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METHOD OF MAKING SOLID SOLUTION CARBIDE-GRAPHITE COMPOSITIONS

Filed May 12, 1967

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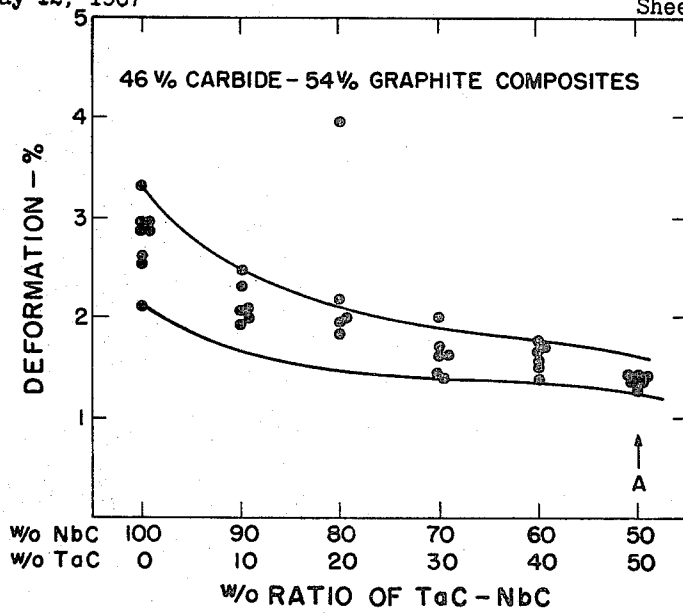


Fig. 1

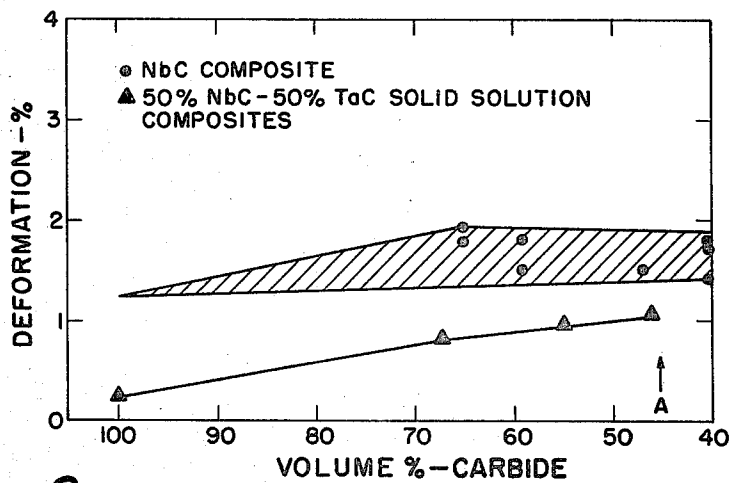


Fig. 2

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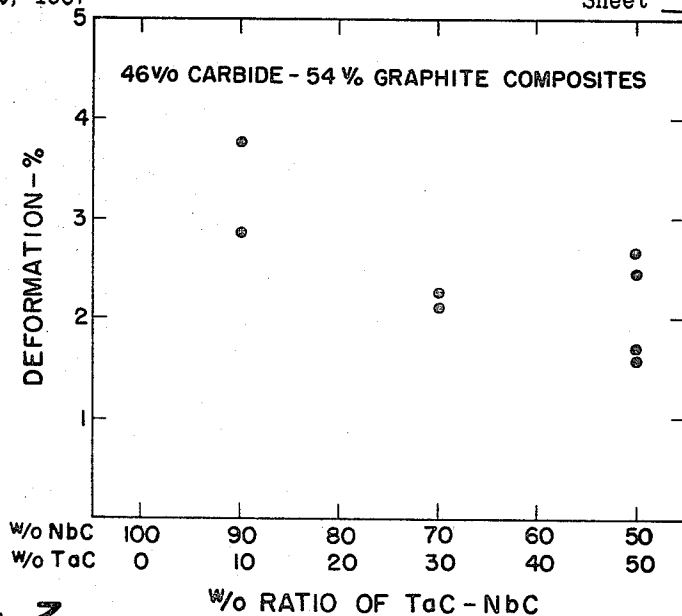


Fig. 3

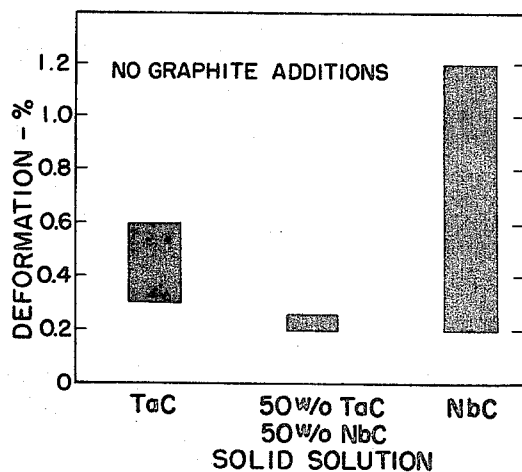


Fig. 4

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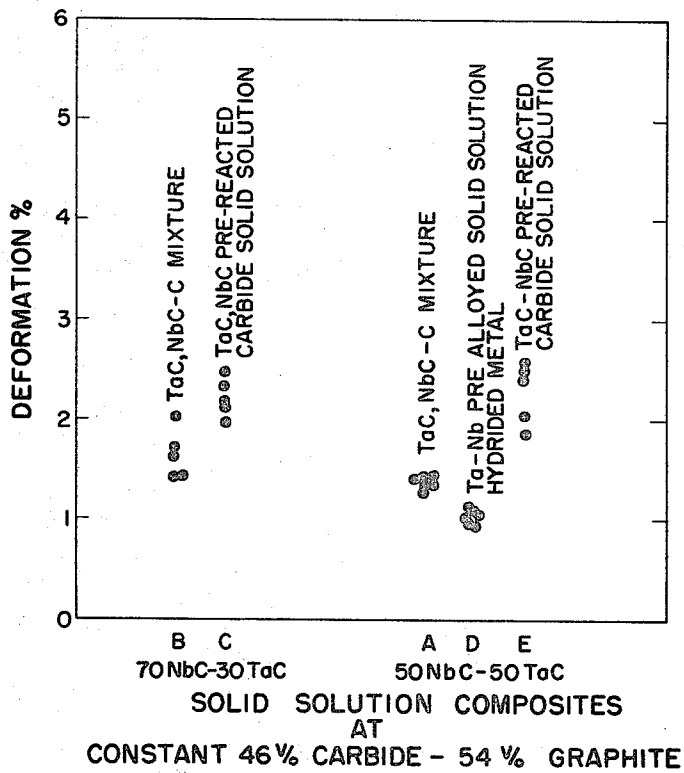


Fig. 5

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3,419,656

**METHOD OF MAKING SOLID SOLUTION
CARBIDE-GRAPHITE COMPOSITIONS**

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America as represented by the United States Atomic
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ABSTRACT OF THE DISCLOSURE

The characteristics of a composite composed of graphite and metal carbide are improved by utilizing a solid solution carbide in the metal carbide-graphite composite.

The invention described herein was made in the course of, or under, a contract with the U.S. Atomic Energy Commission.

Carbide-graphite composites have recently received considerable attention since these materials exhibit favorable strength properties at high temperature, even in corrosive atmospheres. Such composites have been described in a Los Alamos Scientific Laboratory report LA-3569-MS distributed Oct. 19, 1966, available from the Clearinghouse for Federal Scientific and Technical Information, National Bureau of Standards, United States Department of Commerce, Springfield, Va.

It has been found that resistance to deformation at high temperatures is increased substantially if the NbC in a graphite composite system is replaced with a solid solution of TaC and NbC. It has also been found that limitation of metallic contaminants favorably affects resistance to deformation of solid solution carbide-graphite composite systems as well as metal carbide-graphite composite systems as reported in U.S. application Ser. No. 611,179 filed Jan. 23, 1967 now abandoned (July 27, 1967) by the inventors herein.

FIGURE 1 is a plot of deformation versus weight percent ratio of TaC to NbC at a constant total carbide to graphite ratio.

FIGURE 2 is a plot of deformation of selected carbide-graphite composites versus volume percent of total carbide.

FIGURE 3 is a plot utilizing the same parameters as FIGURE 1 except that the starting carbides have high iron impurity levels.

FIGURE 4 is a bar graph showing the range of deformation of the monocarbides of Ta and Nb as compared with a 50 w/o TaC-50 w/o NbC alloy solid solution carbide.

FIGURE 5 is a plot of deformation for solid solution composites at constant total carbide-to-graphite ratio comparing solid solution carbide-graphite composites obtained by different methods, all according to the present invention.

The formation of the carbide solid solution-graphite composite can be accomplished by four techniques:

(1) By using two or more carbides, combining them with carbon and hot pressing to form the solid solution carbide-graphite composites.

(2) By pre-reacting two or more carbides to form an alloy solid solution which would be crushed to powder and combined with carbon and hot pressed to form a shape.

(3) By adding two or more metal powders in the proper proportions to graphite, blending, and hot pressing to form the carbide solid solution composite.

(4) By pre-alloying two or more metals by melting,

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hydriding and crushing to powder, combining with carbon and hot pressing to form the carbide solid solution composite.

The charge formulation was based on weight percents of the combination of Nb, Ta, TaC, NbC and graphite desired. The metal or metal carbide constituents were weighed to the nearest 0.1 gram, placed into a glass jar with aluminum agitator wires, sealed and blended for 4 hours. The desired quantity of graphite flour was then added and this mixture was blended for an additional 4 hours. The blend was removed from the jar and screened through a 50-mesh screen. At this point the blend was ready to load into a graphite die as a predetermined weighed charge. If for any reason the blend was allowed to sit around for longer than an hour or two before loading the dies, it was reblended for 20 minutes immediately prior to use.

Hot pressing was performed in an induction heated hot press. The pressing was done at 3050° C. and 3200 p.s.i. for 10 minutes at temperature.

The pressing assumed a very slight barrel shape as a result of the hot pressing and had to be cut from the die. The pressing was then machined to 1.0 in. diameter by 1.0 in. long to remove any skin effect. Machining was accomplished by standard techniques using diamond tooling.

The machined specimens were weighed and measured, and then placed between the punches of an oversize die and tested. The deformation test data were obtained by heating the specimens to 2700° C. At this point a load of 2000 p.s.i. was applied and held for 30 minutes after which the load was removed and the specimen cooled to room temperature. The specimens were removed from the die, measured and the amount (percent) of deformation recorded.

The benefits of solid solution strengthening of NbC with additions of TaC are most evident in the 46 v/o (50 w/o NbC-50 w/o TaC)+54 v/o graphite hot pressed composites. The actual composition by weight is 39.7 w/o TaC+39.7 w/o NbC+20.6 w/o graphite.

In preparing such a composite by method 1 (mixing two or more carbides) a 590-gram blend of the various constituents weighed to the nearest 0.10 gram was made at one time to provide sufficient material for two hot pressings. The procedure consisted of weighing 234.2 grams of TaC and 234.2 grams of NbC and pouring the two powders into a glass jar equipped with fixed aluminum wires, sealed shut, and roll blended for 4 hours.

The jar was then opened and 121.6 grams of graphite flour was added, the jar sealed again, and the powders blended for an additional 4 hours.

The blended powders were weighed into two 295-gram charges and carefully loaded into graphite dies. The loaded dies were positioned in the induction coils of two hot presses, the furnaces closed, and the tanks flushed with argon. After flushing the tank, the dies were heated to 3050° C. while a load of 3200 p.s.i. was gradually applied. Both furnaces are heated simultaneously by a single 150 kw. motor-generator set. The pressing is held for ten minutes at temperature and pressure, after which the power is turned off, the pressure is released, and the assembly allowed to cool.

This particular charge formulation corresponds to the data points on FIGURES 1 and 2 found on a line with the arrow indicated by A.

Method 2 (pre-reacting two or more carbides) may be employed as in the following example. The TaC-NbC solid solution powders were formed by hot pressing the desired blended compositions, crushing to -325 mesh and blending with graphite for the desired carbide-graphite composition. Specifically the 50 w/o TaC-50 w/o NbC

composition was prepared by roll blending 600 grams of TaC and 600 grams of NbC in glass bottles with fixed aluminum wires for 4 hours.

Each of two graphite dies was loaded with 600 grams of the 50 w/o TaC-50 w/o NbC blend and hot pressed at 2950° C. for 10 minutes with a load of 1800 p.s.i. The resulting pressings were crushed through -325 mesh and blends made which contained 468.4 grams of the TaC-NbC solid solution and 121.6 grams of graphite. The charges were roll blended in glass bottles with fixed aluminum cutting wires for 4 hours. The 285 gram charges were weighed and loaded into the graphite dies for hot pressing as previously described.

Preparation of the solid solution using elemental Ta and Nb powders (method 3) was accomplished by blending 232 grams of Ta and 232 grams of Nb powder in a glass jar with fixed aluminum wires for 4 hours. To the blend 176.5 grams of graphite powder was added and the powders blended again for 4 hours. The blend was divided into two charges and the previously described procedures utilized for die loading and hot pressing.

Method 4 (pre-alloying the metals) may be illustrated by the following example. Preparation of the 50 w/o Ta-50 w/o Nb was accomplished by button arc-melting 500 grams each of Ta and Nb sheet scrap (high purity and acid cleaned) together in an argon atmosphere. The alloy plate obtained (3¼ in. x 3¼ in. x ¼ in. thick) was rolled to 0.050 in. thick sheet. The sheet was sheared into ¾ in. wide x 3 in. long strips which were hydrided three times and dehydrided in between. The resulting alloy hydride was crushed in a WC mortar and pestle to -325 mesh powder in an argon atmosphere dry box.

A powder blend (a quantity for two hot pressings) consisted of 463.5 grams of the Ta-Nb solid solution alloy powder and 176.5 grams of the graphite powder which was roll blended for 4 hours in a glass bottle with fixed aluminum wires. Die loading and hot pressing was performed identical to that previously described.

FIGURE 1 shows the effect of using a TaC-NbC solid solution mixture-graphite composite in place of an NbC-graphite composite. These pressings were made by taking the individual carbides and graphite, blending, and hot pressing to form the solid solution mixture. Prealloyed powder of the metals or carbides could also be used. For purposes of comparison of the deformation results, all data were obtained at a constant v/o (volume percent) graphite composition obtained by method 1. It will be noted that although the data are somewhat scattered, over a 1% decrease in percent deformation is obtained by using alloy composition A (50 w/o NbC-50 w/o TaC) over using 100 w/o NbC. Furthermore, it is clear that, at all levels, the presence of tantalum carbide decreases the amount of deformation at high temperatures.

FIGURE 2 shows the effect of varying total volume percent of the carbides at constant 50 w/o NbC-50 w/o TaC solid solution (obtained by method 1) as compared to the NbC-graphite system not incorporating TaC. Although the NbC-graphite data are shown as a scatter band it is noted that at all levels improvement in the amount of deformation is found by utilizing a 50 w/o NbC-50 w/o TaC solid solution.

FIGURE 3 shows the deformation at a constant 54 v/o total carbide as a function of the weight percent ratio of TaC-NbC. FIGURE 3 would be comparable to FIGURE 1 except that the data of FIGURE 3 were obtained utilizing carbide powders (in method 1) as starting ma-

terials which had in excess of 2000 p.p.m. of metal impurities (Fe, Ni, etc.) in the starting carbides. Conversely, FIGURE 1 shows data for materials having a lower concentration of metal contaminants in the starting carbides (i.e., less than about 500 p.p.m.). It is seen that high levels of metal contaminants are detrimental to the strengths of solid solution composite mixtures.

There are no data available yet to show how homogeneous the solid solution mixtures represented in FIGURES 1 to 3 are. Increasing the homogeneity of the solid solution would be expected to increase the strength of the solid solution carbide-graphite composite systems. FIGURE 4 shows the result of tests run on pressings of TaC, NbC and a 50 w/o solid solution of TaC and NbC. The data show that the homogeneous alloy solid solution formed during hot pressing was dramatically more resistant to deformation than the individual carbides.

The specific procedure set forth (A on FIGURES 1 and 2) was selected since it has been found that this composition is very advantageous in withstanding thermal shock. For example, samples of this composition have been tested and found to hold up at varying thermal strains up to about 500° C. per second.

FIGURE 5 compares deformation at constant total carbide-to-graphite compositions for solid solution carbide-graphite composites made by the various specific methods of the present invention. Materials B and C are 70 w/o NbC-30 w/o TaC while compositions A, D and E are 50 w/o NbC and 50 w/o TaC. Compositions A and B are formed by method 1, C and E by method 2, and D by method 4. It would appear that the high deformations for compositions C and E are a result of utilizing high metal impurity carbides as starting materials.

What is claimed is:

1. A method of forming solid-solution carbide-graphite composites, the improvement comprising mixing powdered graphite with powdered carbides of tantalum and niobium, hot pressing the resulting powdered mixture at a temperature of about 3050° C., a pressure of about 3200 p.s.i., for a period of about 10 minutes, said mixture having a composition of 54 volume percent graphite-46 volume percent carbides, and the weight percent ratio of niobium carbide to tantalum carbide being in the range of 70 to 50 percent.

2. A method as in claim 1 wherein the solid solution composite mixture has 54 volume percent graphite-46% total carbides and the carbides are present in the ratio 50 w/o NbC and 50 w/o TaC.

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