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PREPARATION OF MANGANESE ALLOYS

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This invention relates to manganese alloys and is especially concerned with the manufacture of objects made of manganese alloys by mixing their component elements in more or less powdered form, compressing into the finished or partially finished form of the object desired, and forming an alloy by heating to a suitable temperature for diffusion of the metal particles into one another. The so-formed objects may be further formed by hot or cold pressing, machining and the like, and may, with certain alloys, be improved by suitable heat treatment.

The practice of producing metal and alloy objects by the general means described above is already known. Such practice, however, has been restricted to metals which can readily be obtained in powdered form and likewise to mixtures of metals in which diffusion takes place sufficiently rapidly at a temperature below the melting point to make the processes practicable. I am also familiar with attempts to use manganese in such compositions and with the difficulties which have attended these attempts. I have found that these difficulties are due, in part, to the problem of preparing manganese metal, such as silico-thermic manganese or alumino-thermic manganese, in a state of fine subdivision because of its hardness. All silico-thermic manganese or alumino-thermic manganese which I have examined contains a film of oxides such as silicon dioxide and aluminum oxide surrounding the grains. I have discovered that the existence of these oxides around the metal grains in metals produced by alumino-thermic and similar processes greatly reduces, if not completely inhibits, the diffusion of this kind of manganese into other metals at temperatures below the melting point of the manganese.

In accordance with my invention, these difficulties are obviated by using electrolytic manganese which is friable, easily powdered, retains a bright surface in air, and contains no oxide films around the grains. The electrolytic manganese which I employ contains at least 99.9% manganese.

In the production of many pressed objects, powdered, electrolytic manganese may be used without further treatment. In the pressing of certain objects, however, particularly those which are composed of a major proportion of manganese, I find it desirable to give the manganese powder a degree of ductility so that it will more accurately fit the mold. I accomplish this by heating the powdered manganese at a temperature above 1000 degrees C. with approximately 4% of finely powdered copper. The copper is intimately mixed with the manganese, and if oxygen and nitrogen are excluded from the powder during the heating operation, sufficient diffusion of the copper into the manganese will take place in a short time, usually approximately thirty minutes, to produce a ductile manganese powder which lends itself readily to mixtures for forming under the press. Where copper is an objectionable constituent of the alloys even in these small amounts, nickel may be used, although with somewhat less satisfactory results, as a considerably longer heating time is required. I have also found that ductile manganese powder may be formed by heating the manganese in ammonia gas at about 450 degrees C. for a short time and subsequently heating in the absence of oxygen to a temperature of approximately 1000 degrees C. Heating in an atmosphere of nitrogen at 1000 degrees C. also brings about a degree of ductility in manganese powder.

While my invention is concerned broadly with the successful use of powdered electrolytic manganese of at least 99.9% purity as a constituent for all types of alloys such as steels, stainless steels, bronzes, "Monel" metal, and similar alloys in which manganese has been used in the past, I find that my present invention may be practiced with conspicuous success to produce the manganese alloys described in my copending applications, Serial No. 219,501, filed July 16, 1938, now Patent 2,286,199, dated June 16, 1942; Serial No. 267,708, filed April 13, 1939; Serial No. 267,706, filed April 13, 1939; and Serial No. 267,707, filed April 13, 1939.

My invention is especially valuable in producing the so-called stainless alloys which are composed essentially of iron and chromium. Nickel has also been used as a constituent of these alloys and, to a less extent, manganese and copper. The production of this type of alloy by the method of mixing has been greatly restricted by the fact that iron, chromium and nickel, which together form more than 95% of most alloys of this type, have approximately the same melting points, all being in the general neighborhood of 1500 degrees C. Diffusion in an object formed of mixed powders of these metals is, therefore, very slow at any temperature below the point at which they are all molten and at which the formed object would therefore lose its shape. I have found that if a considerable proportion of manganese be used in these alloys, either with or without the elimination of nickel or copper, diffusion takes place at a temperature

considerably below the melting point of iron and chromium, which form the major part of the mixture, and consequently homogeneous articles may be obtained without partial fusion or distortion of the part.

As an example of my invention in this regard, I mix 56 parts of iron powder, 18 parts of chromium powder and 26 parts of electrolytic manganese powder of at least 99.9% purity. This mixture is pressed into the desired shape and heated at a temperature of 1200 degrees C. for two hours in an atmosphere of hydrogen. The part is then quenched in water. The object so formed is relatively soft and magnetic. I then straighten the part if any warpage has taken place, and perform any machining or further pressing operations which are necessary to produce the final part. If it is desired to have the final part hardened, I heat the part at about 725 degrees C. for ten minutes and cool in air. The resulting part is hard and stainless.

In another example of my invention, I mix 95 parts of electrolytic manganese powder of at least 99.9% purity with 5 parts of copper powder. This mixture is heated, without being compressed, in an atmosphere of hydrogen at 1000 degrees C. for two hours. It is then cooled in hydrogen and mixed with 27 parts of powdered nickel. The resulting alloy is readily pressed into an accurate form because of the ductility of the metal powder and is heated in a hydrogen atmosphere for thirty minutes. The resulting part is strong and ductile and possesses a coefficient of expansion of 25×10^{-6} cm./cm./deg. C.

In still another example of my invention, I mix 60 parts of copper powder with 20 parts of electrolytic manganese powder of at least 99.9% purity and 20 parts of powdered nickel. This mixture is pressed into the desired parts and heated in a non-oxidizing atmosphere at a temperature of 800 degrees C. for two hours. The object is then quenched in water and is in suitable form for machining or additional forming operations. If it is desired to have the part in hardened form, it may be hardened by heating for twelve hours at 450 degrees C.

In yet another example of my invention, I mix 70 parts of zinc powder with 20 parts of electrolytic manganese powder and 10 parts of copper powder of at least 99.9% purity. This mixture is pressed into the desired form and heated to a temperature of 400 degrees C. for 5 hours in a stream of hydrogen. The resulting part has a hardness of approximately Rockwell C 15 and is tough and strong.

These examples make clear the practice of my invention. It will be obvious that the pressures which will be used for forming the parts will depend upon the density and strength desired in the finished objects. I have found that pressures of 50,000 pounds per square inch are usually adequate, but lower or higher pressures may be used, the latter particularly where it is desired to form very dense and strong parts.

While I prefer to use my invention for the preparation of alloys of manganese, it also encompasses the preparation of objects of pure manganese metal. The preparation of such objects by casting is not possible because of the expansion of manganese which takes place on its transformation from the higher temperature form to the lower temperature form. My invention is, therefore, applicable to the production of products in the alpha form of manganese by compressing powdered electrolytic manganese of at least 99.9% purity under high pressures and heating to a temperature below 742 degrees C. I prefer to carry out the heating under pressure, but satisfactory results may be obtained without pressing in this way.

In another phase of my invention, a ductile powder is prepared, consisting principally of manganese, by alloying electrolytic manganese of at least 99.9% purity with one or more of the metals, nickel and copper, in an amount from 4% to 15%, and in the usual way, that is, by melting the metals together. Such an alloy, when quenched from a temperature above 1000 degrees C., is ductile and may be suitably worked into relatively thin strips by rolling. These strips are now heated at a temperature of from 600 degrees C. to 740 degrees C. whereupon they become embrittled. This embrittled material may be readily pulverized and, after pulverization, is heated in a non-oxidizing atmosphere at a temperature above 750 degrees C., preferably at about 1000 degrees C., and cooled. The resulting powder is ductile and suitable for formation into parts by pressing or for mixing with other metal powders for pressing and alloying by diffusion at a relatively high temperature.

As a specific example of this aspect of my invention, an alloy is made of 4 parts of copper and 96 parts of electrolytic manganese of at least 99.9% purity. This alloy is heated at 1100 degrees C. and quenched. It is then rolled into strips approximately ¼ inch thick. These strips are heated at a temperature of 700 degrees C. for 24 hours. They are then ground to a powder passing 100 mesh by a combination of hammer mill and ball mill treatment. The powdered alloy is then packed loosely in a heat resisting container and heated for ten minutes at a temperature of 1100 degrees C. The powder is allowed to cool in the container to avoid oxidation. This powder is now compressed into suitable forms under pressure of about 150,000 pounds per square inch. After this compression, it is again heated at 500 degrees C. to relieve strains and otherwise condition it. The objects formed in this way are found to have an abnormally high damping capacity and are suitable for many uses where elimination of vibration is necessary.

What I claim as new and desire to protect by Letters Patent of the United States is:

1. An alloy formed by sintering a compressed mixture of metal powders containing a major proportion of powdered electrolytic manganese of at least 99.9% purity.

2. A malleable article containing a major proportion of manganese, prepared by sintering a compressed mixture of powdered electrolytic manganese of at least 99.9% purity with copper.

3. An alloy, substantially entirely devoid of carbon and having as major constituents, iron, manganese and chromium, formed by sintering powdered electrolytic manganese of at least 99.9% purity with the other constituent metals in powdered form after compressing to form a compact object, the manganese constituting at least 20% of the composition.

4. A method of making manganese alloys containing at least 20% manganese, which comprises providing powdered electrolytic manganese having a purity of at least 99.9%, compressing the same together with another metal powder into an object of desired shape, and heating the resulting shaped object at a temperature sufficiently high, but below the melting point of the

metal powders, to cause diffusion of the metal powders into each other.

5. A method of preparing manganese alloys containing at least 20% of manganese and substantially entirely devoid of carbon, which comprises providing powdered electrolytic manganese having a purity of approximately 99.9%, compressing said powdered electrolytic manganese together with powdered iron and powdered chromium, to produce an article of desired shape, and heating the resulting article at an elevated temperature, but below the melting point of the alloying constituents, to an extent sufficient to cause diffusion of the metal powders into each other.

6. An alloy formed by sintering a compressed shaped mixture of metal powders containing at least 20% of powdered electrolytic manganese having a purity of approximately 99.9%.

7. A method of making manganese alloys which comprises providing powdered electrolytic manganese having a purity of at least 99.9% and which has rendered ductile by a treatment including subjection to elevated temperatures, compressing the same together with another metal powder into an object of desired shape, and heating and resulting shaped object at a temperature sufficiently high, but below the melting point of the metal powders, to cause diffusion of the metal powders into each other.

8. The method of making manganese alloys which comprises providing powdered electrolytic manganese having a purity of at least 99.9% and which has been rendered ductile by alloying the same with a minor percentage of at least one metal selected from the group consisting of copper and nickel, compressing the powdered ductile electrolytic manganese together with another metal powder into an object of desired shape, and heating the resulting shaped object at a temperature sufficiently high, but below the melting point of the metal powders, to cause diffusion of the metal powders into each other.

9. A method of making manganese alloys containing at least 20% manganese, which comprises providing powdered electrolytic manganese having a purity of at least 99.9% and which has been rendered ductile by alloying therewith approximately 4% of copper, compressing the same together with another metal powder into an object of desired shape, and heating the resulting shaped object at a temperature sufficiently high, but below the melting point of the metal powders, to cause diffusion of the metal powders into each other.

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