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**METHOD OF MAKING COMPOSITE ARTICLES**  
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This invention relates to a method of making fine-grained, hard alloys utilizing the principles of soliquidus (solidus-liquidus) component interchange, and to a method of making shaped articles thereof.

In the prior art practice of making alloys hardened by high melting point compounds, the usual procedure involves the steps of melting all of the constituents in an induction furnace, heating to the "top side," i.e., a temperature sufficiently high to melt all of said constituents (usually over 4000° F.), and thereafter casting. The resultant castings of this procedure are characterized, in the main, by a very coarse dendritic distribution and the segregated condition of the cast material is such that a tremendous amount of working is required before any degree of structural homogeneity is obtained which permits substantially uniform physical properties. As indicated heretofore, the ultimate melting temperature of alloying constituents is quite high, from which fact it necessarily follows that requirements for materials of construction, e.g., furnace linings, crucibles, molds, etc., are very rigid and constitute a distinct disadvantage. In addition, the manufacture of hard alloy shapes by prior art methods is attended by the further disadvantage of high capital investment. As an illustrative example of the prior art, consider an attempt to prepare a nickel base alloy containing an appreciable volume fraction of  $TiB_2$ . In such case, the temperature range between the melting point of the matrix metal, i.e., nickel, and the melting point of the compound, i.e.,  $TiB_2$ , is greater than 1000° F. and constitutes a soliquidus spread of such magnitude that density differences and cooling rate practicalities are virtually prohibitive of the obtention of a final alloy having a substantially distributed, high volume fraction of said compound.

Accordingly, a principal object of the present invention is to provide an improved method of making alloys containing high melting point compounds which method is unattended by the foregoing disadvantages of the prior art.

Another object of the invention is to provide a method of making substantially segregation-free alloys comprising a ductile matrix containing a high volume fraction of hard melting-point compounds.

A further object of the invention is to provide a method of making shaped articles of substantially segregation-free alloys hardened by refractory compounds, which articles are not readily made by other methods.

Other objects of the invention will be apparent from the following description.

In general, the method of the invention contemplates the preparation of fine grained, hard alloys comprising a matrix metal and a high volume fraction of a high melting point compound by mixing two or more ingredients, the resultant admixture containing all of the essential components of said high melting point compound and the individual compositions of said ingredients being so formulated that each ingredient contains no more than a relatively small amount of all of said components and at least one of said ingredients has a liquidus temperature which is far below that of said high melting point compound and substantially below that of said matrix metal. This latter requirement is important in the sense that as the liquidus temperature of the most refractory phase

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of the starting ingredients approaches the liquidus temperature of the most refractory phase of the final alloy, the advantage of the method vanishes. To accrue the principal advantages of the inventive method, the liquidus temperatures of those starting ingredients which are melted during the practice of said method should be sufficiently low to simplify materials of construction problems, such as those associated with choice of crucible materials, and the temperature at which the sought high melting point compound forms should be sufficiently lower than the melting point thereof as to constitute effectively a substantial super-cooling. In this latter connection, what is meant is that the high melting point compound should form at a temperature below the melting point of the compound and at least one of the components thereof should derive from a material in the liquid state. Ordinarily, formation of a solid high melting point compound at a temperature lower than its melting point would be accomplished by super-cooling the molten compound. In such case the difference between the melting point and the temperature at which the solid compound actually forms is the measure of super-cooling. In accordance with the practice of the instant invention, for the same system, the measure of super-cooling is the same. However, beyond this feature similarities cease to exist. Obviously, the prior art method necessitates initially attaining a temperature above the melting point of the high melting point compound, whereas the inventive method does not. A major disadvantage of the prior art method is its lack of effective control over compound coarsening and distribution. This result accrues from cooling of the molten mass which forms phases in the order of decreasing refractoriness, thus permitting the growth of more refractory phases to trap lesser refractory phases resulting in dendritic segregation. On the other hand, the inventive method exhibits greater control over the size and distribution of high melting point compounds within the matrix metal since such compounds form only at the expense of the low melting starting mixture, i.e., the components of said compounds are necessarily extracted from said mixture, the liquidus temperature of which is thereby raised. Ensuing solidification of the mixture effectively holds the high melting point compounds at formation sites and segregation is thus minimized or obviated entirely.

In accordance with the inventive concept, soliquidus component interchange may take place between starting ingredients while each is present only as a liquid phase or while one is present as a liquid phase and another is present as a solid phase. Exemplary of the former case is the mixing of molten starting ingredients or the mixing of solid starting ingredients having the same or approximately the same melting points, followed by heating to effect melting of all of said ingredients. Exemplary of the latter case is the mixing of solid starting ingredients having dissimilar melting points, followed by heating to effect melting of the lower melting ingredient. In this latter case it is, of course, necessary that the higher melting ingredients be finely divided or powdered in order that a maximum surface area be available to promote component interchange between the liquid and solid phases. An inherent advantage of the invention accrues from the fact that this requirement is unnecessary where an ingredient undergoes melting, in which case granular or even lump material may be employed.

The invention also contemplates soliquidus component interchange reactions involving both liquid-liquid and liquid-solid reactions, either consecutively or simultaneously during the course of the formation of a desired final alloy. Thus, it will be seen that the invention requires the provision, in each contemplated system, of at

least one starting ingredient having a melting point appreciably lower than that of the lower melting material, i.e., the matrix metal, of the desired final alloy. For this purpose, certain low melting point compositions are useful, e.g., eutectic or near-eutectic compositions.

Illustrative of alloys produced in accordance with the present invention, together with the low melting starting mixtures therefor, are the examples given below in Table I:

Table I

| Low melting starting mixture |                           | Final alloy               |                                 |
|------------------------------|---------------------------|---------------------------|---------------------------------|
| Alloy 1                      | Alloy 2                   | Matrix                    | High melting point compound     |
| Ni+B                         | Ni+Ti                     | Ni                        | TiB <sub>2</sub>                |
| Ni+Co+B                      | Ni+Ti+(Fe, W, Mo, Cb, Cr) | Ni+Co+(Fe, W, Mo, Cb, Cr) | TiB <sub>2</sub>                |
| Ni+Fe+C                      | Ni+Fe+Ti                  | Ni+Fe                     | TiC                             |
| Ni+Co+Fe+C                   | Ni+Ti+(Fe, W, Mo, Cb, Cr) | Ni+Co+Fe+(W, Mo, Cb, Cr)  | TiC                             |
| Fe+C                         | Ni+Ti                     | Fe                        | TiC                             |
| Fe+Ni+Co+C                   | Fe+Ti+(Ni, Co, Cr, Mo)    | Fe+Ni+Co+(Cr, Mo)         | TiC                             |
| Co+C                         | Co+Ti                     | Co                        | TiC                             |
| Co+B                         | Co+Ti                     | Co                        | TiB <sub>2</sub>                |
| Cu+B                         | Cu+Ti                     | Cu                        | TiB <sub>2</sub>                |
| Cu+Si                        | Cu+Ti                     | Cu                        | Ti <sub>3</sub> Si <sub>2</sub> |
| Cu+B                         | Cu+Zr                     | Cu                        | ZrB <sub>2</sub>                |
| Ni+B                         | Ni+Zr                     | Ni                        | ZrB <sub>2</sub>                |

NOTE.—In general, Zr and Hf can be substituted wherever Ti appears in Table I.

In the case of the examples listed in Table I, the selection of Alloy 2 is based essentially upon the existence of a low melting point eutectic comprising a potent compound former, e.g., Ti, and a useful matrix metal, e.g., Ni. Alloy 1 is selected with the thought in mind of providing a sufficient amount of a particular non-metal, e.g., B, which will combine with the compound former of Alloy 2 to provide a high volume fraction of a high melting point compound. To secure the chief advantages of the invention, such a compound should exhibit a minimum super-cooling effect of about 400° C. While all of the Alloy 1 examples of Table I are denoted as alloys of the matrix metal and the non-metal component of the high melting point compound, e.g., Ni+B (Ni containing B either in solid solution or as a dissociable compound), nevertheless, it is within the scope of the invention to provide the non-metal in elemental form either in place of Alloy 1 or as a separate addition thereto.

Although the principles of the inventive method as applied to the mixing of liquids require essentially that no one of the low melting starting mixture alloys should contain all of the essential components of the high melting point compound of the final alloy, a small admixture may in some cases be desirable for the purpose of altering characteristic of a melt or for adding more of a component than a single melt can hold within the temperature requirements. In any case, the bulk, e.g., over 60%, of the high melting point compound must be formed in situ after mixing melts of the starting alloys in order to realize the full advantages of the invention.

As indicated heretofore, the mixing of more than two melts is within the scope of the present invention. In such case, however, the justification for any additional advantage to be gained thereby should be weighed against the additional complication of necessarily mixing a number of melts simultaneously and with great rapidity.

Exemplary of the aspect of the invention involving principally liquid-liquid reaction is the procedure of preparing two melts, the one a eutectic composition of Ni+B, melting point less than about 2000° F., the other eutectic composition of Ni+Ti, also having a melting point less than about 2000° F., followed by mixing said melts to form TiB<sub>2</sub> crystallites, with effectively at least a 1000° F. super-cool and hence, a very high nucleation rate. While the reaction is strongly exothermic, it is important to note that the degree of exothermicity is insufficient to cause reheating to a temperature approaching that of the TiB<sub>2</sub> liquidus. Solidification of the super-cooled "mush" can

occur in situ or upon casting into any desired form and results in a fine-grained structure in contrast to the coarse-grained structure obtained by following the "top side" temperature practice of the prior art.

Where the principles of soliquidus component interchange are to be applied by way of reheating a low melting starting mixture of alloys in solid form, it is advantageous in certain instances to add part or even all of one or some of the essential components of the high

melting point compound as a separately prepared powder. This may greatly simplify comminution of said components or permit additions thereof in quantities considerably beyond solubility limits.

The liquid-solid reaction aspect of the invention may be illustrated by application thereof to melts of Ni+B and Ni+Ti which, as aforementioned, are amenable also to the liquid-liquid reaction procedure. In this case the two melts are separately solidified and granulated (fine powders not being necessary or desirable), mixed, and heated to a temperature slightly higher than the melting point of the lower melting component, i.e., Ni+B. Immediately thereafter, pressure is applied to the heated mix, e.g., by spinning the mold or forcing the mix through orifices into a multiplicity of molds. Micromixing is accomplished by wetting and penetration (ultrasonics may also be valuable here), and is aided by the exothermic reaction involved.

In another case, such as Ni hardened by a large volume fraction, e.g., 30 to 80%, of TiC, the nickel melt will hold only a small fraction of the required carbon, and comminution of the solidification alloy is very difficult without loss of carbon, the latter being present as graphite. Hence, rather than employing the mixing of liquids procedure the preparation of the desired alloy preferably proceeds by the heating of intimately mixed powders of graphite and an approximate eutectic composition of Ni+Ti, the latter being chosen so as to have a melting point no higher than about 1200° C.

While some or most of the Ni could be added as Ni powder, most (at least 90%) of the Ti must be added as a low melting alloy. Otherwise, the inventive method will show little or no advantage over prior art powder metallurgy methods wherein the high melting compound, in this case TiC, is pre-prepared and used as such. To illustrate, a mixture of 10 grams of finely divided graphite, 60 grams of granular Ti-30% Ni eutectic alloy, and 80 grams of granular Ni, upon heating under light pressure to about 1200° C., results in a mush or pasty mix comprising a matrix of Ni throughout which there is uniformly distributed 50 volume percent of TiC. For a short period of time, up to a few seconds or minutes, after reaching the eutectic melting temperature, the pasty condition of the mix remains and permits of ready plastic deformation, e.g., forcing into molds. After solidification the resultant fine-grained, hard alloy has a density which approaches the theoretical, and soaking for the purpose of densification is entirely unnecessary. However, sev-

eral hours of soaking for the purpose of homogenization may in some cases be desirable after removal of the alloy from the mold. This would be done at temperatures increasing with time up to within about a hundred centigrade degrees of the solidus temperature of the alloy.

Among the outstanding advantages flowing from the practice of the present invention are the following: modest requirements for materials of construction; low to moderate gauge pressures encountered even at the highest temperatures employed; feasibility in many instances of utilizing granular material, e.g., about minus 100 mesh, as well as finely powdered material, e.g., micron particle size; ability to obtain a finer and more uniform distribution of high melting point compounds in a massive piece than is possible by prior art techniques; ability to make some compositions which cannot be made at all by prior art techniques.

While only a restricted number of examples have been given in the above specification, it is understood, of course, that the present invention is not limited thereto, since many modifications thereof may be made and the appended claims intend to cover such modifications as fall within the true spirit and scope of the invention.

I claim:

1. A method of making shaped metallic articles having a fine grained microstructure and exhibiting improved hardness and comprising an alloy containing a matrix metal and at least one high melting point compound, comprising: preparing in a form an admixture of at least two substances, the one substance consisting of a molten alloy, said alloy having a melting point lower than that of said matrix metal, and the other substance comprising at least one member selected from the group consisting of a non-metal and an alloy thereof, said substances providing all of the essential components of said high melting point compound and in such amount as to result in a substantial increase in the melting point of the mass when reaction between components in different ones of said substances occurs, said substances being so composed individually that each contains no more than a relatively small amount of all of said components; the energy released from a chemical reaction causing formation of said compound by chemical reaction of components in said substances being such in relation to the amounts and heat capacity of materials present as to raise the temperature of the system to a temperature not exceeding the melting point of the matrix metal; and maintaining the temperature of said admixture substantially less than the melting point of said matrix metal until solidification of said mass occurs.

2. A method of making shaped metallic articles having a fine grained microstructure and exhibiting improved hardness and comprising an alloy containing a matrix metal and at least one high melting point compound, comprising: preparing an admixture of at least two substances, the one substance consisting of a molten alloy, said alloy having a melting point lower than that of said matrix metal, and the other substance comprising at least one member selected from the group consisting of a non-metal and alloy thereof, said substances providing all of the essential components of said high melting point compound and in such amount as to result in a substantial increase in the melting point of the mass when reaction between components in different ones of said substances occurs, said substances being so composed individually that each contains no more than a relatively small amount of all of said components; casting said admixture into molds; the energy released from a chemical reaction causing formation of said compound by chemical reaction of components in said substances being such in relation to the amounts and heat capacity of materials present as to raise the temperature of the system to a temperature not exceeding the melting point of the matrix metal; and maintaining the temperature of said admixture substantially less than the melting point

of said matrix metal until solidification of said mass occurs.

3. A method as in claim 2 wherein the step of casting is accompanied by the application of pressure to said admixture.

4. A method as in claim 3 wherein said application of pressure is accomplished by spinning said molds.

5. A method as in claim 3 wherein said application of pressure is accomplished by forcing said admixture through orifices into a multiplicity of molds.

6. A method of making fine grained, hard alloys containing a matrix metal, M, and at least one high melting point compound, C, said method comprising: preparing an admixture of at least two substances, A and B, said substances having a melting point lower than that of said matrix metal, M, and being present in such amount as to result in a substantial increase in the melting point of the mass upon reaction between components in different ones of said substances occurs, wherein at least one of said substances is molten and wherein A, B, M and C are selected from the same grouping consisting of one of the following groupings:

| Grouping | A               | B                                 | M                                 | C                               |
|----------|-----------------|-----------------------------------|-----------------------------------|---------------------------------|
| 1-----   | Ni+B-----       | Ni+Ti-----                        | Ni-----                           | TiB <sub>2</sub>                |
| 2-----   | Ni+Co+B-----    | Ni+Ti+<br>(Fe, W, Mo,<br>Cb, Cr). | Ni+Co+<br>(Fe, W, Mo,<br>Cb, Cr). | TiB <sub>2</sub>                |
| 3-----   | Ni+Fe+C-----    | Ni+Fe+Ti-----                     | Ni+Fe-----                        | TiC                             |
| 4-----   | Ni+Co+Fe+C----- | Ni+Ti+<br>(Fe, W, Mo,<br>Cb, Cr). | Ni+Co+Fe+<br>(W, Mo,<br>Cb, Cr).  | TiC                             |
| 5-----   | Fe+C-----       | Fe+Ti-----                        | Fe-----                           | TiC                             |
| 6-----   | Fe+Ni+Co+C----- | Fe+Ti+<br>(Ni, Co,<br>Cr, Mo).    | Fe+Ni+Co+<br>(Cr, Mo).            | TiC                             |
| 7-----   | Co+C-----       | Co+Ti-----                        | Co-----                           | TiC                             |
| 8-----   | Co+B-----       | Co+Ti-----                        | Co-----                           | TiB <sub>2</sub>                |
| 9-----   | Cu+B-----       | Cu+Ti-----                        | Cu-----                           | TiB <sub>2</sub>                |
| 10-----  | Cu+Si-----      | Cu+Ti-----                        | Cu-----                           | Ti <sub>2</sub> Si <sub>3</sub> |
| 11-----  | Cu+B-----       | Cu+Zr-----                        | Cu-----                           | ZrB <sub>2</sub>                |
| 12-----  | Ni+B-----       | Ni+Zr-----                        | Ni-----                           | ZrB <sub>2</sub>                |

and maintaining the temperature of said admixture substantially less than the melting point of said matrix metal, M, until solidification of said mass occurs.

7. A method of making fine grained, hard alloys containing a matrix metal and at least one high melting point compound, said method comprising: preparing an admixture of at least two substances, the one substance consisting of a molten alloy, said alloy having a melting point lower than that of said matrix metal, and the other substance comprising a member selected from the group consisting of a non-metal and an alloy thereof, said substances providing all of the essential components of said high melting point compound and in such amount as to result in a substantial increase in the melting point of the mass when reaction between components in different ones of said substances occurs, said substances being so composed individually that each contains no more than a relatively small amount of all of said components, the energy released from a chemical reaction causing formation of said compound by chemical reaction of components in said substances being such in relation to the amounts and heat capacity of materials present as to raise the temperature of the system to a temperature not exceeding the melting point of the matrix metal, said step of preparing an admixture comprising admixing said molten alloy with said other substance in molten form; and maintaining the temperature of said admixture less than the melting point of said matrix metal until solidification of said mass occurs.

8. A method of making fine grained, hard alloys containing a matrix metal in at least one high melting point compound, said method comprising: preparing an admixture of at least two substances, the one substance consisting of a molten alloy, said alloy having a melting point lower than that of said matrix metal, and the other substance comprising a member selected from a group

consisting of a non-metal and an alloy thereof, said substances providing all of the essential components of said high melting point compound and in such amount as to result in a substantial increase in the melting point of the mass when reaction between components in different ones of said substances occurs, said substances being so composed individually that each contains no more than a relatively small amount of all of said components, the energy released from a chemical reaction causing formation of said compound by chemical reaction of components in said substance being such in relation to the amounts and heat capacity of materials present as to raise the temperature of the system to a temperature not exceeding the melting point of the matrix metal, the step of preparing an admixture comprising individually comminuting said substances, admixing the resultant comminuted substances, and heating the resultant admixture to a temperature slightly higher than the melting point

of the lower melting of said substances, said heating being immediately followed by application of pressure to said admixture; and maintaining the temperature of said admixture less than the melting point of said matrix metal until solidification of said mass occurs.

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