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SEMI-CONDUCTOR COMPOSITION

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18 Claims. (Cl. 252—503)

This is a continuation-in-part of our co-pending application S. N. 357,906 filed May 27, 1953, now abandoned.

This invention relates to a semi-conductor composition and more particularly to a glass-phase ceramic composition having special electrical and physical properties.

It is an object of our invention to provide a composition, the resistance of which is readily controlled within wide limits. It is another object of our invention to provide a glass phase-ceramic composition, the resistance of which is accurately controlled to within narrow limits by the addition of reducing agents.

The ceramic compositions disclosed in our parent application are basically titanates and stanno-titanates which have been modified to obtain semi-conductor materials having stable and reproducible electrical characteristics, i. e. resistance, low thermal coefficient of conductivity and low voltage coefficient of resistivity.

We have found that the presence of Ta^{+5} reduces the resistivity of the titanate and stanno-titanate material to a marked extent. Ta^{+5} has about the same ionic radius as Ti^{+4} but has a higher ionic charge and is visualized as going into the titanium crystal structure with an incomplete bond thus forming electronic imperfections or "holes." It has been found that as little as 2% of Ta_2O_5 lowers the resistivity considerably and the addition of said compound in the amount of 10% reduces the resistance to 1/10 of that without the addition. Such addition was found to have no effect on the voltage coefficient of resistivity of the composition.

It was also found that V_2O_5 acts in a manner similar to Ta_2O_5 though to a lesser degree. For this reason we prefer to use Ta_2O_5.

It was also found that the presence of molybdenum or tungsten oxides, alone or in combination, in the titanate or stanno-titanate compositions greatly reduced the voltage coefficient of resistivity. We prefer to use the molybdenum oxide inasmuch as its effect on the voltage coefficient is greater than that of the tungsten oxide.

In order to obtain the characteristics desired, it is necessary to thermally react the semi-conductor constituents. However, it has been found that the reacted composition was not as stable as required for some applications. Stability has been attained by the introduction of certain ceramic materials into the mixture prior to calcination. Such materials as tabular corundum, magnesia, mullite, zircon, chrome oxide, etc., have been found to be suitable. We prefer to use tabular corundum, a high temperature calcined alumina, on the basis of results obtained from test.

The range of compositions yielding the best results are as follows:

Material:	Limits, parts
TiO_2	15–60
SnO_2	0–50
Ta_2O_5	up to 15
MoO_3	0–10
Al_2O_3	20–40

The preferred composition varies with the particular application in mind. As an example, where the semi-conductor material is to be utilized in a creep gap or resistor the composition may be

	Parts
TiO_2	60
SnO_2	20
Ta_2O_5	10
MoO_3	4
Al_2O_3	40

The semi-conductor material in accordance with this invention may be prepared, after weighing out the desired amounts, by thoroughly dry mixing in a Lancaster mill, the constituents being of such size as to pass a 325 mesh screen (43 microns) with most particles being less than 10 microns. The batch is then placed in a suitable container and calcined at a temperature of around 1400° C. in an atmosphere that may be slightly oxidizing, though this is not essential and we do not wish to be limited thereto. For example, a reducing atmosphere may be used thereby giving further control of the resistivity of the material. The calcined material is then ground to the desired state of subdivision, preferably finer than 200 mesh. If desired, the material may be briquetted before firing. The semi-conductor material so formed is then suitable for application in whatever form desired.

We have found that the admixture of our semi-conductor material with glass not only produces a dense, non-porous structure but also results in a composition the resistance range of which is subject to ready control by selection of the type of glass used.

In accordance with our invention, the use of a barium-borate glass in admixture with our semi-conductor material yields a structure which has a very low range of electrical resistance whereas the use of an alkali-boro-silicate glass yields a structure which has a very high range of resistance. However, a magnesium-borate glass, in contrast to the barium-borate, gives a high range of electrical resistance. Likewise, a boro-aluminum-silicate glass has a very high range of resistance. Thus, it can be seen that the coarse resistance range can be varied widely by a change in composition of the glass phase. Likewise, as pointed out hereinbefore, coarse control of the resistance of the composition is obtained by varying the amount of Ta_2O_5 in our semi-conductor material.

The fine control of the resistance of our final composition is obtained by the addition of reducing agents, the resistance being lowered as the amount of reducer is increased. We have found that the addition in very small quantity of such reducing agents as powdered aluminum and carbon, the latter having a particle size of about 0.3 micron and being available commercially as Thermax, enables almost precision-like control of the resistance of the final product. The amount of reducer added should be so small as to exist in the product as a discontinuous phase and function not as a conductor material but solely as a reducing agent. Though the exact nature of the interaction of the materials in the composition is not known, it is theorized that the glass phase acts to form a multitude of reaction bombs each containing reducer and semi-conductor material which react in the course of hot-pressing the desired element to form a glass-like semi-conducting structure. The reaction in the glass-phase apparently also results in the materials being integrated therewith.

It has been noted that the aluminum has a greater effect in reducing the resistance than has the carbon and we have been able to obtain very satisfactory results by using quantities of each, though it should be understood that this is not essential.

In the hot pressing operation, the mold or die contain-

ing the semi-conductor composition is heated at a definite temperature necessary to develop the plastic flow characteristics of the glass phase. Various types of glasses require different temperatures and we have found that a temperature of 1550° F. to 1850° F. suffices for most glasses. At the same time, a pressure sufficient to cause the glass to flow into the mold contour and produce a relatively non-porous article is applied, the article being kept under pressure while cooling until the glass has become rigid.

We have found that the amount of the particular glass used, as distinguished from the amount of reducer used, has no appreciable effect on the resistance of the composition within the limits of about 25 to 40 parts by weight of the composition. Likewise, though the composition of the glass phase does not affect the temperature coefficient of resistance or voltage coefficient of resistance of the semiconductor composition, it is undesirable to mix two or more types of glass since we have found that such mixing tends to reduce the stability of the temperature and voltage coefficients otherwise obtained.

The fluidity of the final composition, as exhibited during the hot pressing operation, is controlled by the presence of a filler or diluent material which does not react chemically with the other constituents of the composition. We have been able to obtain very satisfactory results with a −48 to +100 mesh mullite though other materials such as borolon, zircon, chromium oxide and aluminum oxide, etc. may be used. The filler or diluent material may be added to the semi-conductor composition or may be only that amount present in the semi-conductor (stanno-titanate) material. It has been noted that the filler also increases the temperature resistance of the formed element after hot pressing, the composition becoming more refractory and less fluid than on the first heating.

Since the glass phase semi-conductor composition is best handled in a granulated form, a binder such as bentonite, a very plastic aluminum silicate, is added to bond the particles together during processing.

The range of composition may vary widely depending on the electrical, thermal and voltage characteristics desired. We have found the following range to be suitable for most purposes:

	Parts
Glass	25–40
Semi-conductor material	25–75
Filler	0–40
Reducing agent	0–6

The preferred composition varies with the particular application in mind and the following are examples of compositions preferred for use in resistors and creep gaps:

Resistance (approximate)—ohms	1,000	10,000	100,000	250,000
	Parts	*Parts*	*Parts*	*Parts*
Glass (Barium-borate type)	25			
Glass (Magnesium-borate type)		25		
Glass (Boro-aluminum-silicate type)			25	25
Semi-conductor material	45	50	75	75
Filler	30	25		
Aluminum	0.8	1	3	1
Carbon (Thermax)	0.8	1	3	1
Bentonite	3	3	3	3

The composition of the semi-conductor material is:

	Parts
Titania, TiO_2	60
Tin oxide, SnO_2	20
Tantalum oxide, Ta_2O_5	10
Molybdenum oxide, MoO_3	40
Aluminum oxide, Al_2O_3	40

The semi-conductor composition of our invention may be prepared in granular form by first dry mixing the materials and then adding water to make a plastic mass. The plastic mass is then forced through a 20 mesh screen and the resulting granules dried. The dried material is then regranulated through a 28 mesh screen and the material retained between 28 and 100 mesh is used. This sizing has been found to produce granules which are most suitable for uniform volumetric feed. Alternatively, the materials may be dry mixed and formed into a free-flowing slip by addition of water. The slip is then passed into a spray-drying tower where the desired agglomerates are formed.

At this point it should be noted that the sizing of the semiconductor composition of our invention may be varied in accordance with the requirements of the specific application. Likewise, it should be understood that while we have disclosed our invention as it relates to particular glasses, other glasses may be used, the semi-conductor composition being then formed by a hot pressing operation into a vitrified article of the desired shape and having the required physical and electrical characteristics.

It is thus apparent from the above description that we have provided a glass phase semi-conductor composition adapted to be readily formed with a substantially non-porous, vitrified, ceramic article of manufacture, the electrical properties of which may be readily controlled to satisfy predetermined requirements.

While we have disclosed our invention with reference to certain preferred embodiments thereof, it is to be understood that modification may be made within the limits of our disclosure and as defined by the scope of the attached claims which follow.

What is claimed is:

1. A ceramic composition exhibiting stable electrical properties consisting essentially of a substantially electrically stable mixed metal oxide semi-conductor material in admixture with glass and a reducing agent which latter constituent controls the resistance of the composition and is present in such small amount as to act as a discontinuous reducer phase, said semiconductor material consisting essentially of 15–60 parts of TiO_2, 0–50 parts of SnO_2, up to 15 parts of Ta_2O_5, 0–10 parts of MoO_3 and 20–40 parts of Al_2O_3.

2. A ceramic composition as set forth in claim 1 wherein said glass is of the group consisting of the borate and silicate type glasses.

3. A ceramic composition as set forth in claim 1 wherein said glass is a borate type glass.

4. A ceramic composition as set forth in claim 1 wherein said glass is a silicate type glass.

5. A ceramic composition as set forth in claim 1 wherein said reducing agent is at least one of the materials from the group consisting of aluminum and carbon and said glass is a barium borate glass.

6. A ceramic composition as set forth in claim 1 wherein said reducing agent is at least one of the materials from the group consisting of aluminum and carbon and said glass is a magnesium borate glass.

7. A ceramic composition as set forth in claim 1 wherein said reducing agent is at least one of the materials from the group consisting of aluminum and carbon and said glass is a boro-aluminum-silicate glass.

8. A composition of matter consisting essentially of 25 to 40 parts glass, 25 to 75 parts of a substantially electrically stable semi-conductor material, 0 to 40 parts filler, 0 to 6 parts reducing agent selected from the group consisting of aluminum and carbon and 0 to 6 parts binder, said semi-conductor material consisting essentially of 15–60 parts of TiO_2, 0–50 parts of SnO_2, up to 15 parts of Ta_2O_5, 0–10 parts of MoO_3 and 20–40 parts of Al_2O_3.

9. A composition of matter composed of 25 parts barium borate glass, 45 parts of a substantially electrically stable mixed metal oxide semi-conductor material, 30 parts filler, 0.8 part powdered aluminum, 0.8 part carbon and 3 parts bentonite, said aluminum and carbon being present as a discontinuous reducer phase, and said semi-

conductor material consisting essentially of 15–60 parts of TiO_2, 0–50 parts of SnO_2, up to 15 parts of Ta_2O_5, 0–10 parts of MoO_3, and 20–40 parts of Al_2O_3.

10. A composition of matter composed of 25 parts magnesium borate glass, 50 parts of a substantially electrically stable mixed metal oxide semi-conductor material, 25 parts filler, 1 part aluminum, 1 part carbon and 3 parts bentonite, said aluminum and carbon being present as a discontinuous reducer phase, and said semi-conductor material consisting essentially of 15–60 parts of TiO_2, 0–50 parts of SnO_2, up to 15 parts of Ta_2O_5, 0–10 parts of MoO_3, and 20–40 parts of Al_2O_3.

11. A composition of matter composed of 25 parts boro-aluminum-silicate glass, 75 parts of a substantially electrically stable mixed metal oxide semi-conductor material, 3 parts powdered aluminum, 3 parts carbon and 3 parts bentonite, said aluminum and carbon being present as a discontinuous reducer phase, and said semi-conductor material consisting essentially of 15–60 parts of TiO_2, 0–50 parts of SnO_2, up to 15 parts of Ta_2O_5, 0–10 parts of MoO_3, and 20–40 parts of Al_2O_3.

12. A composition of matter composed of 25 parts boro-aluminum-silicate glass, 75 parts of a substantially electrically stable mixed metal oxide semi-conductor material, 1 part powdered aluminum, 1 part carbon and 3 parts bentonite, said aluminum and carbon being present as a discontinuous reducer phase, and said semi-conductor material consisting essentially of 15–60 parts of TiO_2, 0–50 parts of SnO_2, up to 15 parts of Ta_2O_5, 0–10 parts of MoO_3, and 20–40 parts of Al_2O_3.

13. A resistance element having stable electrical properties formed by hot-pressing a composition consisting essentially of a dense vitrified mixture of 25 to 40 parts glass, 25 to 75 parts of a substantially electrically stable semi-conductor material, 0 to 40 parts filler, 0 to 6 parts reducing agent and 0 to 6 parts binder, said semi-conductor material consisting essentially of 15–60 parts of TiO_2, 0–50 parts of SnO_2, up to 15 parts of Ta_2O_5, 0–10 parts of MoO_3, and 20–40 parts of Al_2O_3.

14. A resistance element having stable electrical properties formed by hot-pressing a composition consisting essentially of a dense vitrified mixture of 25 parts barium borate glass, 45 parts semi-conductor material, 30 parts filler, 0.8 part aluminum, 0.8 part carbon and 3 parts bentonite, said semi-conductor material consisting essentially of about 60 parts TiO_2, about 20 parts SnO_2, about 10 parts Ta_2O_5, about 4 parts MoO_3 and about 40 parts Al_2O_3.

15. A resistance element having stable electrical properties formed by hot-pressing a composition consisting essentially of a dense vitrified mixture of 25 parts magnesium borate glass, 50 parts semi-conductor material, 25 parts filler, 1 part aluminum, 1 part carbon and 3 parts bentonite, said semi-conductor material consisting essentially of about 60 parts TiO_2, about 20 parts SnO_2, about 10 parts Ta_2O_5, about 4 parts MoO_3 and about 40 parts Al_2O_3.

16. A resistance element having stable electrical properties formed by hot-pressing a composition consisting essentially of a dense vitrified mixture of 25 parts boro-aluminum-silicate glass, 75 parts mixed metal oxide semi-conductor material, 3 parts aluminum, 3 parts carbon and 3 parts binder, said semi-conductor material consisting essentially of about 60 parts TiO_2, about 20 parts SnO_2, about 10 parts Ta_2O_5, about 4 parts MoO_3 and about 40 parts Al_2O_3.

17. A resistance element having stable electrical properties formed by hot-pressing a composition consisting essentially of a dense vitrified mixture of 25 parts boro-silicate glass, 75 parts semi-conductor material, 1 part aluminum, 1 part carbon and 3 parts bentonite, said semi-conductor material consisting essentially of about 60 parts Ti_2O, about 20 parts SnO_2, about 10 parts Ta_2O_5, about 4 parts MoO_3 and about 40 parts Al_2O_3.

18. In a ceramic composition having a semi-conductor material in admixture with glass, the improvement which consists of using an electrically stable mixed metal oxide semi-conductor together with a small amount of reducing agent selected from the group consisting of carbon and aluminum sufficient to produce the desired resistance upon hot-pressing the composition, said reducing agent being present as a discontinuous reducing phase and said semi-conductor material consisting essentially of 15–60 parts of TiO_2, 0–50 parts of SnO_2, up to 15 parts of Ta_2O_5, 0–10 parts of MoO_3, and 20–40 parts of Al_2O_3.

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UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

Patent No. 2,864,773 December 16, 1958

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It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 3, line 71 for

"Molybdenum oxide, MoO_3---- 40

read

-- Molybdenum oxide, MoO_3---- 4 --.

Signed and sealed this 14th day of April 1959.

(SEAL)
Attest:

KARL H. AXLINE
Attesting Officer

ROBERT C. WATSON
Commissioner of Patents