Automation of thermal processes constitutes an important advance in production technology. Control over thermal processes taking place at high temperatures calls for suitable temperature gauges which must also be reliable and convenient in operation. For example, completely closed open-hearth, converter, and blast furnace production cycles depend upon the provision of an automatic gauge system capable of continually monitoring the temperature of molten metal during the whole heat. The conditions under which such control is to be exercised are quite complex. The gauges must have good resistance to chemical attack by molten metals and minimum thermal inertia, must give stable indications, and must be convenient in operation. Such requirements are fulfilled by thermocouples protected against their environment by sheaths made of highly refractory materials.

Depending on the service for which they are required, protective thermocouple sheaths may be made in a variety of materials. At temperatures of up to 1000-1200°C, porcelain, stainless steel, and quartz are used. Quartz sheaths have had extensive application in metallurgy for the short-time measurement of iron and steel temperatures. For measurements over longer periods of time, use is made of sheaths made in oxide ceramics, cermets, graphite, and silicon carbide. Oxide sheaths do not afford adequate protection to thermocouples against rupture in aggressive media. Their failures are usually due to intergranular rupture and to thermal crack generation induced by a longitudinal temperature gradient set up during rapid heating and cooling. To improve the operating qualities of sheaths, various composites based on oxides and other materials have been developed. Thus, for the protection of thermocouples in electric arc steel-melting and open-hearth furnaces, sheaths made from mixtures of alumina and titania, magnesia and zirconia, chromic oxide and alumina, and zirconia with various additions are employed [1-5].

Sheath materials based on oxygen-free refractory compounds include silicon carbide [6, 7], for temperature measurements in molten nonferrous metals, molybdenum disilicide, for molten glass, and zirconium diboride, for molten iron and steel [8, 10]. Industrial tests in an open-hearth furnace have shown that the useful life of a zirconium diboride sheath is 2.5-3 h. Sheaths made in a zirconium diboride-molybdenum alloy have a longer life (up to 6 h) because of the high density of the alloy. During prolonged exposure to liquid steel, zirconium diboride sheaths rupture and their structure undergoes appreciable changes. Even more rapid is the rupture of zirconium diboride sheaths in an oxygen converter, where their life does not exceed five heats. This suggests that their rupture in liquid steel is due to oxidation-reduction processes occurring in melts, rather than to a chemical reaction between the diboride and iron. It is known that zirconium diboride exhibits virtually no reaction with iron nor is it wetted by iron.

In liquid steel containing dissolved oxygen and the oxides FeO, SiO₂, CaO, and MgO in the form of slag, zirconium diboride reacts with the oxygen, with the formation of zirconium dioxide and boric anhydride. As an acid oxide, the latter vigorously reacts with both the iron and basic oxides, resulting in the
formation of borate salts which pass into slag. A zirconium dioxide film remains on the zirconium diboride surface, and the subsequent process might be expected to involve diffusion through this film [11]. However, zirconium dioxide does not adhere firmly to the smooth zirconium diboride grains and flakes off under the action of a moving mass of boiling steel, the process being particularly pronounced at grain junctions. To prevent zirconium dioxide from flaking off, it is necessary to ensure that the substrate material has a fine-grained structure with a well-developed network of tortuous boundaries. Investigations have shown that such a structure can be obtained by alloying zirconium diboride with tungsten [12, 13].

In the work described below, protective thermocouple sheaths in zirconium diboride-tungsten alloys were produced by a standard powder metallurgy process comprising charge preparation, shaping, and sintering as the principal operations. The zirconium diboride powder employed, manufactured (to TU 17-66 specification) at the Institute of Materials Science, Academy of Sciences of the Ukrainian SSR, contained 81.3% Zr, 18.5% B, 0.1% C, and 0.1% Fe. The powder was mixed, and at the same time comminuted, with 20-30% of tungsten powder (to TsMTU 4789-56 specification, of 99.98% W content) in an M10 vibratory mill under ethyl alcohol for 2 h. After milling, the specific surface of the charge material was not less than 0.5-1 m²/g.

For plasticizing such a charge, various materials can be employed. In our work, a study was made of the processing characteristics of 20% starch paste and a 2% solution of rubber in benzine. Each of the plasticizers has its advantages and disadvantages both in the preparation of a mixture for extrusion and in subsequent operations.

Starch paste-plasticized charges, containing 15-20% of the plasticizer, were mixed for 30-45 min in a colander to obtain a homogeneous plasticized mass, which was then dried in a vacuum dryer to a moisture content of 10-12% and rubbed through a sieve with a No. 0315 screen (to GOST 3584-53 standard). The resultant granulated charges were extruded within 2-4 h, because starch paste loses its plasticizing qualities with the passage of time, even when the mixture is stored in an enclosed desiccator. Parts extruded from starch paste-plasticized charges were dried in drying cabinets with a controlled moisture content.

Charges containing a solution of rubber in benzine were plasticized by mixing for 2-4 h in a steel-ball mill. After mixing and subsequent air drying, the mixtures were granulated by rubbing them through sieves with No. 0315 screens. Such granulated mixtures retained their plasticity for a long time and did not have to be extruded immediately.

Prior to extrusion, a small amount of plasticizer (5-7 wt. %) was added to the charges, which were then mixed by hand. Sheaths extruded from the rubber-plasticized charges were mechanically much less strong than those extruded from the starch paste-plasticized charges, but could be dried in air at room temperature without any special precautions.

Protective thermocouple sheaths can be shaped from nonplastic materials by a number of methods, the most widely used being those of ramming and vibratory densification, hydrostatic and die extrusion.