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METHOD OF MANUFACTURING ALUMINUM-CONTAINING ALLOYS

Victor O. Allen, Madison, N. J., assignor to Wilbur B. Driver Company, Newark, N. J., a corporation of New Jersey

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This invention relates to metallurgy and has for its object the provision of an economically practical method of eliminating aluminum oxide, nitride and hydride compounds from metallic alloys containing the same. More particularly the invention relates to and has for its object the provision of an economically practical method of eliminating aluminum oxide, nitride and hydride compounds from alloys consisting predominately of one or more of the metals consisting of the group iron, nickel and copper and in lesser proportions one or more of the elements Mn, Si, Cr group metals, Zr group metals, V group metals, Co, Mg, rare earth group metals and the like, commonly associated therewith, with or without aluminum in amounts ranging from fractional or substantially residual percentages up to about 30%. Another object is to improve the ductility and hot and cold workability of Al-containing alloys, particularly iron, nickel and copper alloys which either contain aluminum in alloyed percentages or have been deoxidized and degasified by additions of aluminum, by eliminating therefrom aluminum oxide, nitride and hydride compounds. Other objects and advantages will be apparent as the invention is more fully hereinafter disclosed.

Aluminum is added to many alloys and especially to iron, nickel and copper base alloys either as a deoxidizing and degasifying agent, per se, or in alloyed amounts ranging from fractional percentages upward to about 30% to impart thereto desired physical and chemical properties. In all such alloys, irrespective of associated metallic and metalloid constituents, the chemical activity of the aluminum with respect to oxygen, nitrogen and hydrogen is such that substantially all oxide, nitride and hydride compounds present in the bath are converted into aluminum oxide, nitride and hydride compounds which are highly refractory and of low solubility in the molten metal bath and which are of such low specific gravity that they are usually retained dispersed as relatively small particles throughout the bath.

Even when present in relatively small amounts these aluminum oxide, nitride and hydride compounds have a marked deleterious effect upon the physical properties of the solid metal and upon the grain growth and recrystallization characteristics of the same, which is most generally reflected in the ductility and workability of the alloys.

Many of the iron, nickel and copper base alloys containing aluminum are desired in relatively

small sized wire and relatively thin sheet or strip form, particularly those utilized in the electrical industry for its magnetic or electrical resistance properties. Many of the alloy compositions heretofore prepared are not obtainable in such form by known or by economically practical mechanical deformation methods. I have discovered that by eliminating aluminum oxide, nitride and hydride constituents from these said iron, nickel and copper base alloys the hot and cold ductility and workability of the alloys are markedly increased and all such alloys that I so far have experimented with, when substantially free of such aluminum compounds, have been found to be amenable to mechanical deformation by economically practical methods to the relatively thin wire, sheet or strip form desired with practically no difficulty and most of the alloys may be subjected to extensive cold mechanical deformation subsequently to hot deformation of the cast metal to condition the same for such cold working without developing excessive amounts of work hardening strains seriously impairing the physical properties of the same.

To accomplish the elimination of aluminum oxide, nitride and hydride compounds from molten metal baths, particularly molten iron, nickel and copper base alloys containing aluminum, from substantially residual amounts to relatively large amounts approximating 30%, I have found that the molten metal bath must be vigorously agitated while in contact with a flux that is non-reducible or reactive with aluminum but reactive with the said aluminum oxide, nitride and hydride compounds to decompose the same forming compounds therewith that are either soluble in or miscible with the said flux.

Flux materials that are non-reactive with aluminum falling generally within the scope of the present invention comprise alkali, alkaline earth, aluminum and ammonium halide and double halide compounds. Many different combinations of these compounds are suitable for the purpose of the present invention and the selection of the same depends primarily upon the temperature of the molten metal bath and the fluidity of the flux at that temperature. Additions of ammonium halide and double halide salts are effective in increasing the fluidity of the flux and in stabilizing the same against oxidation decomposition.

Materials falling generically within the scope of compounds reactive with aluminum oxide, nitride and hydride compounds comprise any lithium salt or compound that is either soluble

in or miscible with the flux mixture employed. The lithium salt or compound is added to the flux in such proportions relative to the volume of metal being treated and the known amount of aluminum oxide, nitride and hydride compounds contained therein, as will effect substantial elimination of these said aluminum compounds within an economically practical time interval. Preferably, and in treating most metals, I employ a lithium halide compound, such as lithium fluoride. However, I have found that additions of lithium oxide alone or in addition to the halide (fluoride) compound are equally as effective and, in the presence of excessive amounts of nitride and hydride compounds, are perhaps more effective in the removal of the same than is lithium fluoride alone.

As a specific embodiment of the practice of the present invention, I may employ cryolite as a flux and add thereto from 10 to 30% of lithium fluoride or from 10 to 30% of a mixture of 90% lithium fluoride and 10% lithium oxide in the event the molten metal bath is more highly nitrogenized than usual. Alternatively, I may employ a mixture of sodium and potassium chlorides or fluorides and incorporate therein 10 to 30% lithium fluoride or 10 to 30% of a mixture of 90% lithium fluoride and 10% lithium oxide. A mixture of alkali and alkaline earth metal fluorides are equally as effective as a slag or flux and additions of lithium fluoride or of a mixture of lithium fluoride and oxide as hereinabove described will render the same reactive with the aluminum compounds present in the molten metal bath.

In the practice of the present invention additions of lithium compounds alone to the molten metal bath without any flux additions is effective to eliminate aluminum oxide, nitride and hydride compounds from the bath. However, in the absence of a flux means to dissolve or absorb or mix with the double $AlLi$ compounds formed, the elimination of the same from the molten metal bath will be difficult. Moreover, where the metal bath is being heated under more or less oxidizing conditions, extensive reoxidation of the bath is often obtained before cleansed metal may be cast.

In the practice of the present invention, vigorous agitation of the bath and the lithium-containing flux contacting therewith is preferably obtained by means of induced electric currents, as by this means the temperature of the bath may at the same time be controlled and maintained. However, alternatively I may employ any other type of means effective to obtain either emulsification of the flux in the metal bath or intimate association of the same with the metal sufficient for the purpose in view, as one skilled in the art will perceive.

As a specific embodiment of the practice of the present invention the adaptation of the same to iron base alloys will be described.

Binary iron-aluminum alloys, for example alloys containing from 2 to 10% Al, have heretofore been proposed in the art for use as magnetic alloys. The magnetic permeability and watt loss in such alloys is directly effected by the amount of oxide, nitride and hydride compounds present therein, where all other associated metallic and non-metallic impurities have been substantially eliminated. Moreover, the presence of these oxide, nitride and hydride compounds deleteriously effect the ductility and workability of the alloys and also markedly influence the grain

growth and recrystallization properties of the same.

I have found that these alloys may be made substantially free from aluminum oxide, nitride and hydride compounds by melting down the alloy in an induction furnace of the Ajax-Northrup type and subjecting the alloy to treatment for a prolonged time interval with the reactive flux composition of the present invention for a period of time effective to remove therefrom the aluminum oxide, nitride and hydride compounds contained therein. Preferably a flux consisting of cryolite containing about 20% lithium fluoride is employed.

The resultant alloy product after casting will be found to be substantially free from aluminum oxide, nitride and hydride compounds and may be mechanically deformed to relatively thin sheet, strip or wire by subjecting the same first to hot mechanical deformation to condition the same for cold mechanical deformation, at a temperature approximating 2000° F. to about 50% reduction in area, finishing at a temperature well below its recrystallization temperature, which in most alloys will approximate 1000° F. Thereafter the alloy may be subjected to cold mechanical deformation to final desired thickness or diameter, sheet, strip or wire without intermediate annealing.

The tertiary iron-chromium-aluminum alloys and the quaternary iron-chromium-cobalt-aluminum alloys, heretofore proposed in the art for use as electrical resistant alloys, when treated similarly also will evidence improved ductility and workability over those alloys not so treated, to such an extent that many of the alloys not heretofore obtainable in fine wire or thin sheet or strip form may be so obtained as a result of the practice of the present invention.

As an example, Fe.Cr.Al alloys containing 20% Cr, and from 3% to 10% Al, balance substantially all Fe, except for incidental and unavoidable impurities, have been prepared and treated in accordance with the present invention and have been found on microscopical examination to be uniformly free from seams and stringers heretofore characterizing the untreated alloys and have been found to evidence consistently markedly superior ductility and workability properties over those characteristic of the untreated alloys.

As an indication of the extent of improvement obtained, the 3% Al alloy (Cr 20%, bal. Fe) so treated as hereinabove described with lithium fluoride-containing cryolite flux, when cast into an ingot 4" x 4" and cogged at 2000° F. into a 2" x 2" billet finishing under 1500° F., was found to be substantially free from surface seams or stringers characteristic of such alloys not so treated. The billet when reheated to 2000° F. and rolled on a falling temperature gradient to a $\frac{1}{8}$ inch rod finishing at a temperature under but approximating 1000° F. was found to be capable of being subjected to cold mechanical deformation at room temperatures to wire size and additional cold drawing to .001 inch wire without intermediate annealing. The tensile strength of such cold drawn wire was found to be 85,700 p. s. i which is materially lower than any heretofore obtained, the elongation was 24%, which was materially higher than any heretofore obtained, and the electrical resistance was found to be 650 ohms per c. m. f., a figure that is also materially higher than that obtained with similar alloys not so treated. Hardness tests indicated that the treated alloy was materially softer

than the untreated alloy, confirming the tensile and elongation tests above given. The material above described has been cold flat rolled from the $\frac{1}{8}$ inch rod to .010 inch strip size without intermediate annealing with comparable results to the wire results above given.

Iron-chromium alloys containing 4, 6, 8 and 10% Al and 20% Cr were all capable of extensive hot and cold mechanical deformation to relatively small sized strip and wire without intermediate annealing, as were also various quaternary types of alloys. Microscopical examination of the alloys treated in accordance with the present invention, after prolonged heat-treatment to obtain a stabilized grain structure and agglomeration of contained non-metallic inclusions, indicate by the presence of clean cut grain boundaries and no discernible agglomeration of non-metallic particles that the metal consistently was produced substantially free from aluminum oxide, nitride and hydride impurities as contrasted to material not so treated.

One of the marked advantages obtained by the practice of the present invention is that the Al-containing iron and iron-chromium alloys treated in accordance with the present invention, even after prolonged heat treatment inducing recrystallization and grain growth in the cold mechanically deformed metal, uniformly retain surprising ductility which differentiates the metal from alloys not so treated.

Having hereinabove described the present invention generically and specifically and given several specific embodiments and examples of the

practice of the same, it is believed apparent that many modifications and adaptations may be made therein without essential departure therefrom and all such are contemplated as may fall within the scope of the following claims.

What is claimed is:

1. The method of treating molten heavy metal baths to effect the removal therefrom of aluminum oxide, nitride and hydride compounds, which comprises vigorously agitating the bath over an extended time interval while in contact with a flux comprised of a mixture of alkali metal, alkaline earth metal and aluminum halide compounds non-reducible by aluminum, the major portion of said mixture consisting of compounds having a solubility towards aluminum oxide and the minor portion of said mixture consisting of lithium compounds having a reactivity towards aluminum nitride and hydride compounds and the total amount of said mixture relative to the mass of said molten metal being at least sufficient to dissolve and react with substantially all of the aluminum oxide, nitride and hydride compounds contained in said molten metal.

2. The method of claim 1, said major portion consisting of 70 to 90% cryolite and said minor portion consisting of 10 to 30% of a mixture of lithium fluoride and lithium oxide.

3. The method of claim 1, the said mixture consisting of from 70 to 90% cryolite and from 10 to 30% of a lithium fluoride and lithium oxide mixture containing 90% lithium fluoride and 10% lithium oxide.

VICTOR O. ALLEN.