

UNITED STATES PATENT OFFICE

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METALLIC CARBIDES USED AS MICROPHONE RESISTANCE GRANULES

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This invention relates to microphones containing metal carbides in granular form as the pressure responsive elements thereof.

It is a well-known desire, that a microphone which is to transform variations of the pressure in air, water or another medium into electrical current variations should have a sufficient sensitivity, that is, give rise to great variations of the resistance with small variations of the pressure. The relative variations of the contact resistance must chiefly be proportional to the relative variations of the pressure. At the same time such a static contact resistance is desired, as can through suitable treatment be varied within certain limits at the same volume of granules in the transmitter inset. A relatively great static resistance is especially valuable. A more favourable matching of the static resistance of the transmitter to the input impedance of the connected telephone line is thereby obtained. A high resistance also requires a lower current and consequently a lower current consumption. The granulated material in the transmitter should also be chemically and physically constant.

These requirements are not met with to a sufficient degree in the granulated materials for transmitters known until now.

A condition for obtaining a high sensitivity and good qualities in other respects is that the granulated material has a low external resistance within each granule in relation to the contact resistance between the different granules. It has been tried to achieve this by coating metal granules with a layer of poor conducting material. These experiments have however not given any practical results.

According to this invention a material is used, the external resistance of which does not differ

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chosen, for example a semi-conductor of the excess- or the defect conductor type. An example of a semi-conductor of the excess conductor type is the material obtained from SnO_2 by reduction with hydrogen gas, whereby oxygen atoms are removed and there arise divergences in the stoichiometric composition of SnO_2 . This reduction (which in certain cases can also aim at a reduction of a metalloid component) entails a liberation of metal valences, which considerably increases the conductivity. The condition is the inverse for defect conductors (also called oxidation- or hole conductors). We take for example Cu_2O with a conductivity $\geq 10^{-10}$ $1/\Omega$ cm. and obtain by oxidation with oxygen a defect conductor $\text{Cu}_2\text{O} + x\text{O}$, where x expresses the number of oxygen atoms (resp. metalloid atoms). This compound has thereby a conductivity $\leq 10^{-2}$ $1/\Omega$ cm. By "oxidation" is here also meant introduction of another metalloid than oxygen, for example iodine.

Some typical examples of excess conductors are:

Initial material	Conductivity at near stoichiometric composition	Conductivity at great divergence from stoichiometric composition (after reduction)
ZnO.....	1.10^{-10} $1/\Omega$ cm.....	$0.1.10^1$ $1/\Omega$ cm.
TiO ₂	1.10^{-10} $1/\Omega$ cm.....	$0.4.10^1$ $1/\Omega$ cm.
Fe ₂ O ₃	1.10^{-10} $1/\Omega$ cm.....	$2.1.10^1$ $1/\Omega$ cm.
Ta ₂ O ₅	1.10^{-11} $1/\Omega$ cm.....	1.10^{-8} $1/\Omega$ cm.
SnO ₂	1.10^{-8} $1/\Omega$ cm.....	$9.4.10^1$ $1/\Omega$ cm.
WO ₃	$5.6.10^{-6}$ $1/\Omega$ cm.....	$0.5.10^{-1}$ $1/\Omega$ cm.
U ₃ O ₈	1.10^{-7} $1/\Omega$ cm.....	$2.4.10^{-4}$ $1/\Omega$ cm.
Nb ₂ O ₅	$1.8.10^{-7}$ $1/\Omega$ cm.....	$1.2.10^1$ $1/\Omega$ cm.
MoO ₃	$<1.3.10^{-7}$ $1/\Omega$ cm.....	$2.5.10^2$ $1/\Omega$ cm.
SiC.....		

Some typical examples of defect conductors are:

Initial material	Conductivity	Defect conductor after oxidation	Conductivity
Cu_2O	10^{-10} $1/\Omega$ cm. (20° C.).....	$\text{Cu}_2\text{O} + x\text{O}$	$>10^{-2}$ $1/\Omega$ cm. (20° C.).
Cu_2J	10^{-3} $1/\Omega$ cm. (20° C.).....	$\text{Cu}_2\text{J} + x\text{J}$	>1 $1/\Omega$ cm. (20° C.).
CoO	10^{-7} $1/\Omega$ cm. (300° C.).....	$\text{CoO} + x\text{O}$	$>10^{-2}$ $1/\Omega$ cm. (300° C.).
UO_2	10^{-3} $1/\Omega$ cm. (20° C.).....	$\text{UO}_2 + x\text{O}$	$>10^{-1}$ $1/\Omega$ cm. (20° C.).

considerably from the external resistance of the granule, but the contact resistance of which can be made considerably higher, thereby allowing greater variations at changes in the contact pressure. According to the invention, this is achieved by making use of the known fact, that the contact resistance of a certain material grows with the hardness. A material with great hardness is

It has appeared that excess and respectively defect conductors with two or more free valences are considerably more stable chemically and physically than conductors with one free valence.

Especially good results have been obtained with SnO_2 , which is found in nature in the shape of cassiterite as large crystals or small granules, mixed with sand. Its colour varies from diamond

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shining clear yellow to black, depending on the percentage and the nature of the impurities. The black kind, containing iron as the most probable impurity, shows a hardness up to 170,000 kg./cm.². This material is practically an insulator in spite of the impurities.

For the production of excess conductors in the shape of granulated material it is possible to proceed from cassiterite, which is crushed to the desired granule size. It is then reduced in a current of hydrogen gas at a certain temperature, for example between 500-700° C. and for a certain time, for example one hour. An excess conductor having two free metal valences for each reduced oxygen atom is thereby obtained. Unreduced SnO₂ can however occur in the core of the granule. Such an excess conductor can also be produced from SnO₂ in other compounds than cassiterite, for example by oxidation of pure tin in favourable conditions to SnO₂ and thereafter suitable reduction.

Carbides such as TiC, VC, WC, Mo₂C and TaC have also been proved. They have been produced from waterfree (that is glow) oxides with carbon at a high temperature. The lowest possible temperature was for vanadium carbide (VC) 1100° C. and for tantalum carbide (TaC) 1250° C. These two carbides have shown the greatest changes of resistance at certain changes of the pressure.

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A granulated material with varying composition, contact resistance and hardness can be obtained by reduction and respectively oxidation in different manners at different temperatures, pressures and times.

We claim:

1. A microphone containing, as the pressure-dependent electrical resistance, granules of a metal carbide.

2. A microphone containing, as the pressure-dependent electrical resistance, granules of vanadium carbide.

3. A microphone containing, as the pressure-dependent electrical resistance, granules of tantalum carbide.

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