

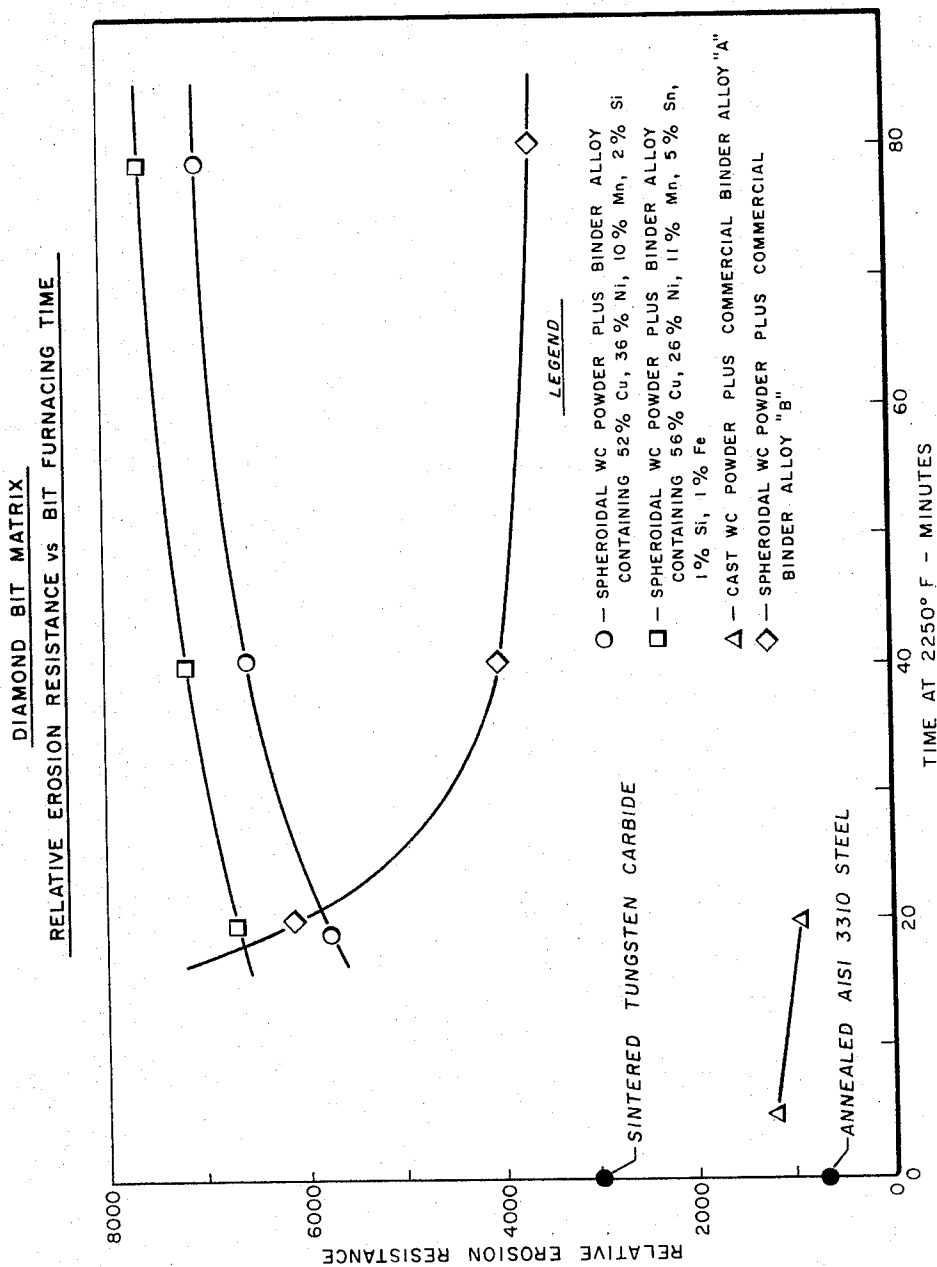
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LIQUID PHASE SINTERING PROCESS

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1

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LIQUID PHASE SINTERING PROCESS

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The present invention relates to metal alloys and is particularly concerned with binder alloys for use in the liquid phase sintering of hard metal carbides and other refractory materials.

Binders containing iron, nickel or cobalt as the principal constituent are widely used for the liquid phase sintering of powdered hard metals to produce composite materials. The sintering process employed generally involves either the compaction of a mixture of powdered hard metal and binder as it is heated to a temperature above the binder melting point or the infiltration of a molten binder into the interstices in a porous compact of powdered hard metal formed prior to infiltration. In either case, the binder metal employed has a pronounced effect upon the final properties of the composite material. Studies have shown that binders employed in the past generally attack and partially dissolve the hard metal powder during furnacing and that the furnacing period must be carefully controlled to avoid a loss in the hardness of the powder granules and other adverse effects. Binders which do not attack and dissolve the hard metal to a significant extent and therefore do not require close control of the furnacing operation often fail to produce a satisfactory bond between the powder granules and may result in a product which lacks the mechanical strength, erosion resistance and other properties required in the finished composite material. Efforts to avoid these and related difficulties have in the past been largely unsuccessful.

In accordance with this invention, it has now been found that many of the difficulties encountered in the liquid phase sintering of hard metal carbides and similar refractory hard metals with binders employed in the past can be avoided by utilizing certain binder alloys which contain copper as the principal constituent and include lesser amounts of manganese and a metal from Group VIII, Series 4 of the Periodic Table. Tests have shown that these alloys permit the satisfactory bonding of refractory hard metal particles under a variety of different time and temperature conditions but that they do not attack or dissolve the particles to such an extent that the hardness, erosion resistance and other properties of the hard metal particles are seriously affected. As a result of these and other beneficial characteristics, composite materials prepared with these binders are generally superior to those prepared with binders available in the past.

The nature and objects of the invention can best be understood by referring to the following detailed description of the alloys and their use in liquid phase sintering operations and to the accompanying drawing showing the results of erosion tests of composite materials prepared with the alloys.

The alloys employed for purposes of the invention are copper-base alloys containing from about 10 to about 25 weight percent manganese and from about 20 to about 40 weight percent of one or more transition metals Group VIII, Series 4 of the Periodic Table. The combination of copper and iron, nickel or cobalt over the composition range utilized produces a strong, erosion-resistant alloy which has good "wetting" properties but does not cause excessive dissolution of hard metal car-

2

bides and similar refractory hard metal materials. The use of nickel, alone or in combination with lesser amounts of iron or cobalt, is preferred. The manganese promotes wetting, improves fluidity, depresses the freezing point of the ternary copper-nickel-manganese system, and imparts toughness to the material. It also serves to deoxidize the metal, tends to tie up sulfur present, and slows down attack of the transition metal at the surfaces of the hard metal particles by forming diffusion-barrier carbides and similar hard metal reaction products. Copper, manganese and one or more of the transition metals are thus all essential alloy constituents. In addition to these constituents, the alloys may also contain silicon in amounts up to about 5 percent by weight, tin in quantities up to about 10 percent by weight, and sulfur in amounts up to about 0.2 percent by weight. The silicon and tin strengthen the alloy by the precipitation of silicides and insoluble tin complexes with copper, manganese and the transition elements. They also reduce the melting point of the alloy, improve fluidity at the sintering temperature, and serve as deoxidizing agents. The sulfur is normally present as an impurity and should be limited to the amounts indicated above. Other elements such as carbon, chromium, silver, phosphorus, zinc and the like may also be present as impurities.

Typical alloy compositions containing the constituents set forth above include: (a) copper, 52.0%; nickel, 36.0%; manganese, 10.0%; silicon, 2.0%; (b) copper, 48.5%; nickel, 21.3%; cobalt, 12.4%; manganese, 11.8%; silicon, 2.5%; tin, 3.5%; (c) copper, 43.5%; nickel, 38.2%; manganese, 12.3%; silicon, 3.0%; tin, 3.0% (d) copper, 46.0%; nickel, 24.3%; iron, 8.4%; manganese, 14.2%; silicon, 1.2%; tin, 6.9%; (e) copper, 55.2%; nickel, 28.0%; manganese, 13.1%; silicon, 3.7%; (f) copper, 56.0%; nickel, 26.1%; iron, 0.7%; manganese, 11.2%; silicon, 1.0%; tin, 5.0%; (g) copper, 34.5%; nickel, 40.0%; manganese 20.5%; silicon, 3.0%; tin, 2.0%; (h) copper, 36.1%; nickel, 33.8%; iron, 0.8%; manganese, 25.0%; tin, 4.2%; sulfur, 0.1%; (i) copper, 28.0%; nickel, 39.8%; iron, 0.2%; manganese 23.0%; tin, 9.0%; (j) copper, 56.0%; nickel, 29.1%; iron, 0.6%; manganese, 11.9%; silicon, 1.0%; tin, 1.2%; sulfur, 0.2%; (k) copper, 40.0%; nickel, 30.0%; cobalt, 10%; manganese, 20.0%; (l) copper, 20.9%; nickel 38.7%; iron, 1.0%; manganese, 24.8%; silicon, 4.6%; tin, 10.0%; (m) copper, 48.0%; cobalt, 21.3%; manganese, 21.2%; silicon, 1.5%; tin, 8.0%; (n) copper, 42.0%; nickel, 31.1%; cobalt, 2.8%; iron, 2.8%; manganese, 12.2%; silicon, 3.2%; tin, 5.6%; phosphorus, 0.1%; sulfur, 0.1%; carbon, 0.1%; (o) copper, 49.7%; cobalt, 12.6%; iron, 8.1%; manganese, 23.6%; tin, 6.0%; and the like.

The alloys employed in accordance with the invention can be prepared by heating the constituents at a temperature of about 2400° F. or higher under a borax slag until they have dissolved into a single liquid phase. The resultant material can then be cast into water to produce shot suitable for remelting, atomized or otherwise disintegrated to produce fine powder, or cast into bars or ingots. The method utilized will depend in part upon the particle size required. This in turn is governed to some extent by the particular type of liquid phase sintering operation in which the alloy is to be used. Alloys for use in hot pressing operations are generally employed in the form of very fine powders; while those intended for use in infiltration type operation may be prepared in the form of shot or pellets.

In utilizing the alloys described above in hot pressing operations, alloy powder reduced to -325 mesh or smaller in size is generally used. The finely divided alloy is mixed with powdered tungsten carbide, titanium carbide, tantalum carbide, chromium carbide, vanadium car-

bide or a similar refractory hard metal to produce a uniform mixture. This is preferably done by wet milling the hard metal and alloy powders together in a ball or rod mill but may be carried out by other methods if desired. The mixture will generally contain from about 1 to about 30% by weight of the alloy and from about 70 to about 99% by weight of the hard metal. This mixture is then placed in a suitable mold and pressed at a pressure of 10,000 pounds per square inch or higher. Simultaneously, the mold and its contents are heated to a temperature above the melting point of the binder alloy under vacuum or in a hydrogen atmosphere. Under these conditions, the hard metal particles are coated with the alloy and sintered together to form a composite material having a compressive strength over about 200,000 pounds per square inch, a transverse rupture strength above about 100,000 pounds per square inch and hardness values in excess of about 2500 V.H.N. in the hard metal phase.

The binder alloys referred to herein can also be employed in infiltration type operations. Here powdered tungsten carbide, tantalum carbide, titanium carbide or a similar refractory hard metal powder is first placed in a carbon or graphite mold of the desired shape. The powder may be compacted and may be presintered to form a porous skeletal structure if desired. Pellets of the binder alloy to be used are placed in the mold above the powder and the mold and its contents are then heated to an infiltration temperature above the melting point of the binder. As it approaches this temperature, the molten alloy flows into the interstices between the powder granules. This results in the liquid phase sintering of the granules and, after the material has cooled, provides a hard composite product having high resistance to erosion and abrasion. The infiltrated mass can be pressed as it cools to further increase the hardness and density if desired.

It will be understood that the use of the alloys set forth herein is not limited to the particular applications described above. Other liquid phase sintering operations in which the alloys may be employed have been described in the metallurgical and patent literature and will therefore be familiar to those skilled in the art.

The improved properties obtained with the alloys de-

furnace after 20 minutes, after 40 minutes and after 80 minutes and were cooled to room temperature. Examination showed that the alloy had infiltrated uniformly and completely and that the resultant composite materials were free of porosity. They had an average transverse rupture strength of 106,922 pounds per square inch. The carbide granules bonded within the materials had Vicker's microhardness values of about 2800 kilograms per square millimeter.

Following preparation of the first group of specimens as described above, additional specimens containing the same tungsten carbide powder and a different binder alloy were prepared. This second alloy contained 56% copper, 26% nickel, 11% manganese, 5% tin, 1% silicon and 1% iron. The infiltration conditions employed were identical to those used earlier. Specimens were again removed from the furnace after 20 minutes, after 40 minutes and after 80 minutes. Examination showed that these specimens had physical properties similar to those prepared with the first alloy.

The specimens produced as described in the preceding paragraph were subjected to an erosion test to determine the suitability of the materials for use on oil field diamond bits and in other applications where erosion by fluids containing suspended solids may present difficulties. To provide a basis for comparison, similar tests were carried out with annealed samples of 3310 steel, with samples of a commercial cemented tungsten carbide containing 10% cobalt by weight as the cementing agent, with samples of a diamond drill bit matrix material containing cast tungsten carbide powder and a commercial binder alloy, and with samples of a composite material containing the same tungsten carbide powder used in the materials prepared as described above and a second commercial binder alloy used in diamond bits. Each test was carried out by directing a high velocity jet stream of a slurry of aluminum oxide powder in water against the side of a cylindrical specimen 1/2 inch in diameter and 1 inch long for a period of two hours. The reciprocal of the weight loss for each specimen was multiplied by a constant to obtain the relative erosion resistance. The results of these erosion tests are set forth in the following table and are shown graphically in the accompanying drawing:

Relative Erosion Resistance

Material	Furnacing Temp., ° F.	Furnacing Time, Min.	No. of Specimens	Relative Erosion Resistance
Annealed 3310 Steel.....	-----	-----	2	960
Sintered Tungsten Carbide containing 10% cobalt as the cementing metal.....	-----	-----	15	3,031
Diamond Bit Matrix containing cast WC powder and commercial binder alloy A.	2,150	5	2	1,149
	2,150	20	2	950
Composite Material containing WC powder and commercial binder alloy B.	2,250	20	10	6,083
	2,250	40	7	4,065
	2,250	80	2	3,717
Composite Material containing WC powder and alloy consisting of 52% Cu, 36% Ni, 10 Mn, and 2% Si.	2,250	20	2	6,621
	2,250	40	2	7,368
	2,250	80	2	7,631
Composite Material containing WC powder and alloy consisting of 56% Cu, 26% Ni, 1% Fe, 11% Mn, 5% Sn. and 1% Si.	2,250	20	2	5,739
	2,250	40	2	6,504
	2,250	80	2	7,067

scribed above are shown by the results of liquid phase sintering operations carried out with the alloys and tungsten carbide powder. The powder employed consisted of spheroidal granules of tungsten carbide between about 200 and about 325 mesh in size. Cylindrical graphite molds 1/2 inch in diameter and one inch long were first filled with this powder. The molds containing the powder were then heated in air in an electric furnace to an infiltration temperature of 2250° F. A binder alloy containing 52% copper, 36% nickel, 10% manganese and 2% silicon heated to the same temperature was introduced into the upper part of each mold and permitted to infiltrate downwardly into the interstices between the tungsten carbide granules. Specimens were removed from the

It can be seen from the table that the relative erosion resistance of the steel was low. The sintered tungsten carbide containing cobalt as the cementing metal had a relative erosion resistance about three times that of the steel. The erosion resistance of the diamond bit matrix containing cast tungsten carbide powder and commercial alloy A fell between that of the steel and that of the sintered tungsten carbide. This is typical of conventional diamond drill bits and similar tools. The relatively soft binder metal is quickly eroded away and hence such tools may fail rapidly at high fluid circulation rates. Metallurgical examination of the specimens prepared with this matrix material showed that it was soft and highly porous, probably because of the vaporization of zinc or a similar

5

low boiling constituent in the binder alloy. The alloy used does not infiltrate readily at temperatures below about 2150° F. and thus such porosity is difficult to avoid.

The composite material prepared with the spheroidal tungsten carbide powder and commercial binder alloy B had a much higher erosion resistance than the materials tested previously. The data show, however, that the resistance obtained was strongly dependent upon the furnacing time used in manufacturing the material. As the furnacing time was increased, the relative erosion resistance decreased rapidly. This indicates that the binder alloy probably attacks and partially dissolves the tungsten carbide powder, resulting in the precipitation of multiple carbides which are much less satisfactory than the tungsten carbide powder started with. This behavior is typical of most binder alloys having very high nickel, iron or cobalt contents. The furnacing time during the manufacture of large drill bits and similar tools is generally at least 30 minutes and often considerably longer. The loss of erosion resistance and other desirable properties which takes place during this extended furnacing undoubtedly restricts the useful life of such tools.

The data in the table and the drawing show that the composite materials prepared with the alloys utilized in accordance with the invention have better relative erosion resistance than the conventional materials and that this erosion resistance increases with increasing furnacing time. Similar results have been obtained with other alloys employed in accordance with the invention. It is thus apparent that these binders behave in an entirely different manner from the materials tested earlier and that an increase in the furnacing period permits the manufacture of a more erosion-resistant tool than can be obtained otherwise. This makes the alloys employed in accordance with the invention attractive for use in diamond drill bits, nozzles and other devices where high resistance to erosion is important.

What is claimed is:

1. In a liquid phase sintering operation wherein

6

particles of a refractory hard metal are bonded together with a molten binder alloy to produce a composite material, the improvement which comprises bonding said particles together with an alloy consisting essentially of about 20 to 40 percent of at least one metal from Group VIII, Series 4 of the Periodic Table, about 10 to 25 percent manganese, about 0 to 5 percent silicon, about 0 to 10 percent tin, about 0 to 0.2 percent sulfur, and the balance copper.

2. A sintering operation as defined in claim 1 wherein said metal from Group VIII, Series IV of the Periodic Table is nickel.

3. A sintering operation as defined in claim 1 wherein said alloy contains about 52% copper, about 36% nickel, about 10% manganese and about 2% silicon.

4. A sintering operation as defined by claim 1 wherein said alloy contains about 56% copper, about 26% nickel, about 11% manganese, about 5% tin, about 1% silicon and about 1% iron.

5. A sintering operation as defined by claim 1 wherein said refractory hard metal is tungsten carbide.

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