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TREATMENT OF AGE-HARDENABLE COPPER-NICKEL-ZINC ALLOYS AND PRODUCT RESULTING THEREFROM

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The present invention relates to copper-nickel-zinc alloys and, more particularly, to an improved treatment for imparting new and improved characteristics of good hot workability to special age-hardenable copper-nickel-zinc alloys and also to the improved products resulting therefrom.

As is well known to those skilled in the art, certain copper-nickel-zinc alloys which are often referred to as "nickel silvers" commonly contain about 45% to 72% copper, 9% to 20% nickel and 10% to 43% zinc. Such alloys include the alpha type, in which the amounts of copper, nickel and zinc are so proportioned that the alloys have a single-phase matrix of alpha phase copper-nickel-zinc solid solution with a face-centered-cubic structure, and also include the alpha-beta type, in which the amounts of copper, nickel and zinc are in such proportions that the alloy has a dual phase matrix comprising both alpha phase and beta phase. For example, an alloy containing about 17% to 19% nickel, 16% to 18% zinc and balance copper is an alpha nickel silver alloy and an alloy containing about 11% to 13% nickel, 42% to 44% zinc and balance copper is an alpha-beta nickel silver alloy. It is understood by those skilled in the art that, in the broad sense, the compositional difference between the alpha and the alpha-beta nickel silver alloys is determined by the phase boundary between the alpha phase and the alpha-beta phase in the copper-nickel-zinc alloy system.

Alpha type nickel silvers are characterized by good corrosion resistance and good cold working characteristics, such as are required for cold rolling thin sheet, which are generally superior to the corrosion resistance and cold working characteristics of alpha-beta nickel silvers. Heretofore, experimental results have shown that alpha nickel silver alloys can be rendered age hardenable and, thus, increased strength and hardness can be obtained, by incorporating small amounts of aluminum, with or without titanium, in the alloys.

Now, of course, it would be highly desirable to produce age-hardenable alpha nickel silvers having good hot workability characteristics in order to obtain, among other attributes, the commercial advantages which would flow from producing the alloys in ingots of large size and accomplishing reductions of ingot thicknesses by hot working. However age-hardenable alpha nickel silver alloys which have been prepared using prior art melting practices for making ingots have been detrimentally characterized by hot shortness, e.g., extremely small limited ranges of hot malleability, if hot malleable at all, and other characteristics detrimental to hot workability. Various melting practices including melting under charcoal and/or treatment with manganese, phosphorus, zirconium and magnesium have been tried in preparing nickel silver alloys for making ingots but have not successfully produced age-hardenable alpha nickel silver alloys having good hot workability even though the alloys may have had excellent cold workability. In view of such poor hot-working characteristics, commercial production of wrought age-hardenable alpha nickel silver products, particularly sheet and strip, and commercial utilization of the advantageously high strength and other desirable characteristics of such alloys has been seriously hindered.

Accordingly, there has been a need for a process which would provide improvement in the hot working characteristics of age-hardenable alpha nickel silver alloys.

Although many attempts were made to overcome the foregoing difficulties and other difficulties and disadvantages, none, as far as I am aware, was entirely successful when carried into practice on a commercial scale.

It has now been discovered that highly satisfactory characteristics of hot workability can be achieved in age-hardenable alpha nickel silver alloys by a new process.

It is an object of the present invention to provide a new process for treating an age-hardenable alpha nickel silver alloy when in the molten condition during the preparation thereof whereby new and improved characteristics of good hot workability are imparted to the alloy so treated.

It is a further object of the invention to provide hot-workable age-hardenable alpha nickel silver alloys and products thereof made in accordance with the new process for treating the alloys.

Other objects and advantages will become apparent from the following description.

Generally speaking, the present invention contemplates a new process for imparting new and improved hot working characteristics to age-hardenable alpha nickel silver alloys which comprises introducing into a molten bath for such an alloy a magnesium-carbon alloyed composition to introduce small amounts of magnesium and carbon into said molten bath, said small amounts being effective to impart new and improved characteristics of hot workability to the resulting alloy. In order to obtain satisfactory results in accomplishing the process of the invention it is necessary that the bath be treated with a magnesium-carbon addition agent having magnesium and carbon in intimate association with each other such as is characteristic of magnesium and carbon when associated together in an alloy and that a cleansing treatment be performed after the magnesium-carbon treatment. For example, the invention contemplates a process for making a hot workable, age hardenable, alpha nickel silver alloy comprising treating a molten bath for such an alloy by introducing into the bath, prior to a cleansing treatment, an amount of an alloy containing magnesium and carbon sufficient to provide at least about 0.01% retained magnesium in the nickel silver alloy after solidification thereof and sufficient to introduce at least about 0.001% carbon into the bath along with the magnesium.

Alloys comprising magnesium, carbon and a third metal having substantial miscibility and/or solubility with magnesium and carbon, e.g., nickel, are especially advantageous for magnesium-carbon alloyed addition agents in accordance with the invention. Thus, magnesium-carbon additions in accordance with the invention are advantageously made by introducing into the bath a nickel-base alloy containing at least one part of carbon for each 30 parts of magnesium, advantageously, about 1 part of carbon for each 10 parts of magnesium (parts by weight). Such an alloy can contain about 1% to about 4% carbon, about 10% to about 30% magnesium and balance nickel, e.g., about 1.5% carbon, about 15% magnesium and balance nickel. Mixtures of unalloyed powders of carbon and magnesium are not satisfactory magnesium-carbon addition agents for the process of the invention. The magnesium-carbon addition agent is thoroughly dispersed throughout the bath and for this object it is advantageous to plunge the addition agent into the bath. Most advantageously, to accomplish good retention of magnesium in the bath, the agent containing magnesium and carbon is plunged into the bath very shortly, e.g., not more than three minutes, before the bath is tapped from the furnace. Elements having strong tendencies to combine with carbon are highly detrimental to the effectiveness of the magnesium-carbon addition and in order that the magnesium-carbon addition be effective, the molten bath is maintained substantially devoid of carbide-forming elements such as titanium, columbium, molybdenum and vanadium at the time the magnesium-carbon addition is made thereto. For instance, when the magnesium-carbon agent is introduced, the bath should not contain more than about 0.02% titanium or about 0.01% columbium. All compositional percentages set forth herein are by weight and all percentages of amounts introduced or added to the bath are based on the weight of the bath to which the addition is made.

When treating an alloy in accordance with the process of the invention, the alloy bath must be low in dissolved sulfur and oxygen immediately prior to introduction of the magnesium-carbon alloyed composition. In practice such a bath condition is very satisfactorily obtained by adding manganese to the bath in an amount sufficient to effectively fix any sulfur present and deoxidize the bath, e.g., by adding at least about 0.05% manganese, to the bath. Where the molten bath initially contains at least about 0.05% manganese and/or where the bath is otherwise well deoxidized and is of a low sulfur content, e.g., contains less than 0.005% sulfur, addition of manganese to remove and/or combine with sulfur may not be necessary and, accordingly, it is to be understood that processes whereby age-hardenable alpha nickel silver alloys are rendered hot workable by treatment with a magnesium-carbon composition without addition of the manganese to the alloy are within the contemplation of the invention.

For the process of the invention, it is also important that the alloy be cleansed of detrimental deoxidation and desulfurization products after the treatment with a magnesium-carbon composition. A particularly satisfactory method for cleansing the alloy after the magnesium-carbon composition is introduced is to add a fluxing agent such as phosphorus, e.g., about 0.01% phosphorus, to the molten alloy so that impurities such as oxides and sulfides are readily floated from the alloy.

In carrying the invention into practice, it is advantageous to further control the amounts of any manganese and phosphorous added to the alloy and the amount of magnesium-carbon composition introduced into the bath so as to provide that the retained amounts of these elements (retained when the alloy has solidified) are each not greater than about 0.5% manganese, about 0.05% magnesium and about 0.04% phosphorous. Manganese is advantageously maintained not greater than about 0.5% in order to avoid detrimentally affecting hot malleability of the alloys. The retained amount of magnesium should be not greater than about 0.05%, advantageously about 0.01% to about 0.03%, since greater amounts tend to reduce the tensile elongation and increase the work hardening rate of the treated alloy. Carbon is known to have only very slight solubility in either molten or solidified alpha nickel silver alloys and it will be readily understood by those skilled in the art that carbon in amounts exceeding the solubility limit will be rejected from the molten alloy without harmful effects on the characteristics of the solidified alloy. Thus, additions of carbon which are in excess of the amount of carbon required or desired for effectiveness are not detrimental inasmuch as excess carbon is rejected from the molten alloy. Use of a cover of charcoal, such as charcoal chips, over the melt during melting nickel silver alloys is a commonly employed practice that is not detrimental but does not serve as an equivalent substitute for introducing carbon in alloyed association with magnesium in accordance with the process of the invention. Carbon introduced from sources other than a magnesium-carbon alloyed addition agent in accordance with the invention does not provide the hot workability advantages obtained with the process of the invention. Phosphorous should be kept not greater than about 0.04% retained since greater amounts of phosphorus reduce the ductility of the alloy and tend to segregate, thereby forming hard spots in the alloy. Thus, an advantageous embodiment of the process of the invention, whereby age hardenable alpha nickel silver alloys are treated so as to be characterized by good hot workability and other advantageous characteristics referred to herein, comprises establishing a molten nickel silver alloy bath containing about 0.1% to about 0.5% manganese, e.g., by introducing about 0.15% to about 0.6% manganese into the bath when substantially free of manganese, plunging into the bath an alloy containing magnesium and carbon in amounts sufficient to provide about 0.01% to about 0.05% retained magnesium and sufficient to introduce at least about 0.001% carbon, e.g., about 0.001% to about 0.01% or more, carbon into the bath along with the magnesium, and thereafter adding about 0.01% to about 0.04% phosphorus to the bath. The thus treated bath is thereafter tapped and cast into ingots, thereby producing hot workable, alpha nickel silver alloy ingots in accordance with the invention. Alloy products so produced generally contain, when solidified, about 0.1% to about 0.5% manganese, about 0.01% to about 0.05% magnesium, about 0.001% to about 0.01% carbon and about 0.01% to about 0.04% phosphorus.

It is known in the metallurgical art that retention of magnesium in molten alloys is dependent upon such variables as the composition of the alloy bath, the temperature of the bath when magnesium is added and the length of time the alloy is molten after magnesium is added and it will be understood that it is usually necessary to add a greater amount of magnesium than the amount which is desired to be retained in the treated melt. For instance, in making magnesium-carbon additions in the process of the invention when the bath temperature is about 2150° F. to about 2250° F. and the magnesium-carbon addition is plunged into the bath shortly before casting the alloy, e.g., about one minute to about three minutes before casting, about 0.02% to about 0.05% magnesium, based on the weight of the bath, is added in the form of a nickel-magnesium-carbon alloy to obtain a retained magnesium content of about 0.01% to about 0.03%. More generally, the amount of retained magnesium will ordinarily be about 25% to about 75% of the amount added in accordance with the invention.

Nickel silver alloys which are produced in accordance with the invention are age-hardenable alpha-phase copper-nickel-zinc-aluminum alloys and particularly include alloy compositions containing about 5% to about 25% nickel, about 5% to about 20% zinc, about 0.5% to about 2% aluminum, up to about 0.5% manganese, up to about 0.4% titanium, up to about 1.5% columbium, up to about 1.5% tantalum provided that the total amount of aluminum, titanium, columbium and tantalum does not exceed about 2%, and balance copper with the said nickel, zinc and copper present in proportions which characterize the matrix by a single phase face-centered-cubic structure. Where the balance of a nickel silver alloy is referred to herein as essentially copper, it is to be understood that "balance essentially copper" does not exclude residuals of elements introduced by the treatment process of the invention and does not exclude small substantially harmless amounts of other elements and impurities. For instance, nickel silver referred to herein may contain up to 2% cobalt. Iron, thin, zirconium and silicon are undesirable impurities and should not be present in amounts greater than about 0.1% iron, 0.1% tin, 0.05% zirconium or 0.05% silicon. Sulfur is commonly present as an undesirable impurity in amounts up to about 0.01% in the alloy and in the treatment of the invention, manganese is incorporated in the bath in order to help fix any sulfur present. When at hot working temperatures, e.g., 1450° F. to 1850° F., nickel silver alloys treated in accordance with the invention have an alpha-structured matrix which is satisfactorily hot workable and essentially free from undesirable, low melting point, metallurgical segregates that, if present, would be detrimental to good hot workability.

The invention particularly contemplates production of hot-workable age-hardenable alpha nickel silver alloy products made of alloys containing about 10% to about 20% nickel, about 10% to about 15% zinc, about 0.5% to about 1.25% aluminum, up to about 0.2% titanium with balance essentially copper. These alloys which contain about 0.5% to about 1.25% aluminum have an especially advantageous combination of characteristics including good hot malleability combined with the capacity of being age-hardened to ultimate tensile strengths of at least about 65,000 pounds per square inch (p.s.i.) when in the condition obtained by heat treating at about 1550° F. to about 1700° F. for about 15 minutes to about 30 minutes, water quenching, followed by aging at about 800° F. to about 1200° F. for about 1 hour to about 8 hours and thereafter air cooling. For obtaining especially high levels of tensile strength, it is advantageous, when alloys of this last described composition contain titanium, that the amounts of aluminum and titanium therein be correlated such that the ratio of aluminum to titanium is from about 7 to 1 up to about 10 to 1 (Al:Ti ratio is about 7:1 to 10:1).

The process of the invention does not detrimentally affect the normally good cold-working characteristics of alpha nickel silver. Accordingly, alloys which have been treated by the process of the invention and thereafter hot worked can then be cold worked by known methods, preferably prior to age-hardening, e.g., when in conditions such as hot-worked conditions or hot-worked-and-annealed conditions. High strengths such as ultimate tensile strengths of 100,000 p.s.i. or higher, e.g., 110,000 p.s.i. or 125,000 p.s.i., can be obtained by cold working the alloy between the solution-annealing and aging treatments.

For the purpose of giving those skilled in the art a better understanding of the invention and/or a better appreciation of the advantages of the invention, the following illustrative examples are given:

Example

A molten bath of an age-hardenable alpha nickel silver alloy containing about 12% nickel, 12% zinc, about 1% aluminum, about 0.2% manganese and balance copper was established by melting together copper, nickel and zinc in proportions by weight of about 12 parts nickel, 12 parts zinc and 75 parts copper, adding about 1 part aluminum and thereafter adding to the bath about 0.25% manganese. The bath was provided with a charcoal cover during melting and treatment. A magnesium-carbon addition of about 0.05% magnesium along with about 0.005% carbon was made by plunging into the bath about 0.35% (by weight of the bath) of a nickel-magnesium-carbon alloy containing about 15% magnesium, about 1.4% carbon and balance nickel. Immediately after plunging the magnesium-carbon addition, the bath was tapped into a ladle and about 0.02% phosphorus was added to the alloy in the ladle, the phosphorus addition being made as an alloy containing about 15% phosphorus and balance copper. Thereafter, the alloy was cast into ingot molds and solidified into ingots, which were of an age-hardenable alloy (Alloy 1) containing about 12% nickel, about 12% zinc, about 1% aluminum, about 0.2% manganese, about 0.02% magnesium, about 0.002% carbon, about 0.015% phosphorous and balance copper.

Specimens of alloy 1 from the foregoing example were satisfactorily upset forged by each of the following procedures: forged at 1800° F. to fifty percent reduction in thickness; forged at 1800° F. to eighty-six percent reduction in thickness; and forged at 1725° F. to fifty percent reduction in thickness. All of the upset forged specimens from the foregoing example were satisfactorily free of surface cracking and internal bursts and were of generally highly satisfactory quality. Thus, it is evident

that the ingot products of the example were characterized by good hot workability over a wide temperature range.

In contrast to the results obtained with the product of the foregoing example of the invention, it was found that when age hardenable alpha nickel silver alloys containing about 12% nickel, about 12% to about 13% zinc, about 0.75% to about 1.25% aluminum and balance copper, and also other nickel silvers containing similar amounts of zinc, aluminum and copper and about 21% nickel, with and without about 0.2% titanium, were treated by other melting practice treatments, which are referred to hereinafter as Treatments A, B and C and which are not in accordance with the invention, the alloys produced thereby were hot short and had poor, unsatisfactory hot working characteristics.

Treatment A consisted of establishing a molten bath of an age hardenable alpha nickel silver alloy, adding thereto about 0.2% manganese, plunging into the bath an addition of a carbon-free nickel-magnesium alloy, which addition comprised about 0.05% magnesium based on the weight of the bath, and thereafter adding to the bath about 0.2% phosphorus as a copper-15% phosphorus alloy. Even though a charcoal cover was used over the baths during melting and treatment and the retained magnesium content of the alloys was about 0.01% to about 0.03%, the alpha nickel silver alloys treated by Treatment A were seriously hot short, thus, not satisfactorily hot-workable, and were found to contain a detrimental grain-boundary phase that tended to be molten during hot working.

For each of the Treatments B and C a charcoal cover was provided over the bath and about 0.2% manganese was added to the bath prior to the hereinafter described treating steps. In Treatment B, about 0.05% magnesium and about 0.005% carbon in the form of the nickel-magnesium-carbon alloy used for the foregoing were added to the melt in the ladle, with a retention of about 0.02% magnesium, but no phosphorus or other fluxing agent was added thereafter. Treatment C comprised adding about 0.25% titanium to the bath and thereafter plunging an addition of about 0.05% magnesium in the form of the aforedescribed nickel-magnesium-carbon alloy and adding about 0.2% phosphorus using a copper-15% phosphorus alloy for the addition. Retained magnesium from Treatment C was about 0.02%. When the alloys were tested for hot workability using the same foregoing test procedure as for the alloy made in the example of the invention, the hot workability at 1725° F. of the alloy made with Treatment B was very poor and the hot workability of the alloy made with Treatment C was also poor. Where alloys containing titanium or other strongly carbide-forming elements are to be produced in accordance with the invention, the magnesium-carbon addition must be made before titanium or any other carbide forming element is added to the bath and if such alloys are to be remelted, the carbide forming elements should be removed, e.g., by oxidizing titanium from the alloy, prior to retreatment of the alloy.

As additional examples of the invention, hot workable ingots made of alpha nickel silver Alloys Nos. 2 through 6, having chemical compositions set forth in Table I hereinafter, were produced by embodiments of the process of the invention. Thus, a molten bath containing requisite amounts of nickel, zinc, copper and aluminum for each of these alloys was established and each bath was treated by sequentially adding thereto about 0.2% manganese, about 0.02% to 0.03% magnesium and about 0.002% to 0.003% carbon alloyed together in a nickel-magnesium-carbon alloy, and about 0.02% phosphorus. About 0.2% titanium was added to the bath of Alloy No. 5 after making the phosphorus addition. The thus treated alloys were cast into molds and solidified to make ingot products. Ingots of the alloys were satisfactorily hot worked to about 90% reduction in cross-sectional area, i.e., to reduce the cross sections thereof to about 11% of the original cross-sectional area. Portions of the hot worked alloys were further processed, in order to obtain the alloys in the conditions referred to in Table I, by heat treating and/or cold rolling as shown in Table II. Test results showing mechanical characteristics of Alloys Nos. 2 through 6, when in the indicated conditions, are set forth in Table I hereinafter.

TABLE I

Alloy No.	Ni, percent	Zn, percent	Al, percent	Ti, percent	Cu	Condition	U.T.S. (p.s.i.)	Y.S. (p.s.i.)	Elong., percent
2	12	13	0.8		Bal.	A	77,850	42,400	25
						B	111,900	100,400	12
3	12	13	1		Bal.	A	89,150	54,050	19
						B	123,450	113,150	10
4	12	13	1.2		Bal.	A	94,200	60,950	15
						B	126,150	118,700	7
5	12	13	0.8	0.1	Bal.	A	96,700	55,800	22
						B	123,150	111,250	11
6	18	13	1		Bal.	A	94,900	54,200	28

U.T.S. (p.s.i.)=Ultimate tensile strength in pounds per square inch.
Y.S. (p.s.i.)=Yield strength, at 0.2% offset, in pounds per square inch.
Elong. (percent)=Percent elongation in one inch.
Bal.=Balance (includes any residuals from treatment with manganese, nickel-magnesium-carbon alloy and phosphorus).

TABLE II

Condition	Solution treatment	Cold work	Aging treatment
A	1,600° F.-1,700° F., ½ hour; W.Q.		1,050° F.-1,100° F., 3 hours; A.C.
B		45% R.A.	900° F., 3 hours; A.C.

W.Q.=Water quench.
A.C.=Air cool.
R.A.=Reduction in cross-sectional area.

The present invention is particularly applicable to the production of wrought nickel silver articles, including fasteners, keys, jugs, leaf springs, e.g., electrical contact leaf springs, and also including tableware such as forks, knives, spoons, water pitchers, bread dishes, etc. The process of the invention is applicable to treating molten alpha nickel silver alloys in processes for producing hot-workable, age-hardenable alpha nickel silver alloy products including ingots and also including hot worked blooms, billets, bars, plates, rods and the like products which are capable of being further hot worked and also cold worked.

Although the present invention has been described in conjunction with preferred embodiments, it is to be understood that modifications and variations may be resorted to without departing from the spirit and scope of the invention as those skilled in the art will readily understand. Such modifications and variations are considered to be within the purview and scope of the invention and appended claims.

I claim:

1. In a process for refining and cleansing a molten alloy bath for the production of an age-hardenable alpha nickel silver alloy product the improvement comprising introducing into the molten bath for said alloy, prior to a cleansing thereof, a magnesium-carbon alloyed composition to introduce small amounts of magnesium and carbon into said molten bath, said small amounts of magnesium and carbon being effective to render the said age-hardenable alpha nickel silver alloy hot workable.

2. A process as set forth in claim **1** wherein the magnesium-carbon alloyed composition is a nickel-base alloy containing magnesium and carbon with at least one part of carbon for each 30 parts of magnesium.

3. A process as set forth in claim **1** wherein the magnesium-carbon alloyed composition is a nickel-base alloy containing about 1% to about 4% carbon, about 10% to about 30% magnesium and balance nickel.

4. A process for treating an age-hardenable alpha nickel silver alloy to impart new and improved characteristics of hot workability to the alloy comprising establishing a molten bath of an age-hardenable alpha nickel silver alloy containing about 5% to about 25% nickel, about 5% to about 20% zinc, about 0.5% to about 2% aluminum, about 0.05% to about 0.5% manganese, said bath being substantially devoid of metal from the group consisting of titanium, columbium, tantalum, molybdenum and vanadium, with balance substantially copper and with the said nickel, zinc and copper present in proportions which characterize the matrix of the alloy, when solidified, by a single-phase face-centered cubic structure, introducing into said molten bath a magnesium-carbon alloyed composition to introduce small amounts of magnesium and carbon into said molten bath, said small amounts of magnesium and carbon being effective to render the said nickel silver alloy hot workable and thereafter adding about 0.01% to about 0.04% phosphorus to the bath.

5. A hot workable age-hardenable alpha nickel silver product produced by treating an alloy in accordance with the process set forth in claim **1** and thereafter casting and solidifying the thus treated alloy.

6. A process as set worth in claim **4** wherein the amounts of magnesium and carbon in the magnesium-carbon alloyed composition are sufficient to provide about 0.01% to about 0.05% retained magnesium in the alloy and to introduce at least about 0.001% carbon into the bath along with said magnesium.

7. A process as set forth in claim **4** wherein metal from the group consisting of up to about 0.4% titanium, up to about 1.5% columbium and up to about 1.5% tantalum is introduced into a bath after introduction of the magnesium-carbon alloyed composition and said amounts of aluminum, titanium, columbium and tantalum are controlled to provide that the total percentage thereof does not exceed about 2%.

8. A process as set forth in claim **4** wherein the molten alloy bath contains about 10% to about 20% nickel, about 10% to about 15% zinc, about 0.5% to about 1.25% aluminum with balance substantially copper.

9. A process as set forth in claim **4** wherein the magnesium-carbon alloyed composition is a nickel-base alloy containing about 1% to about 4% carbon, about 10% to about 30% magnesium and balance nickel.

References Cited

UNITED STATES PATENTS

2,101,625 12/1937 Munson ---------- 75—157.5

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