This invention relates to powder metallurgy compositions and to strong metal products produced therefrom. More particularly, this invention relates to mixtures of powdered metals and complex metal silicides and to high temperature-resistant metal products prepared from such mixtures.

In recent years there has developed a considerable demand for structural materials capable of withstanding elevated temperatures. Such materials are employed, for example, in the fabrication of turbine blades and nozzles for jet engines, gas turbines, and the like, as well as in high-speed cutting tools and in the construction of high temperature furnaces. It is known that improved high temperature properties may result from the presence in a metal or alloy of a refractory dispersed phase produced, for example, by precipitation during cooling of an alloy melt. Objects containing such phases may also be produced by powder metallurgy techniques. Although many combinations of metals and refractory phases have been investigated, need remains for specific combinations possessing superior properties.

The present invention provides such a superior combination in the form of a novel powder metallurgy composition and strong metal objects prepared therefrom. More specifically, this invention provides a powder metallurgy composition composed of an intimate mixture of powders less than 75 microns in particle size, and consisting essentially of a complex metal silicide and particles of a metal, the ratio of said complex metal silicide particles to said metal particles being in the range of 85:15 to 90:10 by weight.

The complex metal silicide contains on a weight basis, 15-57% silicon, 15-70% of a transition element of atomic number 22-42, i.e., Ti, V, Cr, Mn, Fe, Co, Ni, Zr, Nb, and Mo, and at least one additional component selected from the group consisting of (a) a different transition metal of atomic number 22-42 in an amount of 15-70% and (b) nitrogen in an amount of 1-19%. Preferred complex metal silicides contain at least two elements of atomic number 22-42 which still more preferably are selected from the group consisting of Mo, Fe, Nb, and Ti.

The metal particles in the powder mixture comprise one or more metals of atomic number 22-28, and preferably Ti, Cr, Fe, Co, and Ni, used singly or combined as alloys. Alloys based on the metals of atomic number 22-28, by which is meant alloys containing at least 85% by weight of such metals are also suitable providing they contain less than 5% and preferably less than 2% of nonmetals. Generally the alloys used are ductile.

Strong, heat-resistant shaped objects are prepared by pressing and heating these powders at a pressure of at least 500 p.s.i. and a temperature of at least 1000° C. Such objects have an overall chemical composition as defined above with a mixed silicide/metal ratio in the range of 85:15 to 10:90 by weight, and are characterized by having a much higher transverse rupture strength at 1000° C. and greatly improved oxidation resistance compared to similarly fabricated, unmodified metal. Such objects are also part of this invention.

Suitable complex metal silicides for use in the compositions of this invention are, for example, those described in assignee's U.S. Patent 2,866,259 and 2,878,113 and assignee's copending application Serial No. 773,087 filed November 10, 1958, now abandoned in favor of continuation-in-part application Serial No. 128,264, filed July 31, 1961, which is assigned to U.S. Patent 3,110,589, also suitable for use in preparing the compositions of the present invention. These molybdenum-nitrogen-silicide compositions contain 45-65% Mo, 2-19% N and 19-53% Si.

These or other complex metal silicides as indicated above are first prepared as described in the aforementioned patent applications. In brief, the preparation is carried out by mixing the ingredients in proportions corresponding to the composition desired in the finished product, milling if necessary to homogenize and reduce the particle size of the mixture, sieving to remove any particles larger than about 75 microns, compacting the sieved powder and firing the compact at a temperature of at least 800° C. to produce the complex metal silicide in a form, such as a wafer, convenient for use in the present invention.

The complex metal silicide in the form of wafers or other convenient shapes is broken up, suitably in an iron mortar, and the resulting pieces ball-milled. If contamination with iron is undesirable, it may be removed magnetically before ball-milling. It is convenient to carry out the milling in a porcelain mill containing quartz pebbles employing a charge, for a 1-quart mill, consisting of 200-300 g. of complex silicide, 700-800 g. of pebbles and 250 ml. of benzene. Milling is continued until the resulting powder has been reduced to a particle size below 75 microns which may require a period of several days. Milling times as long as six days are not uncommon. When the desired fineness of particle size has been achieved as indicated by examination of samples withdrawn from time to time from the mill, the charge is removed from the mill and the benzene allowed to evaporate or separated by filtration. The dry powder is then separated from the pebbles and sieved through a 200-mesh screen to remove any incompletely ground material.

The powdered complex metal silicide and the desired metal or metals in powdered or granular form are milled together under the conditions described above, until the components are intimately mixed and the metal has been reduced to the desired particle size. A shorter milling
time than that employed in grinding the complex silicide is usually sufficient and in the examples below a milling time of 72 hours was employed. The powdered product is separated from the mill contents as described above and sieved through a 200-mesh screen to remove any particles larger than 75 microns.

The temperature employed in converting these powder metallurgy compositions to the final metal objects of this invention depends upon a number of factors, including the melting point of the metal, the relative proportions of metal and complex silicide. The temperature will usually be at least 1000° C. and may range as high as 2000° C. In the examples below, a temperature of 1200° C. has been employed for hot-pressing powder metallurgy compositions containing chromium, nickel and cobalt while 1600° C. has been employed with titanium-containing compositions. It is usually preferable that the temperature not be greatly in excess of the melting point of the ductile metal or alloy component of the powder mixture. If desired, the converted shaped objects may be subjected to various metallurgical procedures such as hot-rolling, extrusion and the like, to develop optimum homogeneity and improved properties. The manner of carrying out such treatments is well known in the art.

In these examples, commercially available materials are employed and quantities of ingredients are expressed in parts by weight.

**EXAMPLE I**

Two hundred and ten parts of chromium metal in the form of a powder less than 45 microns in particle size was mixed with 90 parts of powdered molybdenum-iron silicide (30% Mo—40% Fe—30% Si) less than 75 microns in particle size and milled as described above in a porcelain ball-mill using quartz pebbles for a period of 3 days. The resulting powdered mixture of chromium and complex metal silicide was separated from the pebbles and milling liquid, sieved through a 200-mesh screen and hot-pressed in a graphite mold at a temperature of 1200° C. under 3000 lb./sq. in. pressure for 10 minutes. The metallic bar so obtained was ground to dimensions of 1/4" x 1/4" x 2" and used for determination of physical properties. These properties were as follows:

- Bulk density (g./cc.) 6.17
- Transverse rupture strength at 1100° C. 39,884
- Impact strength at room temperature (ft. lb./sq. in.) 28.8
- Knoop Hardness No. at 100 g. load 1024
- Knoop Hardness No. at 1000 g. load 964

The complex molybdenum-iron silicide employed in this example was prepared as described in U.S. Patent 2,866,239 by thoroughly mixing Mo, Fe and 50% ferrosilicon. This mixture, containing molybdenum, iron and silicon in the proportions named, was ball-milled until a particle size below 75 microns was obtained and hot-pressed into the form of wafers at 3000 p.s.i. pressure and 1200° C. for 10 minutes. The resultant wafers were broken up in an iron mortar and ball-milled as described above until they had been reduced to a particle size below 75 microns.

**EXAMPLE II**

This example illustrates modification of an alloy with a complex metal silicide. The following materials in the form of powders less than 75 microns in particle size were mixed thoroughly by tumbling to provide a powder mixture having the elemental composition of a commercial super-alloy: 47.30 parts of nickel, 21.5 parts of chromium, 18.50 parts of iron, 9.00 parts of molybdenum, 1.50 parts of cobalt, 0.60 part of tungsten, 0.50 part of silicon, 0.50 part of carbon and 0.50 part of copper. To this powder mixture was then added a complex molybdenum-iron silicide (50% Mo—25 Mo—25% Si) composition prepared as in Example I as a powder less than 75 microns in particle size in an amount sufficient to provide a complex silicide content in the mixed powders of 20% by weight. The powders were again mixed by tumbling and pressed at 4000 lb./sq. in. at 1100° C. in a graphite mold into the form of bars which test specimens were prepared as in Example I. The properties of these specimens were as follows:

- Bulk density (g./cc.) 7.26
- Oxidation resistance, ΔW 0.03
- Oxidation resistance, AD 1.68
- Transverse rupture strength at 1000° C. (lb./sq. in.) 13,080
- Impact strength (ft. lb./sq. in.) 46
- Knoop Hardness No. at 10 g. load 415
- Knoop Hardness No. at 100 g. load 333

Oxidation resistance was determined by heating the sample in air successively for 16 hours at 500° C., 750° C. and 1000° C. After each heat treatment the sample was cooled, weighed and measured. The change in weight (ΔW) and linear dimensions (AD) following the 1000° C. treatment are reported. A similar bar pressed at 1200° C. under 4000 lb./sq. in. had an impact strength of 60.9 ft./lb./sq. in. By way of comparison with the above, the test specimens of the super-alloy prepared as above without the addition of complex metal silicide exhibited a transverse rupture strength at 1000° C. of only 7,400 p.s.i.

**EXAMPLES III-V**

These examples illustrate the modification of chromium, nickel and cobalt with complex molybdenum-iron silicide. The examples were carried out according to the procedure described in Example I. Details of the individual compositions are shown in Table I and properties of the resultant products in Table II.

**EXAMPLES VI-VIII**

These examples illustrate the use of various ternary silicides with nickel and iron. The general procedure was as described in Example I and details of the preparation and properties are summarized in Tables I and II. The hot pressing conditions employed in Example VI were 1200° C. and 4000 lbs./sq. in. for 5 minutes.

**EXAMPLES IX-XII**

These examples illustrates the use of quaternary silicides in the modification of iron and titanium. The general procedure described above was employed and details of the preparation and properties are collected in Tables III and IV below. The compositions of Examples XI and XII were hot-pressed at 1250°-1260° C. and 4000 lbs./sq. in. for 5 minutes.

**Table I**

<table>
<thead>
<tr>
<th>Example No.</th>
<th>Raw Materials (wt. percent)</th>
<th>Properties of Complex Silicide Components (by wt.)</th>
</tr>
</thead>
</table>

1. Hot-pressing conditions were 4000 lbs./sq. in. at temperatures as follows: Example VIII-A, 1200° C.; Example VIII-B, 1150° C.; Example VIII-C, 1000° C.
2. This ferromagnesium alloy contained by analysis: Fe, 44.6; V, 21.2; Si, 12.5; C, 6.8.
3. Nox.—Mo-Ni-Fe-5% Si was prepared from molybdenum disilicide, silicon nitride and silicon as described in Example IV of aforesaid U.S. Patent 3,128,541.
Table II

METAL/TERNARY SILICIDE PRODUCTS

<table>
<thead>
<tr>
<th>Example No.</th>
<th>Bulk Density (g/cc.)</th>
<th>Transverse Rupture Strength (lbf./sq. in.)</th>
<th>Impact Strength (ft. lb./sq. in.)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>25°C</td>
<td>75°C</td>
<td>1000°C</td>
</tr>
<tr>
<td>III</td>
<td>5.94</td>
<td>58,594</td>
<td>28,542</td>
</tr>
<tr>
<td>III-A</td>
<td>6.17</td>
<td>26,779</td>
<td>16,272</td>
</tr>
<tr>
<td>IV</td>
<td>7.21</td>
<td>141,790</td>
<td>65,320</td>
</tr>
<tr>
<td>V</td>
<td>7.06</td>
<td>83,500</td>
<td>56,520</td>
</tr>
<tr>
<td>VII</td>
<td>7.60</td>
<td>80,100</td>
<td>48,620</td>
</tr>
<tr>
<td>VIII</td>
<td>6.80</td>
<td>80,100</td>
<td>48,200</td>
</tr>
<tr>
<td>XI</td>
<td>6.86</td>
<td>80,100</td>
<td>48,620</td>
</tr>
<tr>
<td>XII</td>
<td>6.68</td>
<td>80,100</td>
<td>48,620</td>
</tr>
</tbody>
</table>

1 Oxidation resistance measured as described in Example II was: At 1100°C, W = 0.45%, D = 0.86%.
2 These products readily cut glass and steel.
3 At 1100°C, neither product showed significant oxidation after the test which was carried out in air.

Table III

METAL/QUARTERNARY SILICIDE PRODUCTS

<table>
<thead>
<tr>
<th>Example No.</th>
<th>Bulk Density (g/cc.)</th>
<th>Transverse Rupture Strength (lbf./sq. in.)</th>
<th>Impact Strength (ft. lb./sq. in.)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>25°C</td>
<td>75°C</td>
<td>1000°C</td>
</tr>
<tr>
<td>IX</td>
<td>7.45</td>
<td>27,180</td>
<td>13,030</td>
</tr>
<tr>
<td>X</td>
<td>7.45</td>
<td>12,450</td>
<td>9,180</td>
</tr>
<tr>
<td>XI</td>
<td>7.45</td>
<td>12,450</td>
<td>9,180</td>
</tr>
<tr>
<td>XII</td>
<td>7.45</td>
<td>12,450</td>
<td>9,180</td>
</tr>
</tbody>
</table>

Table IV

METAL/TERTIARY SILICIDE PRODUCTS

<table>
<thead>
<tr>
<th>Example No.</th>
<th>Bulk Density (g/cc.)</th>
<th>Transverse Rupture Strength (lbf./sq. in.)</th>
<th>Hardness No. at Load of—</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>25°C</td>
<td>75°C</td>
<td>1000°C</td>
</tr>
<tr>
<td>IX</td>
<td>7.45</td>
<td>27,180</td>
<td>13,030</td>
</tr>
<tr>
<td>X</td>
<td>7.45</td>
<td>12,450</td>
<td>9,180</td>
</tr>
<tr>
<td>XI</td>
<td>7.45</td>
<td>12,450</td>
<td>9,180</td>
</tr>
<tr>
<td>XII</td>
<td>7.45</td>
<td>12,450</td>
<td>9,180</td>
</tr>
</tbody>
</table>

Note.—Stress-to-capture and Knoop Hardness data for the products of Examples IX and X were:

<table>
<thead>
<tr>
<th>Stress (lbf./sq. in.)</th>
<th>Air Temp. °C</th>
<th>Hardness No. at Load of—</th>
</tr>
</thead>
<tbody>
<tr>
<td>IX</td>
<td>10,254</td>
<td>900</td>
</tr>
<tr>
<td>X</td>
<td>10,254</td>
<td>700</td>
</tr>
</tbody>
</table>

In the new powder mixtures of this invention, the metal component is ordinarily composed of one or more metals of atomic number 22-28 used singly or in alloy form. As illustrated in Example II, it is sometimes desirable to include additional elements as modifiers for or as alloying agents with this component. When this is done, it is preferred that the metals of atomic number 22-28 be present in a quantity sufficient to provide at least 85% by weight of the metal component. The remainder, i.e., up to 15% of this component, may include tin, molybdenum, niobium, tungsten, as well as the impurities usually present in commercial metals of atomic number 22-28. The presence of non-metals such as carbon, silicon, boron, oxygen, etc. in this component should not exceed 5% and should preferably be less than 2%.

The complex metal silicides employed in these new powder mixtures may be prepared directly from the appropriate elements or from compounds or alloys thereof. It is preferred that nitrogen, if present, be incorporated in the form of silicon nitride. Silicon may be introduced as titanium disilicide, ferrosilicon, molybdenum disilicide, silico-titanium, and the like. In preparing these complex silicides, it is usually preferable to avoid the presence in the starting materials of large amounts of uncombined elements since these may lead to difficulties such as adhesion to mold surfaces during firing.

Although the examples have described the conversion of the powder metallurgy compositions of this invention to metallic shaped objects by hot-pressing, other methods of conversion may be employed if desired. For example, the powders can be compacted into the form of the desired object by pressing at room temperature or can be shaped by slip-casting and drying. Such green shaped objects are then fired to convert them to the final metal-complex metal silicide composition. Green compacts which contain water or other volatiles, however, should be dried before firing to a volatile content of less than about 3% to prevent rupture of the object during firing. If drying is carried out as an initial stage of the firing process, the initial rate of heating, i.e., up to about 350°C, should be slow to permit drying without cracking. Thereafter, the rate of heating and the final firing temperature as well as the appropriate atmosphere (such as air, vacuum, inert gas, reducing or oxidizing atmospheres, etc.) can be determined experimentally as known in the art to produce optimum properties in the final products.

As shown in the examples, the compositions of this invention prepared using preformed complex metal silicides are strong, impact-resistant and resistant to deformation at high temperatures. In contrast, compositions of the same total elemental content prepared without prior formation of the complex silicide are deficient in one or more respects. For example, a composition prepared directly from the elements containing chromium, molybdenum, iron and silicon in the proportions present in the product of Example I had a transverse rupture strength at 1100°C of only 20,696 lb./sq. in. and an impact strength at room temperature of only 8.5 lb./sq. in. Similarly, a composition analogous to Example X, prepared directly from the elements and containing 91% titanium, 6% molybdenum, 1% niobium and 2% silicon had a transverse rupture strength of only 18,598 lb./sq. in. at room temperature and an impact strength of only 10.2 lb./sq. in.

Although the structure of the alloy products of this invention has not been completely elucidated, it is believed that their superior physical properties result from the presence of at least two phases. These phases may be the ductile metal or alloy and the complex metal silicide used to prepare the powder metallurgy composition. These may be present, e.g., as coexistent continuous phases, as the hard phase dispersed in a relatively ductile phase or as a ductile phase dispersed in the hard phase. However, in certain cases, partial reaction apparently occurs during firing resulting in the formation of additional complex silicide phases. The extent of such reactions may vary widely depending on the duration and severity of firing and on the relative amounts and reactivities of the components. Superficial reaction may lead to the formation of a zone intermediate between the ductile and the refractory phases; more extensive reaction may produce a wholly distinct phase. It is important to note that the microstructure of products prepared as described herein differs from that of compositions containing the same elements in the same proportions prepared from mixtures that do not contain preformed complex silicides.

Illustrative of the first type of structure described above
are the products of Example X, which exhibit a matrix of α- and β-titanium having embedded therein grains, up to 20 and 25% in size, of complex metal silicide. Surrounding these grains an intermediate phase produced by reaction of silicide phase and metal phase is apparent. Microhardness measurements by the Knoop method at 100 g. load gave hardness numbers of 440–495 for the matrix and 970–1010 for the dispersed phase. An example of the second type is the product of Example III–A which shows by X-ray in addition to chromium and complex metal silicide, the presence of Cr₃Si.

The new compositions of this invention are resistant to thermal shock and to degradation by heat and oxygen. They are also electrically conductive and, especially when a large proportion of refractory complex metal silicide is employed, exhibit high hardness. These properties give them utility in diverse applications where materials having high strength at high temperatures are desired. These compositions are useful as structural components, for example, in gas turbines, in the construction of jet engine parts, in high-speed cutting tools and dies, and as heating elements.

What is claimed is:

1. A novel powder metallurgy composition of less than 75 micron particle size consisting essentially of chromium and a complex metal silicide consisting essentially of 18–65% Mo, 15–50% Fe, and 17–57% Si, the ratio of silicide to chromium falling within the range of 85:15 to 10:90.

2. A novel powder metallurgy composition of less than 75 micron particle size consisting essentially of nickel and a complex metal silicide consisting essentially of 18–65% Mo, 15–50% Fe, and 17–57% Si, the ratio of silicide to nickel falling within the range of 85:15 to 10:90.

3. A novel powder metallurgy composition of less than 75 micron particle size consisting essentially of cobalt and a complex metal silicide consisting essentially of 18–65% Mo, 15–50% Fe, and 17–57% Si, the ratio of silicide to cobalt falling within the range of 85:15 to 10:90.

4. A novel powder metallurgy composition of less than 75 micron particle size consisting essentially of at least one metal of atomic number 22–28 and a complex metal silicide consisting essentially of 18–65% Mo, 15–50% Fe, and 17–57% Si, the ratio of silicide to metal falling within the range of 85:15 to 10:90.

5. A powder metallurgy composition of particles less than 75 microns in size consisting essentially of

(a) a metal component selected from the group consisting of metals of atomic number 22–28 and alloys thereof containing at least 85% of such metals and less than 5% of non-metals; and

(b) a complex metal silicide consisting essentially of 15–57% silicon, 15–70% of a transition element of the class consisting of titanium, vanadium, chromium, manganese, iron, cobalt, nickel, zinc, niobium and molybdenum, and at least one additional component of the group consisting of

(a) 15–70% of a different one of said transition elements and

(b) 1–19% nitrogen,

the weight ratio of complex metal silicide to metal component being in the range of 85:15 to 10:90.

6. A novel powder metallurgy composition in accordance with claim 5 wherein the complex metal silicide is a molybdenum-titanium silicide containing 18–65% Mo, 15–50% Fe, and 17–57% Si.

7. A novel powder metallurgy composition in accordance with claim 5 wherein the complex metal silicide is a titanium-iron silicide containing 25–47.5% Ti, 20–45% Fe, and 25–45% Si.

8. A novel powder metallurgy composition in accordance with claim 5 wherein the complex metal silicide is a molybdenum-titanium-nitrogen silicide containing 20–50% Mo, 20–50% Ti, 1–8% N, and 15–45% Si.

9. A novel powder metallurgy composition in accordance with claim 5 wherein the complex metal silicide is a molybdenum-titanium-nitrogen silicide containing 45–65% Mo, 2–19% N, and 15–53% Si.

10. A novel powder metallurgy composition of claim 5 wherein the complex metal silicide is selected from the group consisting of molybdenum-titanium silicide, molybdenum-titanium-nitrogen silicide, molybdenum-nitrogen silicide, iron-titanium silicide, niobium-titanium silicide, molybdenum-titanium silicide, and molybdenum-niobium-titanium silicide.

11. A powder metallurgy composition of claim 5 wherein the metal component is a ductile alloy containing less than 2% of non-metals.

12. A powder metallurgy composition of claim 5 wherein the metal component is iron and the complex metal silicide is a molybdenum-titanium-niobium silicide.

13. A powder metallurgy composition of claim 5 wherein the metal component is iron and the complex metal silicide is a molybdenum-titanium-niobium silicide.

14. A strong heat-resistant shaped object consisting essentially of

(a) 15–70% of a different one of said transition elements and

(b) 1–19% nitrogen,

the weight ratio of complex metal silicide to metal component being in the range of 85:15 to 10:90.

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