

Yu. M. Goryachev, V. A. Obolonchik,  
T. M. Mikhlin, and T. M. Yarmola

UDC 537.226+537.311.33

The work described below was undertaken with the aim of examining the problems involved in the synthesis of gadolinium selenides of compositions  $Gd_{1-x}Me_xSe_{1.5-y}$  (where Me is Ta or Re,  $0 < x \leq 0.03$ , and  $0 \leq y < 0.5$ ), studying some thermoelectric properties of these compounds and analyzing the parameters of electrotransport in them. Gadolinium selenide specimens of compositions  $GdSe_{1.5-y}$  (where  $0 < y \leq 0.5$ ) were prepared by a method, developed by the authors based on a solid-phase reaction between gadolinium sesquiselenide and finely divided gadolinium obtained as a result of the decomposition of gadolinium hydride [1].

In all stages of synthesis the amounts of the main components were controlled by chemical analysis. The resultant specimens were subjected to x-ray phase analysis and lattice parameter determinations. To obtain high purity in the compounds, starting materials of extra-high purity — elemental selenium of "extra-pure" grade to TTs 6-09-2521-77 and elemental gadolinium to TU 48-4-210-72 Gd MD-1 specification — were used and sources of contamination in the processes of synthesis and purification of the compounds themselves were, as far as possible, eliminated.

The alloying of the dense, polycrystalline specimens with tantalum and rhenium was performed during their actual preparation (milling, mixing, pressing, and sintering). The formulas of the alloys were established on the basis of their percentage compositions, as determined by chemical analysis. The alloying was assumed to be accompanied by natural cation substitution. Using the results of x-ray phase analyses and lattice parameter determinations, specimens whose parameters matched those reported in the literature for  $Gd_3Se_4$  were chosen for a study of electrophysical properties. No second phases were detected by x-ray phase analysis. All the specimens investigated had cubic structure of the  $Th_3P_4$  type with a lattice constant  $a$  equal to  $8.722 \pm 0.005 \text{ \AA}$ .

Electrical conductivity  $\sigma$  measurements were made by a compensation method on cylindrical specimens produced by pressing and sintering. The thermo-emf coefficient  $\alpha$  was determined, relative to a platinum electrode, at the same time as electrical conductivity (Fig. 1). All specimens proved to be n-type conductors in the whole temperature range investigated. Characteristically, they exhibited semimetallic properties, manifesting themselves in comparatively high electrical conductivities and high absolute values of thermo-emf coefficient. Estimates of the thermoelectric goodness factor demonstrated that some of the alloys investigated might be suitable for use as thermoelectric materials ( $Z \approx 1 \cdot 10^{-3} \text{ 1/deg K}$ ). The dependence of the electrophysical properties on the substitution of tantalum and rhenium for gadolinium was evidence that such alloys do not fit into the framework of the model of standard, strongly degenerate semiconductors with a single type of carrier; an increase in the number of electrons did not lead to a unique increase of  $\sigma$  and decrease of  $\alpha$ .

The parameters of electrotransport in the alloys investigated were analyzed with the aid of the two-zone model of the structure of their electron valence band [2]. Separate determinations were made of  $\sigma$  and  $\alpha$  in each subband. Such circumstances are described by the following system of starting equations:

$$\left\{ \begin{array}{l} \sigma = \sigma_1 + \sigma_2; \\ \alpha\sigma = -\alpha_1\sigma_1 - \alpha_2\sigma_2; \\ m_1\sigma + T \frac{\partial \sigma}{\partial T} = \sigma_2 \left( \frac{e}{k} \alpha_2 - \frac{9 + m_2 - 3m_1}{3} \right); \\ (m_1 - 1)\alpha\sigma + T \frac{\partial}{\partial T} (\alpha\sigma) = \sigma_2 \left[ -\frac{e}{k} \alpha_2^2 + \frac{15 + m_2 - 3m_1}{3} \alpha_2 - \frac{k}{e} \left( \frac{9 - 2m_2}{3} \right) \right], \end{array} \right.$$

Institute of Materials Science, Academy of Sciences of the Ukrainian SSR. Translated from Poroshkovaya Metallurgiya, No. 4(232), pp. 84-87, April, 1982. Original article submitted April 16, 1981.

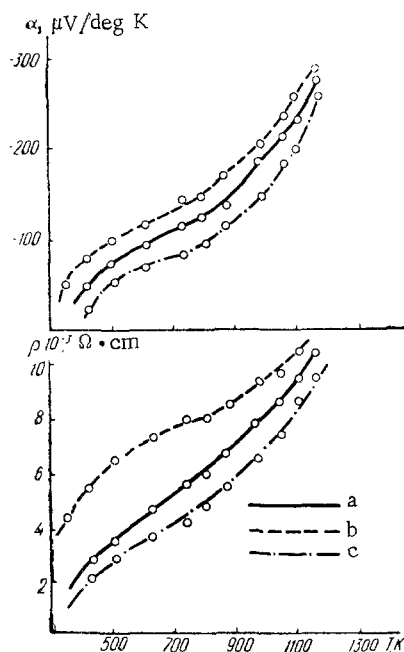


Fig. 1

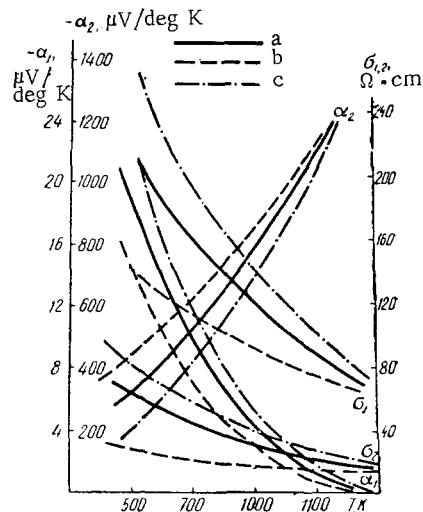


Fig. 2

Fig. 1. Thermoelectric properties of alloys based on gadolinium selenides; a)  $\text{GdSe}_{1.33}$ ; b)  $\text{Gd}_{0.97}\text{Ta}_{0.03}\text{Se}_{1.33}$ ; c)  $\text{Gd}_{0.97}\text{Re}_{0.03}\text{Se}_{1.33}$ .

Fig. 2. Parameters of electrotransport in alloys based on gadolinium selenides. Curve designations as for Fig. 1.

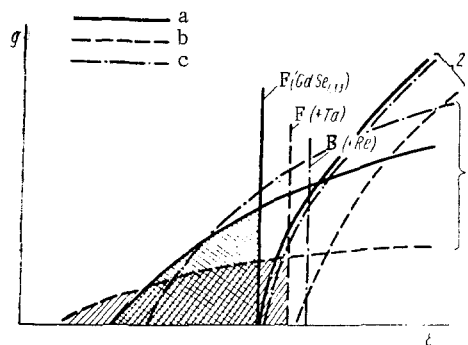


Fig. 3. Dependence of density of electron states  $g$  on energy  $\epsilon$  in 1st (1) and 2nd (2) subzones, respectively, and positions of Fermi levels  $F$  in various alloys based on gadolinium selenides. Curve designations as for Figs. 1 and 2.

where  $\sigma$ ,  $\sigma_1$ , and  $\sigma_2$  are the total electrical conductivity and the conductivities in the first and second zones, respectively;  $\alpha$ ,  $\alpha_1$ , and  $\alpha_2$ , the corresponding coefficients of thermo-emf; and  $m_1$  and  $m_2$ , indices in the equations for the temperature dependence of carrier mobility.

Calculated values of electrotransport parameters for the alloys investigated are shown in Fig. 2. Analysis of the data obtained shows that the electrons responsible for electricity transport in such alloys are located mainly in two subzones, a strongly degenerate (1) and a less degenerate one (2) (Fig. 3). Alloying with rhenium increases the concentration of carriers in both the 1st and 2nd subzones and at the same time markedly increases their localization in the 1st zone. As a result of alloying with tantalum electron localization grows in the 2nd subzone, while in the 1st it substantially decreases, and this is accompanied by a fall in electron concentration.

## CONCLUSIONS

The gadolinium selenide  $\text{GdSe}_{1.3}$  and its alloys are strongly degenerate semimetals of the n-type. These systems can provide a basis for the development of potentially useful thermoelectric materials. Electrotransport in the alloys investigated is effected by electrons in at least two subzones, a strongly degenerate and a weakly degenerate one. Substitution of tantalum and rhenium for gadolinium changes both the carrier concentrations in these subzones and the forms of the subzones (degrees of localization).

## LITERATURE CITED

1. V. A. Obolonchik and T. M. Mikhlin, "Synthesis of the monoselenides of rare-earth metals," *Izv. Akad. Nauk SSSR, Ser. Neorg. Mater.*, 4, No. 2, 286-290 (1968).
2. M. I. Murguzov and Yu. M. Goryachev, "Analysis of electricity conduction in rare-earth-metal chalcogenides," in: *Crystallochemistry of Refractory Compounds* [in Russian], Kiev (1972), pp. 120-127.

## DIFFUSIONAL IMPREGNATION OF SINTERED IRON-TITANIUM MATERIALS WITH CARBON

V. K. Narva, N. T. Salibaev, and O. I. Pershikova

UDC 621.762

The physicomachanical and operating characteristics of iron-base materials can be substantially improved by surface alloying [1]. Physicochemical treatment has a beneficial effect on the surface layers of sintered materials, leaving their cores soft. In the present work a study was made of the diffusional impregnation of sintered iron containing 5, 10, and 15 wt. % Ti with carbon from carbon black packing material. A Höganäs iron powder of  $d_m = 5 \cdot 10^{-5}$  m and an electrolytic titanium powder of  $d_m = 1 \cdot 10^{-4}$  m were employed. Mixtures of the powders were pressed under pressures of  $(3-7) \cdot 10^8$  Pa. The effect of pressing pressure on the density of specimens is shown in Fig. 1.

Diffusional impregnation of the alloys was performed by two methods, combining it with sintering and separately, after sintering. Specimens were sintered in a vacuum electric furnace at temperatures determined in accordance with the Fe-Ti constitution diagram. The alloy with 5% Ti was sintered for  $7.2 \cdot 10^3$  sec at 1473-1523°K, and the alloys with 10 and 15% Ti, for  $5.4 \cdot 10^3$  sec at 1473-1573°K. Carburization consisted in packing alloy specimens in graphite containers filled with lampblack and heating the containers in a graphite-tube resistance furnace in a hydrogen stream.

When impregnation was performed as a separate operation, the process temperature was 1473°K (recommended carbidization temperature range is 1173-1573°K [2]). The duration of impregnation was varied from  $14.4 \cdot 10^3$  to  $43.2 \cdot 10^3$  sec. Specimens with different as-sintered densities ( $\Theta = 77-93\%$ ) were subjected to impregnation. A study was made of the effect of density of sintered materials of varying titanium contents on the distribution of microhardness over the thickness of the diffusion layer and on the actual thickness of this layer.

In chemicothermal treatment combined with sintering the process temperature was chosen in accordance with the Fe-Ti constitution diagram, bearing in mind the need for the simultaneous sintering and carburization of specimens: For the 5% Ti alloy it was 1473, and for the 10 and 15% Ti alloys, 1473-1523°K. The duration of impregnation was  $7.2 \cdot 10^3$  sec. With this variant of chemicothermal treatment a study was made of the effect of density of compacts from powders of various compositions on the distribution of hardness over the thickness of the diffusion layer and on the thickness of this layer ( $\Theta = 69-80\%$ ). The thickness of the diffusion layer was taken to be that thickness in which the microhardness (measured with a PMT-3 tester under a load  $p = 0.98$  N) differed significantly from the hardness of the specimen core.

Data on the effect of density of starting specimens of materials of different compositions after carburization by the two variants are given in Tables 1 and 2. The hardness values are averages for the surface layers and cores. It will be seen that with increasing porosity of specimens in the as-pressed (in the combined process) and as-sintered (with separate impreg-