## July 10, 1956

### W. W. WELLBORN

## 2,753,621

SINTERED CARBIDE COMPOSITIONS AND METHOD OF MAKING THE SAME

Filed Feb. 11, 1953









Fig. 4

INVENTOR. William W. Wellborn

BY Welt, machey & Burden. HIG ATTORNEYS

# **United States Patent Office**

1

#### 2,753,621

#### SINTERED CARBIDE COMPOSITIONS AND METHOD OF MAKING THE SAME

William W. Wellborn, Baldwin Borough, Pa., assignor to Firth Sterling, Inc., Pittsburgh, Pa., a corporation of Pennsylvania

Application February 11, 1953, Serial No. 336,324

#### 11 Claims. (Cl. 29-182.7)

This invention relates to sintered carbide compositions 15 and to a method of making the same. It relates more particularly to sintered chromium carbide compositions containing two different chromium carbides and one or more binder metals such as nickel or cobalt. The composition preferably contains a small proportion of one or more 20 grain refining elements such as copper or tungsten carbide. The proportions of the various ingredients are such that the coefficient of expansion of the sintered carbide composition in the temperature range of  $32^{\circ}$  F. to  $576^{\circ}$  F. is substantially the same as that of steel, i. e.,  $6.3 \times 10^{-6}$  25 inches per inch per ° F.

There are many uses for sintered carbide compositions which have coefficients of expansion substantially equal to that of steel. Such compositions are desirable due to their strength, hardness and wear-resisting qualities, but 30 most of them have coefficients of expansion which differ substantially from that of steel. Sintered carbide compositions according to the present invention, since they have a coefficient of expansion substantially equal to that of steel, find particular application as gauge blocks for measuring steel at different temperatures. They also are desirable for many other uses, for example, as sealing rings for pumps and for bearings where the sintered carbide composition is closely associated with a steel element and it is necessary in order to maintain the desired 40 fit to have the sintered carbide composition and the steel element expand and contract substantially equally.

The accompanying drawings illustrate in a diagrammatic manner a gauge block and a method of making it.

Figure 1 is a plan view of the gauge block,

Figure 2 is a side elevation thereof,

Figure 3 is an end elevation thereof, and

Figure 4 is a side elevation of a billet pressed from powder and given a preliminary sintering treatment, the figure illustrating how the billet is severed into a plurality 50 of gauge blocks.

My sintered carbide composition contains by weight about 40% to 60% Cr<sub>3</sub>C<sub>2</sub>, about 25% to 45% Cr<sub>4</sub>C, the proportion of Cr<sub>3</sub>C<sub>2</sub> to Cr<sub>4</sub>C being between 1:1 and 7:3, the total of said carbides being between about 86% and 55 90%, and about 10% to 12% nickel or cobalt, or both, used as binder metals. In the specification and claims, wherever percentages or proportions are given, they mean percentages or proportions by weight, unless otherwise specified. The preferred binder metal is nickel. The composition preferably, although not necessarily, contains a small amount of one or more grain refining elements such as copper or tungsten carbide. Copper is much preferred over tungsten carbide as a grain refining element. Where copper is used, it is employed in an amount from about 0.5% to 2.0% of the composition. Where tungsten carbide is used, it is employed in an

2

amount between about 0.5% and 3.0% of the composition. A preferred composition is:

	•		Per cent	
5	Cr3C2		 53	
	Cr4C		 	
	Nickel _		 11	
	Copper		 1	
		and the second second second		

My sintered carbide composition may be made in the following manner.

Mix No. 1 is made by mixing  $Cr_2O_3$  and carbon in such proportions that, when reacted, it forms  $Cr_3C_2$  according to Reaction 1.

#### REACTION 1

#### $3Cr_{2}O_{3}+13C=2Cr_{3}C_{2}+9CO$

Mix No. 2 is made by mixing  $Cr_2O_3$  and carbon in such proportions that, when reacted, it forms  $Cr_4C$  according to Reaction 2.

#### **REACTION 2**

#### $2Cr_2O_3 + 7C = Cr_4C + 6CO$

Mixes 1 and 2 are heated separately in a hydrogen furnace to carry out Reactions 1 and 2, employing, for example, a temperature of 2700° F. for two hours. The Cr<sub>3</sub>C<sub>2</sub> and Cr<sub>4</sub>C so produced are crushed and mixed together and the mixture is then ball milled for a period of, say, 48 hours in order to intimately mix the carbides and reduce them to fine particles. The nickel or cobalt, or both, are then added and if the composition is to contain copper or tungsten carbide, they are added and the mixture is ball milled for a period of, say, 72 hours. A pressing lubricant, for example, paraffin, in a small amount, say 11/2%, is added to the powder mixture. The mixture is then pressed into a billet under a pressure which may be 10 tons per square inch and is then given a preliminary sintering at a temperature of, say, 1300° F. in hydrogen for one hour. The billet which has been given a preliminary sintering is then severed into a plurality of bodies and the bodies are then given a final sintering at a temperature higher than the preliminary sintering in order to produce strong articles, the temperature employed being, say, 2700° F. to 2800° F. for a period of 30 minutes to 90 minutes, the sintering being carried out in a 45 hydrogen furnace. Thereafter, the article, if desired, is diamond lapped or otherwise ground or finished to accurate dimensions.

The following example further illustrates my invention:

#### Example

18.625 lbs. of Cr<sub>2</sub>O<sub>3</sub> and 6.375 lbs. of carbon were mixed to form mix No. 1. 15.6 lbs. of Cr<sub>2</sub>O<sub>3</sub> and 4.40 lbs. of carbon were mixed to form mix No. 2. The two mixes were heated separately in a hydrogen furnace at 2700° F. for two hours. Mix No. 1, when reacted according to Reaction No. 1, produced 12.25 lbs. of Cr<sub>3</sub>C<sub>2</sub> containing 13.33% of carbon. Mix No. 2, when reacted according to Reaction No. 2, produced 8.96 lbs. of Cr<sub>4</sub>C containing 5.45% of carbon.

The  $Cr_3C_2$  and  $Cr_4C$  were crushed, mixed together and ball milled for 48 hours. The mixture contained about 57%  $Cr_3C_2$  and 43%  $Cr_4C$ . Nickel and copper in amounts to provide 11% nickel and 1% copper were added to the carbides and the mixture was ball milled for 72 hours. Thereafter, 1½% of paraffin dissolved in a solvent was added to the mixture. The mixture was

5

then further processed to form gauge blocks such as illustrated in Figures 1-3.

Each of the gauge blocks has a length L, a width W and a thickness T. The powder was pressed into a billet 2 as shown in Figure 4, this billet having a length many times greater than the thickness T of the gauge blocks to be formed therefrom. In carrying out the pressing operation, pressure was exerted in the direction of the longitudinal axis of the billet as indicated by the arrow 3. The pressure mounted to 10 tons per square inch. The compressed billet 2 was then subjected to a preliminary sintering in a hydrogen furnace at a temperature of 1300° F. for one hour so as to produce a coherent mass which could be handled and shaped but which was not so hard as to make shaping difficult. The billet was then sawed 15 transversely into a plurality of gauge blocks by sawing along the lines 4. Thereafter, the gauge blocks were subjected to a final sintering in a hydrogen furnace at a temperature of 2700° F.-2800° F. for one hour.

Gauge blocks, or other articles made in the manner de- 20 scribed, may then be diamond lapped or otherwise ground and finished to accurate dimensions.

The article produced according to the example had a coefficient of expansion in the temperature range of 32° F. to 576° F. of  $6.3 \times 10^{-6}$  inches per inch per ° F., a Rockwell A hardness of 90 and a transverse breaking strength of 100,000 pounds per square inch. The Cr<sub>3</sub>C<sub>2</sub> in the sintered composition was in the form of columnar grains, whereas the Cr4C was in the form of substantially equi-axed grains.

By pressing the powder into a billet having a length many times the thickness of the desired article and then severing the billet transversely to form a plurality of the articles as illustrated in Figure 4, articles having substantially the same coefficient of expansion in all direc-tions are obtained. In other words, the coefficient of expansion in the direction of the length L, in the direction of the width W, and in the direction of the thickness T are substantially identical when the method illustrated in Figure 4 is employed.

The invention is not limited to the preferred embodiment but may be otherwise embodied or practiced within the scope of the following claims.

I claim:

1. A sintered carbide composition having a coefficient 45 of expansion substantially equal to that of steel, said composition containing by weight about 40% to 60% Cr3C2; about 25% to 45% Cr4C, the total of said carbides being between about 86% and 90%, the proportion of Cr3C2 to Cr4C being between 1:1 and 7:3, and about 50 10% to 12% of at least one binder metal of the group consisting of nickel and cobalt.

2. A sintered carbide composition having a coefficient. of expansion substantially equal to that of steel, said composition containing by weight about 40% to 60% Cr3C2, 55 about 25% to 45% Cr4C, the total of said carbides being between about 86% and 90%, the proportion of Cr3C2 to Cr4C being between 1:1 and 7:3, about 10% to 12% of at least one binder metal of the group consisting of nickel and cobalt, and about 0.5% to 3.0% of at least 60 one grain refining agent of the group consisting of copper and tungsten carbide.

3: A sintered carbide composition having a coefficient. of expansion substantially equal to that of steel, said composition containing by weight about 40% to 60% Cr3C2, about 25% to 45% Cr4C, the total of said carbides being between about 86% and 90%, the proportion of Cr<sub>3</sub>C<sub>2</sub> to Cr<sub>4</sub>C being between 1:1 and 7:3, about 10% to 12% of at least one binder metal of the group consisting of nickel and cobalt, and about 0.5% to 2.0% 70 copper.

4. A sintered carbide composition having a coefficient of expansion substantially equal to that of steel, said: composition containing by weight about 40% to 60%

being between about 86% and 90%, the proportion of Cr<sub>3</sub>C<sub>2</sub> to Cr<sub>4</sub>C being between 1:1 and 7:3, about 10% to 12% of at least one binder metal of the group consisting of nickel and cobalt, and about 0.5% to 3.0% tungsten carbide.

5. A sintered carbide composition having a coefficient of expansion substantially equal to that of steel, said composition containing by weight about 40% to 60%

- Cr3C2, about 25% to 45% Cr4C, the total of said carbides 10being between about 86% and 90%, the proportion of Cr<sub>3</sub>C<sub>2</sub> to Cr<sub>4</sub>C being between 1:1 and 7:3, and about 10% to 12% nickel.
  - 6. A sintered carbide composition having a coefficient of expansion substantially equal to that of steel, said composition containing by weight about 40% to 60% Cr3C2, about 25% to 45% Cr4C, the total of said carbides being between about 86% and 90%, the proportion of Cr<sub>3</sub>C<sub>2</sub> to Cr<sub>4</sub>C being between 1:1 and 7:3, about 10% to 12% nickel, and 0.5% to 2.0% copper.

7. A sintered carbide composition having a coefficient of expansion substantially equal to that of steel, said composition containing by weight about 53% Cr<sub>3</sub>C<sub>2</sub>, about 35% Cr4C, and about 10% to 12% of at least one binder metal of the group consisting of nickel and co-25 balt.

8. A sintered carbide composition having a coefficient of expansion substantially equal to that of steel, said composition containing by weight about 53% Cr<sub>3</sub>C<sub>2</sub>, about 35% Cr4C, about 10% to 12% of at least one 30 binder metal of the group consisting of nickel and cobalt, and about 0.5% to 2.0% copper.

9. A method of making a sintered carbide composition article having a coefficient of expansion in all directions substantially equal to that of steel, which comprises providing a powder mixture containing by weight about 40% to 60% Cr3C2, about 25% to 45% Cr4C, the total of said carbides being between about 86% and 90%, the proportion of Cr3C2 to Cr4C being between 1:1 and 7:3, and about 10% to 12% of at least one binder metal of the group consisting of nickel and cobalt, pressing said mixture into a billet having a length many times the thickness of the article to be produced therefrom, the pressure being exerted in the direction of the longitudinal axis of the billet, subjecting the billet to a preliminary, sintering to form a coherent mass which can be handled. and shaped, severing the billet transversely into a plurality of articles, and subjecting said articles to further. sintering at a temperature higher than that employed. in the preliminary sintering in order to form a strong article.

10. A method of making a sintered carbide composition having a coefficient of expansion substantially equal. to that of steel, which comprises separately forming Cr3C2, separately forming Cr4C, mixing the Cr3C2, the Cr4C and at least one binder metal of the group consisting of nickel and cobalt to form a batch containing by weight about 40% to 60% Cr3C2, about 25% to 45% Cr4C, the total of said carbides being between about 86% and 90% of the batch, the proportion of Cr3C2 to Cr4C being between 1:1 and 7:3, and about 10% to 12% of at least one of said binder metals, and pressing and sintering said batch.

11. A method of making a sintered carbide composition having a coefficient of expansion substantially equal 65 to that of steel, which comprises separately forming. Cr<sub>3</sub>C<sub>2</sub> by heating to reaction temperature a mixture of chromium oxide and carbon in substantially stoichiometric proportions to form Cr3C2, separately forming Cr4C by heating to reaction temperature a mixture of, chromium oxide and carbon in substantially stoichiometric proportions to form Cr4C, mixing the Cr3C2, the Cr4C and at least one binder metal of the group consisting of nickel and cobalt to form a batch containing by weight about 40% to 60%. Cr3C2; about 25% to 45%; Cr3C2, about 25% to 45% Cr4C, the total of said carbides 75 Cr4C, the total of said carbides being between about

<b>5</b> = <b>5</b>		6	
86% and 90% of the batch, the proportions of CraC <sub>2</sub> to Cr <sub>4</sub> C being between 1:1 and 7:3, and about 10% to 12% of at least one of said binder metals, and pressing and sintering said batch. $5$	1,757,846 2,116,400 2,124,020 2,244,052 2,581,252	Schroter Marth Wirth Comstock Goetzel	May 6, 1930 May 3, 1938 July 19, 1938 June 3, 1941 Jan. 1, 1952
References Cited in the file of this patent		FOREIGN PATENTS	
UNITED STATES PATENTS	502 005	Great Britain	Apr 18 1939

2,753,621

1,728,909

Schroter \_\_\_\_\_ Sept. 7, 1929