OTS: 60-11-513

JPRS: 2526

22 April 1960

SEMICONDUCTOR THERMOCOUPLES FOR HIGH TEMPERATURE USES

- USSR -

by P. S. Kislyy and G. V. Samsonov

Distributed by:

OFFICE OF TECHNICAL SERVICES
U. S. DEPARTMENT OF COMMERCE
WASHINGTON 25, D. C.

U. S. JOINT PUBLICATIONS RESEARCH SERVICE
205 EAST 42nd STREET, SUITE 300
NEW YORK 17, N. Y.

JPRS: 2526

CSO: 3656-N

SEMICONDUCTOR THERMOCOUPLES FOR HIGH TEMPERATURE USES

/This is a translation of an article by P. S. Kislyy and G. V. Samsonov in Izvestiya Akademii Nauk SSSR, Otdeleniye Tekhnicheskikh Nauk, Metallurgiya i Toplivo (News of the AS USSR, Dept. of Technical Science, Metallurgy and Fuel), No 6, Moscow, Nov-Dec 1959, pages 133-137./

One of the basic tendencies of the development of contemporary engineering is the intensification of industrial processes which is frequently attained in metallurgy, chemistry, power engineering and other branches by means of increase of the temperatures of these processes with a simultaneous inclination toward their automation.

For realization of control and automation of high-temperature processes, the creation of thermocouples is necessary, which, on one hand, would provide sufficiently accurate measurements of high temperatures, i.e., have sufficiently high electromotive force and which on the other hand would be stable for the duration of a prolonged time against the action of molten metals, slags, and aggressive gaseous media.

Measuring temperatures by means of optical and radiational pyrometers does not provide sufficient accuracy, due to the dependence of the radiating ability of materials not only on their temperatures but also on the most insignificant changes of their chemical composition, the character of the gaseous medium etc. [1] - without mentioning the fact that the automation of processes in utilization of pyrometric control of temperatures becomes essentially complex and, in some cases, becomes practically impossible.

At the present time, a great number of thermocouples are known; however, they are as a rule unstable in molten metals and many other media and may be exploited only in a vacuum and inert atmospheres, or else the upper limit of temperatures measured with them does not satisfy the requirements of contemporary engineering.

In the present work, an attempt has been made to utilize, for the production of electrodes, thermocouples of high melting compounds, many of which are characterized by high chemical stability. [6]

Since in practice it is not possible to create materials which perform equally well in all media, selection of materials for exploitation in a definite group of media should be performed; specifically, all currently-known high melting materials may be subdivided into the following classes according to this feature:

1. Materials stable up to high temperatures (of the order of 2500-3000°) in inert gases, restoring media, and a vacuum.

To these materials belong many carbides, borides and nitrates of titanium, zirconium, hafnium, vanadium, niobium, tantalum, chromium, molybdenum, and tungsten.

2. Materials stable up to 1500-1800° in oxidizing media. These are silicides of many high melting metals, primarily molybdenum, tugesten, vanadium silicides.

3. Materials stable in many molten metals and alloys with smelting temperatures up to 1000-1200° (lead, tin, zinc, brass, copper, cadmium). According to the data of investigations, many borides belong to such compounds; among them, borides of zirconium, chromium, molybdenum; some carbides, as well as alloys of carbides or borides with high melting metals [7]. Especially high stability in molten metals with the indicated smelting temperatures is possessed by silicon nitride and various alloys of it [8]. This nitride is also stable in many molten salts and in low-melting slag with smelting temperatures to 100-1200°.

4. Materials stable in molten metals with smelting temperatures to 1600-1700°, in particular in molten steel, so far almost unknown. According to preliminary data, among them are titanium nitride and zirconium boride, which are however, unstable against the action of molten slags at these temperatures. To the same kind of materials belong many high-melting oxides.

5. Materials stable in oxidizing media with high temperatures (over 1800°). Among such materials there are

only oxides, their mutual alloys and various silicate compositions.

The selection of materials for high-temperature thermocouples is conditioned not only by their stability in various media but also by their ability, in junctions with one another, to produce a thermoelectromotive force of sufficient magnitude with linear or monotone temperature dependence (but not with inverse).

By means of previously performed measurements, it was shown [9] that many metallic high-melting compounds in pairs with each other possess linear or generally monotone temperature dependence of electromotive force; however, the magnitudes of the latter, as a rule, are small and cannot assure the overwhelming advantage in this respect over the pairs of metals which are used for thermocouples. In connection with this it was decided to stop at high-melting semiconductor compounds, which assure high magnitudes of electromotive force in pairs with high-melting metallic compounds of the type of carbides, nitrides, silicides, and borides. For such semiconductor compounds in the present work, alloys of the system boron-carbon were selected, which are simultaneously characterized by rather high heat resistance and good stability against the action of molten metals. In addition, chromium disilicide was utilized as the semiconductor element whose field of usefulness was limited by the relatively low temperature of its smelting.

For clarification of the nature of temperature dependence and magnitude of electromotive force of alloys in the pairs of high-melting semiconductor compount plus high-melting metallic compound, the following pairs were selected: B_4C-$MoSi_2$, B_4C-TiC, B_4C-TiB_2, B_4C-ZrB_2, $CrSi_2$-TiC, and $CrCi_2$-$MoSi_2$.

The pair B_4C-$MoSi_2$ had previously been studied in detail [10]. The practical investigation of a large number of alloys of boron carbide with molybdenum disilicide showed that in the alloy, as a rule, about 20 mol% of $MoSi_2$ is contained, which is close to the lower limit of homogeneity of a quadruple semiconductor phase. The temperature dependence of the electromotive force of such an alloy has a linear character, beginning with 400°C (Fig. 1);

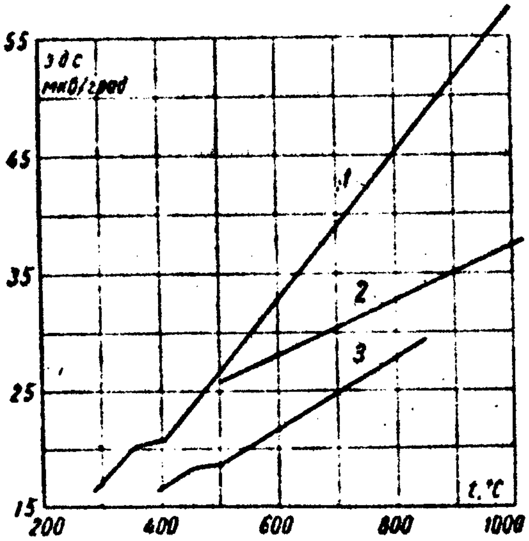

Fig. 1. The temperature dependence of electromotive force of alloys; 20 mol.% $MoSi_2$ + 80 mol.% B_4C (curve 1), 20 mol.% TiC + 80 mol.% $CrSi_2$ (curve 2). 20 mol.% TiC + 80 mol.% B_4C (curve 3).

furthermore, with an increase of temperature, the electromotive force increases considerably, reaching, for example, the value of 55-60 microvolt/degree at 1000°.

In Fig. 1 are also shown the analogous dependencies for alloys which contain 80 mol.% metallic component (TiC) in the pairs of titanium carbide with boron carbide and with disilicide of chromium. In the pair $MoSi_2$(20 mol.%) - $CrSi_2$(80 mol.%), the temperature dependence of the electromotive force has a complex character up to 600°, passing under higher temperature into the linear with magnitudes of electromotive force close to those in the pair TiC-B_4C. All of these experimental "junctions" were prepared by sintering, with hot compression, mixtures of powders of components at temperatures of 2000-2200° for 5-15 min.

The highest electromotive forces are obtained in the pairs of titanium and zirconium borides with boron carbide; furthermore their temperature dependence begins to be linear at 300°.

In all investigated pairs, stable phases are formed whose electric properties in time are practically constant except in the pair $CrSi_2$-$MoSi_2$, where, in selected concentration of $CrSi_2$ in 80 mol.%, an unsaturated hard solution of molybdenum disilicide forms in the chromium silicide [4]. In heating, this passes to saturated with a content of about 70 mol.% of $CrSi_2$ and the liberation of an excess of chromium silicide.

On the basis of the above data, a principal possibility for the creation of semiconductor thermocouples for high-temperature uses was shown which was further developed with respect to construction.

The construction of a thermocouple (Fig. 2) differs in principle from the construction of metal thermocuples and represents a tube of a metallic compound (silicide of molybdenum, boride, carbide, tatanium, zirconium, etc.) which serves simultaneously as one of the electrodes and the jacket of the thermocouple, in which is concentrically located the rod of the semiconductor (boron carbide, chromium silicide) that is the second electrode. Both of these electrodes have been welded at one end, in this respect being closed, and have lead connections at the other end.

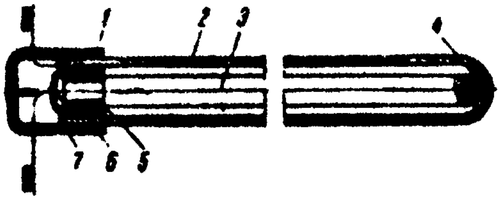

Fig. 2. Semiconductor high temperature thermocouple. 1 and 7 - insulators, 2 - tube of metallic compound, 3 - rod of semiconductor, 4 - junction, 5 and 6 - copper contact bushing.

The especially developed technology for the preparation of high-temperature thermocuples of tubes of high-melting compounds [12-14] consists of pressing out tubular components from material which consists of a powder of the compound with a starch glue and their subsequent sintering.

For preparation of the central electrode-rode in the case of chromium silicide, the same method may be utilized as for tubes. However, in the case of boron carbide, this is difficult, due to bad pressing out and difficulties of sintering semi-finished boron carbide material, which, in addition, is characterized by great fragility. In order to avoid these difficulties and to make the process of production of central rods sufficiently technological and reproducible, it is expedient to utilize rods not of boron carbide but of boron saturated by carbon, or of graphite saturated by boron. In this work the latter variation was selected, i.e., preparation of graphite rods saturated with boron.

For this, graphite rods used for spectral analysis were utilized, as well as graphites of brands B and G. Borating was accomplished by a hard-phase bath consisting of amorphous boron, which usually contains an addition of magnesium which is easily removed under the high temperatures of borating and during the process of the selective diffusion of boron into graphite.

For borating, the graphite rods are covered with a special paste of boron and starch glue prepared according to a special recipe [15]. The ratio of boron and starch glue in the paste is 1:1 by weight. The paste is placed over the rod in an even layer with a thickness of 1.5-2 mm, after which the rods are dried according to this process: placement on the drier at 20°, heating to 150° for the duration of 2-3 hours and keeping at 150° for the duration of 1 hour. Rods prepared in this manner are placed in special linings, made of graphite in a graphite cartridge with lids, into a Tammans oven and are subjected to thermal treatment according to the following method: placement into the oven at 700-800° and keeping them at this temperature for 0.5 hours; raising the temperature to 2350° during 2 hours and keeping them there for the duration of 20-30 min.; cooling with the oven to 1500°, moving forward into the cooler of the oven.

For total borating of the graphite rod with the diameter of 7 mm, used for spectral analysis, this operation is repeated three times, after which the retention of boron equals 22-25% in the rod. Borating from a bath of carbide with borax (1:1 by weight) at 1500° for 2-3 hours also leads to positive results.

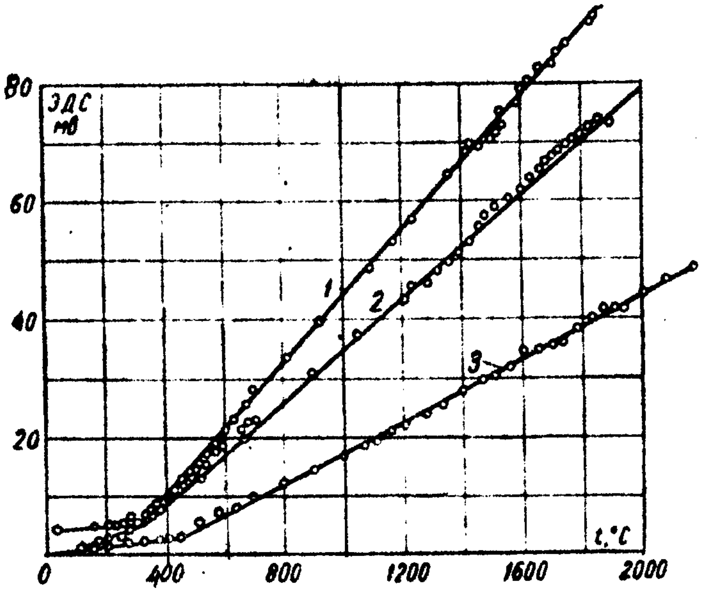

Fig. 3. Calibrated characteristics of thermocouples: 1 - TiB_2-B-C, 2 - ZrB_2-B-C, 3 - $MoSi_2$-B-C

Baked tubes of molybdenum disilicide, intended for the preparation of thermocouples, which work in an oxidizing atmosphere, are oxidized in the air by being heated at 1500-1550° by the direct passed through them of current for the duration of about one hour, or by being heated in ovens with Silit heaters at 1350-1400° for the duration of 4-5 hours.

With this, on the surface of the tube a thin protective film of SiO_2 is formed, which protects it from further oxidation [16].

The junction of the tube with the rod is created by welding. The internal electrode of borated graphite is placed concentrically into the tube and, into the space between them, a layer of molybdenum silicide powder is poured, after which baking under low pressure is conducted in the graphite heater at 1900-2000°.

The welding of the ends of borated graphite thermocouples with titanium carbide or zirconium boride is performed in Tamman's ovens. For this the internal rod is placed into a still-unbaked tube of boride or carbide and is connected at one end by means of the same mixture of which the tube is pressed. Such a preparation is dried and placed into an oven where it is baked at certain temperatures [14].

Lead connections are attached to the electrodes of the thermocouples either by welding to a layer of silver, placed on the cold ends by smearing with a silver paste, or by mechanical pressing by a copper slot bushing to which copper wires are welded.

In Fig. 3, calibrated characteristics of a number of thermocouples are shown (the semiconductor electrode of borated graphite is marked with B-C).

The calibrated characteristics of all thermocouples are linear, beginning at 300-400°; furthermore, the electromotive forces of these thermocouples exceed the electromotive forces of the metallic thermocouples used at the present time in industry. Thus, the electromotive force of the thermocouple containins $MoSi_2$, intended for use in an oxidizing medium is, on the average, three times higher than the electromotive force of platino-platinorhodium thermocouples, and still higher than that of thermocouples containing borides.

Laboratory tests of the stability of the thermocouple during 150 hours in air at 1600° showed that it did not differ from the stability of a platino-platinorhodium thermocouple, tested under the same conditions but at 1200°.

Production experiments conducted in the Alchevskiy Metallurgical Plant imeni Voroshilov for measuring the temperature of escaping gases and warmed air in the vertical channel of a Martin furnace (which was set up from the side of the pouring opening at a level of 1.5 m from the floor of the work platform) showed that it is possible to measure temparatures to 1800-1900° with it for the duration of 10-15 hours in an oxidizing atmosphere.

The thermocouple went out of order after 40-50 hours of work, which was induced by a small thickness at the bottom of the molybdenum silicide, formed in welding, which conditioned the gradual burning out of the borated graphite electrode and the formation of a crater from the end part of the thermocouple. In connection with this it is expedient, after final production of the thermocouple, to weld to its lower end a short hood with a thick bottom which reliably prevents burning through and lets one use the thermocouple under the described conditions for a prolonged time.

Thermocouples of borated graphite with borides and carbides of titanium and zirconium are intended for measuring temperatures to 2200-2300° under vacuum conditions, in a medium of inert and restoring gases.

The thermocouples with an exterior electrode of zirconium boride and some other borides are also stable in molten pig iron at its exit from a blast furnace (Alchevskiy Metallurgical Plant) where they did not show any changes for the duration of 2 hours; in molten brass - 90 hours (Kiev Armature-Machine Works) as well as in molten steel at 1700°.

The described thermocouples may be produced of practically any length.

Since the materials of thermocouple electrodes (especially of the exterior metallic compound) possess a relatively high heat conductance, their cold ends become heated through, which brings a constant error into the temperature measurements. Thus in heating a thermocouple 250 mm long by hot welding to 1700°, the cold ends are warmed to 80-90°. For removal of this error it is possible either to cool the cold ends of thermocouples, or, what is constructionally simpler, to utilize compensation wires which yield about the same electromotive force as the semiconductor thermocouple and the linear dependence of the electromotive force on the temperature. For example, in the linear areas of changes of the electromotive force of the thermocouples to temperatures of 500°, it is more expedient to utilize the compensation of wires made of the pairs Cu-(Cu + 0.9% Ni) - for thermocouple $MoSi_2$-B-C (the electromotive force of such wires is 8-10 microvolts/degree) or Cu(Cu + 3.5% Ni) - for thermocouple TiC-B-C (the electromotive force is 16-18 microvolt/degree). For compensation under higher temperatures, other metallic pairs are selected.

A known drawback of semiconductor thermocouples is their relatively large bulk with the construction selected by us (the minimum cross-section of the thermocouple is 8-10 mm), as well as less durability than metallic thermocouples. In the case of the thermocouple $MoSi_2$-B-C the latter drawback is rather easily removed by the utilization, for the outside tubular electrode, not of a tube of molybdenum silicide but a molybdene tube saturated with silicon for a definite thickness from the inside and the outside. With this, the electric properties of the thermocouple remain unchanged, and the durability, conditioned by the metallic internal part of the tube, increases sharply.

In principle, it is possible in a number of special cases to equip the thermocouple with an additional protective jacket, for example of silicon nitride, which is stable against many molten metals. It is rather difficult to prepare an outside electrode from silicon nitride due to the impossibility of obtaining even somewhat stable welding of nitride with borated graphite.

It follows from the above that the variations of preparation of high-temperature thermocouples of the semiconductor type are not limited by anything in practice, and it is possible rather easily to select electrodes for thermocouples which would assure sufficient electromotive force, sensitivity and the necessary stability in this or that medium.

In the experimental part of the work, A. D. Panasyuk, V. S. Sinel'nikova and V. V. Pen'kovskiy participated.

Conclusions. 1. It was shown that a number of alloys of high-temperature semiconductor compounds of the type of boron carbide or chromium silicide with metallic compounds (carbides, borides) possess high magnitudes and linear temperature dependence of electromotive force in the range of temperatures from 300-400° to 2000-2200°, which, along with the high stability of these compounds and alloys in aggressive media, may be utilized for the construction of high-temperature semiconductor thermocouples.

2. A high-temperature thermocouple has been developed of molybdenum disilicide and borated graphite which possesses an electromotive force that increases linearly within the limits of 400-2000° from 4 to 45 mv, which is characterized by constancy of electromotive force in time and which may be exploited in oxidizing media under temperatures up to 1800-1900°.

3. A series of thermocouples from borated graphite with carbides and borides of titanium, zirconium and other high-melting metals has been developed, which are intended for measuring temperatures in a vacuum, restoring media and inert atmospheres to 2200-2300°, which are also characterized by linearly calibrated characteristics of electromotive force, which changes within the limits of 300-400 to 2200-2300° from 5-6 to 90-120 mv.

4. The possibility of selection of thermocouples with given electric, mechanical properties and stability in various media.

Received 29 June 1959

The Institute of Metalloceramics and
of Special Alloys, Academy of Sciences
Ukrainian SSR, Kiev

BIBLIOGRAPHY

1. Jutmann, K. Entwicklung und Stand der metallurischen Messtechnik des Auslands in den letzten Zehnjahren. Stahl u. Eisen, V. 69, 1949.
2. Rudnitsky, A. A. Thermoelectric Properties of Noble Metals and Their Alloys, p. 5, 13, Publ. Academy of Sciences USSR, 1956
3. L'vovskaya, V. P.; Tarakanova, Ye. F. The Technology of Obtaining and Property of Metalloceramics Alloy for Thermocouple TSNIICHM-1. Bulletin of the Seminar of Heat-Resistant Materials, No. 5, Publ. Academy of Sciences UkrSSR, Kiev, 1959.
4. Tugarinov, N. I.; Moskvichev, G. S.; Yeremin, A. A. A Tunksten Graphite Thermocouple of New Construction.

Lab. head., No. 1, p. 92, 1957.

5. Markovsky, L. Ya.; Orshanskiy, D. L. Pryanishnikov, V. P. Chemical Electrothermics, State Chemical Publ., L., 1952.
6. Samsonov, G. V.; Umanskiy, Ya. S. Hard Compounds of High-Melting Metals. Metallurg-publish., M., 1957.
7. Samsonov, G. V. New Refractory Materials for Melting and Pouring of High-Melting Metals. Refractory Materials, No. 3, p. 122, 1956.
8. Collins, J., Gerby, R. New Refractory Uses, for Silicon Nitride Reported. J. Metals, v. 7, p. 612, 1952.
9. Kolomoyets, N. V.; Neshpor, V. S.; Samsonov, G. V.; Semenkovich, S. A. Thermo-electric Properties of Some Metallic Compounds. ZhTF, v. 28, pp. 2382, 1958.
10. Samsonov, G. V.; Sinel'nikova, V. S.; Kislyy, P. S. Alloys of the Pair Boron-Carbide - Molybdenum Disilicide. DAN UkrSSR, 1959.
11. Nowotny, H.; Kieffer, R.; Schachner, H. Die Strukturuntershuchungen an Siliziden. Mh. Chemie, V. 83, S. 1243, 1952.
12. Samsonov, G. V.; Kislyy, P. S. Tubes and Rods from High-Melting Metals and Their Alloys, DAN Ukr SSR, No. 1, p. 46, 1959.
13. Samsonov, G. V.; Kislyy, P. S. The Technology of Preparation of Tubes and Rods of Molybdenum Disilicide. Refractory Materials. No. 6, 1959.
14. Samsonov, G. V.; Kislyy, P. S. New Technology of Production of Tubes and Rods of High-Melting Metals and Compounds. Publ. Fil. VINITI GNTK USSR and Academy of Sciences USSR, M., 1959.
15. Novikov, A. N. Plastic Forming of Products of Monomineral Composition by Means of Glue. Refractory Materials, No. 1, p. 12, 1957.
16. Samsonov, G. V. Silicides and Their Use in Technology. Publ. Academy of Sciences UkrSSR, Kiev, 1959.

END