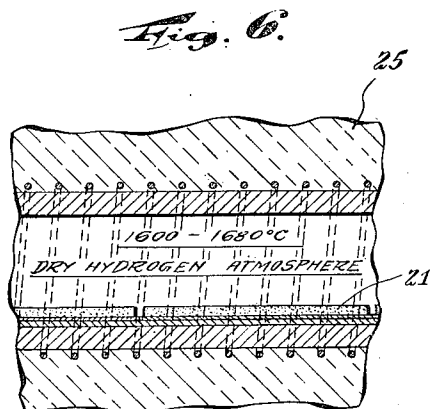
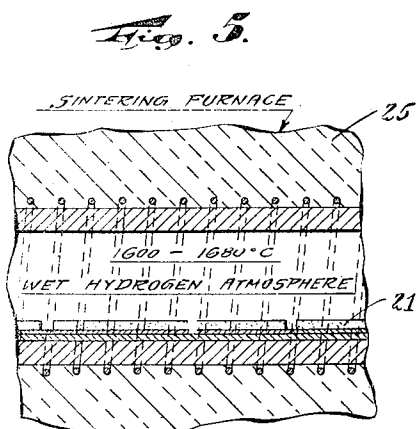
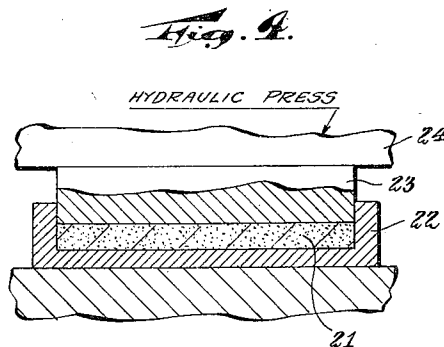
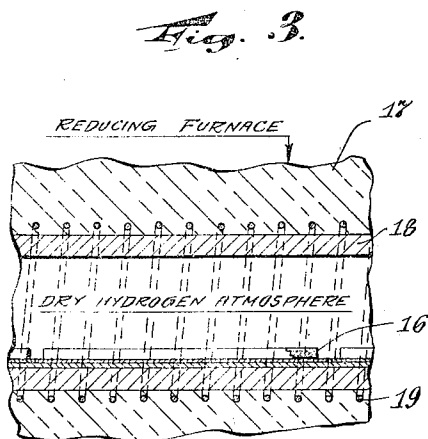
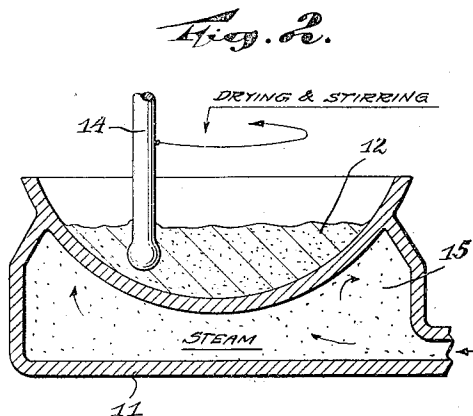
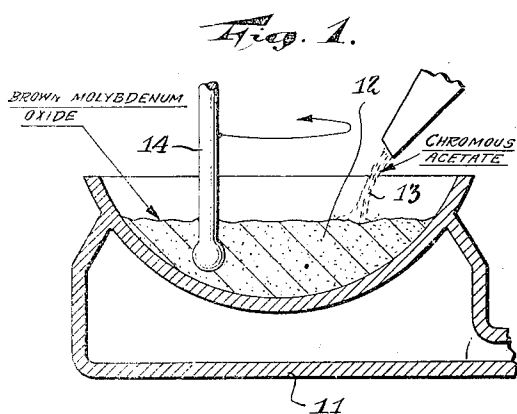


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MANUFACTURE OF ALLOYS
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MANUFACTURE OF ALLOYS

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4 Claims. (Cl. 75-22)

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This invention relates to readily oxidizable refractory metal such as molybdenum, tungsten, and mixtures thereof, alloyed with metal such as chromium, to protect the same against oxidation when heated.

The principal object of my invention, generally considered, is to provide alloys of molybdenum and/or tungsten, containing sufficient chromium, whereby the readily oxidizable refractory metal is protected when used at elevated temperatures in air or oxygen-containing atmospheres.

Another object of my invention is to provide chromium-molybdenum, chromium-tungsten, and tertiary alloys, in which the chromium content, although relatively small, is sufficiently high to protect the molybdenum and tungsten from oxidation at reasonably elevated temperatures, even though not enough to reduce the molybdenum or tungsten melting point, measured in degrees C., more than a few percent.

A further object of my invention is to produce an alloy of molybdenum and chromium, by taking an oxide of molybdenum, such as the sesquioxide or dioxide, Mo_2O_3 or MoO_2 , wet it with a solution of a salt of chromium, such as the acetate, nitrate or chloride, to the proper proportions of chromium, dry, and reduce in hydrogen.

A still further object of my invention is to produce alloys of metals such as molybdenum and tungsten with metal, such as chromium, to protect against oxidation at elevated temperatures, comprising impregnating an oxide of molybdenum, such as the dioxide, or the corresponding oxide of tungsten, with a solution of a salt of chromium, drying with constant stirring to avoid segregation of the liquid, reducing in hydrogen at a relatively low temperature to get molybdenum or tungsten powder and well-distributed chromium oxide, press, treat the article so-produced in wet hydrogen to a well-sintered mass at relatively high temperatures, and finally treat the sintered article in dry hydrogen to hasten and complete the reduction of chromium and its alloying with the other metal.

Other objects and advantages of the invention will become apparent as the description proceeds.

Referring to the drawing:

Fig. 1 is a vertical sectional view of a receptacle for mixing the selected oxide of molybdenum with a solution of the selected salt of chromium.

Fig. 2 shows the apparatus of Fig. 1 during a subsequent stage in which the mixture is being dried, as by means of steam, while stirring.

Fig. 3 is a vertical longitudinal sectional view of an electric reducing furnace in which the molyb-

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denum oxide constituent of the mixture is reduced.

Fig. 4 is a vertical sectional view of a hydraulic press in which slugs of the mixture, reduced in the furnace of Fig. 3, are formed.

Fig. 5 is a vertical sectional view of a sintering furnace in which the slugs, produced in the press of Fig. 4, are sintered.

Fig. 6 is a vertical sectional view of the furnace shown in Fig. 5 during a subsequent treatment in which the wet hydrogen is replaced by dry hydrogen.

I will now describe the preparation of a molybdenum-chromium alloy of proportions such that the melting point will be near that of the molybdenum, that is, above 90% of the melting point of molybdenum measured in degrees C., for small percentages of chromium say from about $\frac{1}{2}$ to 2%, as disclosed in the Anton patent, No. 2,304,297, for example. It will, however, be understood that a similar process is applicable to the manufacture of other molybdenum-chromium alloys, as well as to the manufacture of alloys of tungsten and chromium and tungsten, molybdenum and chromium.

Referring to the drawing in detail, there is shown in Fig. 1 a receptacle 11 in which is placed a desired mass of a powdered oxide of molybdenum 12, such as the brown variety MoO_2 . Upon this mass is poured a solution 13 of a salt of chromium, such as the acetate, nitrate or chloride, which are equivalent for the purpose, as they all are soluble and no deleterious material remains after decomposition. The amount of solution applied depends on the concentration and on the percentage of chromium desired in the alloy. During the addition of the solution, the mass is constantly stirred, as by means of a rod 14, while the receptacle is heated, preferably by means of steam 15. On account of drying with constant stirring, segregation of the liquid is avoided and a mixture of molybdenum oxide uniformly impregnated with the selected salt of chromium, is obtained.

The dry powdered impregnated oxide 12 is then placed in suitable receptacles or "boats" 16 and passed through a reducing furnace 17, comprising a suitably insulated tube 18 of refractory material, such as alumina, surrounded by a coil 19 of molybdenum or tungsten through which electricity is passed to supply the heating power. The atmosphere in the furnace, for reducing the powder as well as protecting the heating coil, is preferably dry hydrogen, although other reducing atmospheres may be used, if desired. The furnace

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may be of the type illustrated in Fig. 1 of the Hall et al. Patent No. 2,431,690, dated December 2, 1947 and owned by the assignee of the present application. During this treatment the furnace need only be operated at a relatively low temperature, just sufficient to effect a reduction of the molybdenum oxide to molybdenum, a schedule for such a reduction being generally in accordance with the Rennie application, Ser. No. 471,604, filed January 7, 1943, now Patent No. 2,402,084, dated June 11, 1946, that is from 400° to 1075° C., except that it is not necessary to use diluted hydrogen because the starting oxide is the dioxide rather than molybdenum trioxide, although any of the reducing atmospheres there suggested may be employed.

After the reduction has been effected, the powder is removed from the furnace and formed into slugs or other desired articles 21, as in a die 22 by means of a plunger 23 operated by a hydraulic press 24, so that sufficient pressure is applied to allow for handling of the formed slugs.

As an alternative, especially where high percentages of chromium are used in making the alloy, it may be desirable to remove the powder from the reduction furnace and treat it in a sintering furnace, such as illustrated in Fig. 5 or Fig. 6, in a dry hydrogen atmosphere at temperatures between 1600° and 1680° C., in order to remove the bulk of the oxygen from the chromium oxide to avoid substantial shrinkage or the possible formation of voids in the slugs or articles subsequently pressed from the powder.

The pressed slugs or other articles 21 are, after removal from the die, placed in a sintering furnace 25 which may be the same or like the furnace 17, except that said slugs are there first treated in a wet hydrogen or other reducing atmosphere, like the molybdenum articles of the Hall et al. Patent No. 2,431,690, previously referred to, and owned by the assignee of the present application to temperatures between 1600° and 1680° C. until the slugs or other articles are well-sintered. This treatment produces sintered molybdenum with partly-reduced chromium oxide well-distributed therethrough.

The treatment is then continued at about the same temperature, that is, between 1600° and 1680° C., as illustrated in Fig. 6, with the substitution of dry hydrogen or other reducing atmosphere, for wet hydrogen or other reducing atmosphere, to thereby hasten the reduction of the chromium and its alloying with the molybdenum until the operation is completed. It will be understood that the same furnace 25 is preferably employed, merely the water content of the treating atmosphere eliminated so that it is dry.

Although it will be understood that chromium is not readily reduced by hydrogen when free, yet in the presence of another metal such as molybdenum which absorbs or alloys with the nascent chromium as it becomes reduced, such reduction is effected and the final product is a well sintered alloy of molybdenum and chromium.

Although I have specifically disclosed the manufacture of an alloy of molybdenum and chromium, it will be understood that a similar process may be employed for manufacturing alloys of tungsten and chromium and molybdenum, tungsten and chromium, the only difference being that for tungsten alloys the sintering temperature is correspondingly raised to that usually employed for tungsten, from that usually employed for molybdenum, when tungsten is substituted for molybdenum.

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Although preferred embodiments of my invention have been disclosed, it will be understood that modifications may be made within the spirit and scope of the appended claims.

I claim:

1. The method of forming an alloy of a metal selected from the group consisting of molybdenum, tungsten and mixtures thereof, with such a proportion of chromium that its melting point will be above 90% of that of the selected metal as measured in degrees C., for protection against oxidation at elevated temperatures, comprising forming an intimate mixture of an oxide of the selected metal with a solution of a salt of chromium in the amount to give the proportion referred to, drying the mixture and heating it in a reducing atmosphere at a relatively low temperature to produce the selected metal with an oxide of chromium well-distributed therethrough, pressing said mixture sufficiently to allow for handling the formed articles, treating said formed articles in a wet reducing atmosphere at a temperature between 1600° and 1680° C. to produce a well-sintered mass of metal, with some reduced chromium, and finally treating the pressed mass in a dry reducing atmosphere at a temperature between 1600° and 1680° C. to hasten the complete reduction of chromium and its alloying with the selected metal.

2. The method of forming an alloy of a metal selected from the group consisting of molybdenum, tungsten and mixtures thereof, with such a proportion of chromium that its melting point will be above 90% of that of the selected metal as measured in degrees C., for protection against oxidation at elevated temperatures, comprising forming an intimate mixture of an oxide of the selected metal with a solution of a salt of chromium in the amount to give the proportion referred to, drying the mixture and heating it in hydrogen at a relatively low temperature to produce the selected metal with an oxide of chromium well-distributed therethrough, pressing said mixture sufficiently to allow for handling the formed articles, treating said formed articles in wet hydrogen at a temperature between 1600° and 1680° C. to produce a well-sintered mass of metal with some reduced chromium, and finally treating the pressed mass in dry hydrogen at a temperature between 1600° and 1680° C. to hasten the complete reduction of chromium and its alloying with the selected metal.

3. The method of forming an alloy of molybdenum with such a proportion of chromium that its melting point will be above 90% of that of molybdenum as measured in degrees C., for protection against oxidation at elevated temperatures comprising forming an intimate mixture of molybdenum oxide with a solution of a salt of chromium, drying the mixture and heating it in hydrogen at a relatively low temperature to produce molybdenum with an oxide of chromium well-distributed therethrough, pressing said mixture sufficiently to allow for handling the formed articles, treating said formed articles in wet hydrogen at a temperature between 1600° and 1680° C. to produce a well-sintered mass of molybdenum, with some reduced chromium, and finally treating the pressed mass in dry hydrogen at a temperature between 1600° and 1680° C. to hasten the complete reduction of chromium and its alloying with the molybdenum.

4. The method of forming an alloy of molybdenum with such a proportion of chromium that its melting point will be above 90% of that of

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molybdenum as measured in degrees C., comprising forming an intimate mixture of molybdenum oxide with a solution of a salt of chromium in the amount to give the proportion referred to, drying said mixture and heating in dry hydrogen at a temperature between 1600° and 1680° C., in order to remove the bulk of the oxygen from the chromium oxide to avoid substantial shrinkage and the possible formation of voids, pressing said mixture sufficiently to allow for handling the pressed mass, treating said pressed mass in a wet reducing atmosphere at a temperature between 1600° and 1680° C. until well sintered, and finally treating the pressed mass in a dry reducing atmosphere at between 1600° and 1680° C. to hasten the complete reduction of chromium and its alloying with molybdenum.

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