effect of chromium, cobalt and nickel, to a material consisting predominantly of copper; bringing the material so prepared to a temperature below 600° C. and into a condition wherein it contains substantial quantities of silicon and hardening metal in solid solution, by the steps of heating the material at a temperature between 750° C. and 975° C. and then quenching it; heating the material at a temperature between about 250° C. and about 600° C. for a sufficient period to develop a substantial proportion of the hardness attainable at such temperature; and finally cooling the material.

6. A process which comprises bringing a material consisting predominantly of copper, and containing substantial quantities of silicon and a metal having the hereindescribed hardening effect of chromium, cobalt and nickel, to a temperature below 600° C. and into a condition wherein it holds in solid solution substantially all of the silicon and hardening metal present; heating the

material at a temperature between about 250° C. and about 600° C. for a sufficient period to develop a substantial proportion of the hardness attainable at such temperature; and finally cooling the material.

7. A process which comprises bringing a material consisting predominantly of copper and containing substantial quantities of silicon and a metal having the hereindescribed hardening effect of chromium, cobalt and nickel, to a temperature below 600° C. and into a condition wherein it holds in solid solution substantially all of the silicon and hardening metal present by the steps of heating the material at a temperature between 750° C. and 975° C. and then quenching it; heating the material at a temperature between about 250° C. and about 600° C. for a sufficient period to develop a substantial proportion of the hardness attainable at such temperature; and finally cooling the material.

8. The process which comprises adding silicon and a metal having the hereindescribed hardening effect of chromium, cobalt and nickel, to a material consisting predominantly of copper; bringing the material so prepared to a temperature below 600° C. and into a condition wherein it holds in solid solution substantially all of the silicon and hardening metal present; heating the material at a temperature between about 250° C. and about 600° C. for a sufficient period to develop a substantial proportion of the hardness attainable at such temperature; and finally cooling the material.

9. A process which comprises adjusting the composition of a material consisting predominantly of copper so that it will contain in substantial quantities the constituents of at least one of the hereindescribed group of hardening silicides, in substantially the proportions in which they occur in said silicides; bringing the material to a temperature below 600° C. and into a condition wherein it holds in solid solution substantially all of the silicon and hardening metals present; heating the material at a temperature between about 250° C. and about 600° C. for a sufficient period to develop a substantial proportion of the hardness attainable at such temperature; and finally cooling the material.

10. A process which comprises adjusting the composition of a material consisting predominantly of copper so that it will contain in substantial quantities the constituents of at least one of the hereindescribed group of hardening silicides, in substantially the proportions in which they occur in said silicides; bringing the material to a temperature below 600° C. and into a condition wherein it holds in solid solution substantially all of the silicon and hardening metals present, by the steps of heating the material at a temperature between 750° C. and 975° C. and then quenching it; heating the material at a temperature between about 250° C. and about 600° C. for a sufficient period to develop a substantial proportion of the hardness attainable at such temperature; and finally cooling the material.

11. A process which comprises adjusting the composition of a material consisting predominantly of copper so that it will contain in substantial quantities the constituents of at least one of the hereindescribed group of hardening silicides, in substantially the proportions in which they occur in said silicides; bringing the material to a temperature below 600° C. and into a condition wherein it holds in solid solution substantially all of the silicon and hardening metals present; heating the material at a temperature between about 250° C. and about 600° C. for a sufficient time to develop substantially the maximum hardness attainable at such temperature; and finally cooling the material.

12. A process which comprises adjusting the composition of a material consisting predominantly of copper so that it will contain in substantial quantities the constituents of at least one of the hereindescribed group of hardening silicides, in substantially the proportions in which they occur in said silicides; bringing the material to a temperature below 600° C. and into a condition wherein it holds in solid solution substantially all of the silicon and hardening metals present, by the steps of heating the material at a temperature between 750° C. and 975° C. and then quenching it; heating the material at a temperature between about 250° C. and about 600° C. for a sufficient period to develop substantially the maximum hardness attainable at such temperature; and finally cooling the material.

13. A process which comprises adding to commercially pure copper substantial quantities of the constituents of at least one of the hereindescribed group of hardening silicides in their approximate combining proportions; bringing the material so prepared to a temperature below 600° C. and into a condition wherein substantially all of the silicon and hardening metal are held in solid solution; heating the material at a temperature between about 250° C. and about 600° C. for a sufficient period to develop a substantial proportion of the hardness attainable at such temperature; and finally cooling the material.

14. A process which comprises subjecting a material consisting predominantly of copper containing silicon and nickel, to an homogenizing treatment at high temperature, thereby bringing substantial quantities of silicon into solid solution; quenching;

and then heating the material at a temperature between about 250° C. and about 600° C. for a sufficient period to develop a substantial proportion of the hardness attainable at such temperature; and finally cooling the material.

15. A process which comprises bringing a material consisting predominantly of copper containing silicon and nickel, to a temperature below 600° C. and into a condition wherein it contains substantial quantities of silicon and nickel in solid solution; heating the material at a temperature between about 250° C. and about 600° C. for a sufficient period to develop a substantial proportion of the hardness attainable at such temperature; and finally cooling the material.

16. A process which comprises adjusting the composition of a material consisting predominantly of copper so that it will contain in substantial quantities the constituents of at least one of the hereindescribed group of hardening silicides, in substantially the proportions in which they occur in said silicides, whereby the material becomes adapted for hardening by the hereindescribed heat treatment.

17. A process which comprises adding to commercially pure copper substantial quantities of the constituents of at least one of the hereindescribed group of hardening silicides in their approximate combining proportions, whereby the copper becomes adapted for hardening by the hereindescribed heat treatment.

18. A process which comprises subjecting a material consisting predominantly of copper containing silicon and nickel to an homogenizing treatment at high temperature, thereby bringing substantially all of the silicon and nickel present into solid solution; quenching; and then heating the material at a temperature between about 250° C. and about 600° C. for a sufficient period to develop substantially the maximum hardness attainable at such temperature; and finally cooling the material.

19. A new material consisting principally of copper and containing substantial quantities of the constituents of at least one of the hereindescribed group of hardening silicides; having good workability, a conductivity of at least 35% and, in a condition wherein it is free from cold-work strains, a Brinell hardness of at least 150, and a tensile strength of at least 95,000 pounds per square inch.

In testimony whereof, I affix my signature.

MICHAEL G. CORSON.