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High-purity rare-earth metals: preparation, properties, and application

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In recent years, the ever-growing interest of investigators to the study of rare-earth metals REM) is observed owing to unique properties of the metals and potential uses in electronics, laser technology, space technology, medicine, and many other high-technology applications. The effectiveness of the works, first of all, is due to the use of high-purity materials in fundamental investigation that, in this case, allow one to eliminated an accidental effect of impurities and subsequently to use objectively the alloying with small amounts of different elements.

To purify commercial non-volatile REM metals of cerium subgroup (La, Ce, and Nd), we use a technique consisting in two sequential melting processes under different conditions.

At the initial stage of the purification, a metal placed in a copper mold is subjected to electron-beam melting; the heating is produced by an "electron gun" bombarding an anode (ingot) with the electron beam under a high vacuum (no worse than 10^{5} mmHg). This melting provides the degassing metals and is used for non-volatile and low-volatile REM metals that cannot be purified by vacuum distillation-sublimation. The high-vacuum melting allows us to prepare rather large ingots (~250-300 g) characterized by low contents of interstitial and volatile elements; the metal losses are no more than 2%－3%.

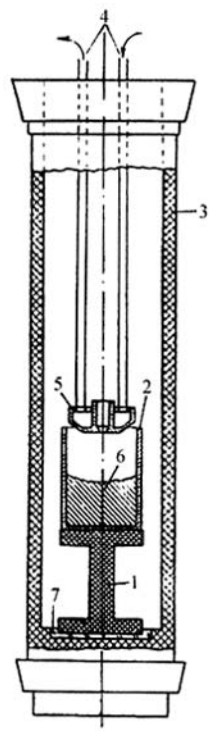

Fig. 1 Scheme of the furnace used for the vacuum distillation of REM in the Baikov Institute of Metallurgy and Materials Science, RAS

As the final stage of purification of La, Ce, and Nd, we use zone melting in a high-purity helium atmosphere. The melting is realized in helium of VCh grade, which is subjected to added purification with activated carbon cooled with liquid nitrogen in order to freeze out water vapor.

The melting is realized in an arc meting using a nonconsumable

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tungsten electrode and water-cooled bottom with a horseshoe-shaped mold 420 mm in length and 30 mm in width. A molten zone 20 mm in width passes along the ingot at a rate of 100 mm/min. We use unidirectional 3 passes along the ingot. This method was used effectively for purification of commercial neodymium, which exhibits a marked increase in the hard magnetic properties of $Nd_2Fe_{14}B$-based magnets.

A technology of purification of rare-earth metals (REM) by vacuum distillation (Y, Pr, Gd, Tb, Lu) and sublimation (Sc, Dy, Ho, Er, Tb, Tm) and optimum regimes of the purification have been developed at the Baikov Institute of Metallurgy and Materials Science. The purification is performed at a residual pressure of 10^{-4}-10^{-5} Pa in a resistor furnace (see Fig. 1) equipped with a graphite heater (3). A purified metal (6) is evaporated from a tantalum crucible (2) and deposited on a water-cooled (4) copper condenser (5) in the form of a druse of small crystal growing together (for some REM, the growth of single crystals is possible). The spacing between the condenser and molten metal is equal to 40-45 mm; the spacing can be varied with graphite tables (1); (7) is a aluminum oxide spacer.

The melting chamber is evacuated with roughing-down and diffusion pumps. Molybdenum cylindrical shields are placed between the graphite heater and furnace walls.

Along with the experimental development of the distillation-sublimation process, we performed thermodynamic analysis of three different types of distillation processes: (1) indoors process; (2) virtually indoors process in the presence of a diaphragm; and (3) evaporation from an exposed surface. When analyzing the indoors process, a generalized Henry law is used. The analytical correlation between the impurity content in the solvent, standard chemical potentials of an impurity in the solution and vapor, activity of an impurity in the solution, and partial pressure of the impurity over the solution is determined using an approximation of complete dissociation of multiatomic impurity molecules in a solvent.

In our case, the evaporation from an exposed surface is realized since the free path of molecules is higher than the spacing between the molten metal and condenser. In this case, we perform the thermodynamic analysis for the condensed substance of a solvent, for which available thermodynamic velocity and energy distributions of molecules are available. The flow of an evaporated component (impurity) from a unit surface of a metal is determined by the number of atoms capable of the thermoemission. The derived analytical expression exhibits the correlation between the flow of evaporated substance and evaporation energy.

On the basis of the performed thermodynamic analysis, we preliminarily estimated the efficiency of separation of principal impurities depending on the amount of evaporated substance and optimized the temperature conditions of the distillation process for some of REM. The total scheme of the process consists in the evaporation of volatile impurities at the beginning stage of distillation, evaporation of the basis metal, and removal low-volatile impurities with a residual metal.

According to laser mass spectrometry data, the content of impurities decreases substantially after the purification and content of matrix metal reaches 99.95%−99.98% (mass fraction). The distilled (sublimed) REM are characterized by low contents of interstitial and metallic impurities; for example, after the purification, the contents of oxygen, nitrogen, and carbon in erbium decrease by 35, 50, and 12 times, respectively.

The substantial decrease in the impurity content manifests itself in the microstructure of metal. For example, the 14-fold decrease in the impurity content in praseodymium leads to the substantial microstructural changes (see Fig. 2).

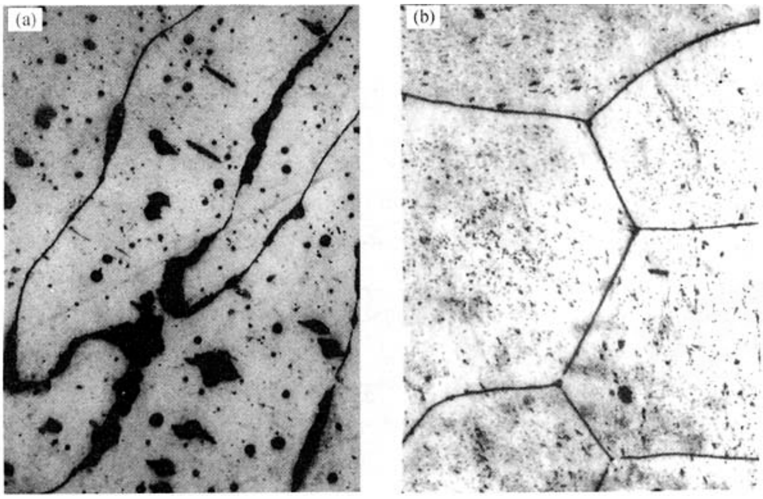

Fig.2 Microstructure (×200) of commercial (a) and distilled praseodymium (b)

The high-purity distilled REM exhibit the following residual resistance ratios ($RRR = R_{300K}/R_{4.2K}$): Dy−210, Er−120, Ho−92, Pr−78, Tm−85, and Y−90.

The high-purity REM were used for measuring and refining principal physical properties, such as the heat capacity, electrical resistivity, magnetic susceptibility, etc. By an example of the low-temperature heat capacity of lutetium, the strong dependence of physical properties on the metal purity is shown.

We studied the low-temperature heat capacity of lutetium samples differing in purity[2]. Figure 3 shows the experimental temperature dependences plotted on the coordinates $C/T-T^2$. The linear dependence is observed in a temperature range of 2-5 K. Reducing the impurity concentration in lutetium reduces its heat capacity over entire temperature range studied. The data for the high-purity lutetium prepared by our technology agree well with earlier results for low-hydrogen samples[3,4,6]. The Debye temperatures and ((electronic heat capacity coefficient) values extracted from our experimental data demonstrate that, with decreasing impurity content (with decreasing heat capacity) the electronic contribution decreases, whereas the lattice contribution rises, in accordance with earlier findings [3,4,6].

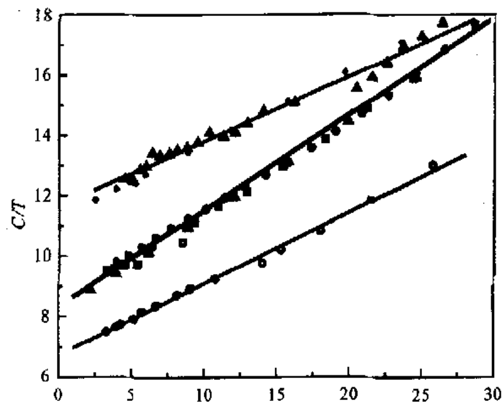

Fig. 3 C/T vs T data for lutetium samples differing in purity

●high-purity Lu (this work); ▲commercial grade Lu (this work); Δhigh-purity Lu[3,6]; □reference[5]; ○reference[4]; + Lu + 15% H [6]

The high-purity REM were used to construct and improve phase diagrams of binary systems: phase equilibria in the Pr-Fe and Pd-Tb systems were refined and the phase diagram of the Lu-Pd system was constructed. The portion of the Pd-Lu phase diagram corresponding to the Pd-based solid solutions, which exhibit anomalously high hydrogen permeability [7], is shown in Fig. 4. A number of compounds exhibiting unique optical properties was found for the Pd-REM systems. The more pronounced optical properties were found for Pd_3Lu and PdLu compounds, which are blue (similar to silicon) and golden, respectively[8].

The Pd-Lu and Pd-Tb systems were studied in a range of compositions of 30%-50% (at. fraction) REM using high purity Lu and Tb (refined by vacuum distillation-sublimation). We identified a berthollide phases of variable composition with a hexagonal structure and lattice parameters changing as a function of REM concentration and heat-treatment conditions [9]. The use of high-purity metals allows us to conclude with certainty that the formation of berthollide phases is an intrinsic property of the REM-Pd systems that is not due to the presence of impurity phases. For each system in which berthollides are formed, there is a critical temperature below which the berthollides undergo a phase transformation to daltonides corresponding to phase diagram.

A procedure of preparation of high-purity (for the contents of impurities and impurity phases) intermetallic binary and multicomponent compounds (based on and with the participation of the high-purity REM) of the REM-(Fe, Ni), REM-Cu, REM-Me_{VIII}, etc. systems have been developed. These compounds are used for fundamental investigation of fine physical effects.

The purity of starting components and the preparation method for high-purity intermetallic compounds play an important role in obtaining preset properties. For example, a high-purity $PrNi_5$ compound (Van Vleck paramagnet) was produced and tested as a nuclear refrigerant capable of reaching millikelvin temperatures. The presence of impurities, in particular, the magnetic elements and $PrNi_x$ phases, causes an irreversible increase in the entropy upon adiabatic nuclear demagnetization.

The quality of distilled Pr and prepared $PrNi_5$ compound based on them permits the use of similar samples for physical experiments at millikelvin temperatures [10].

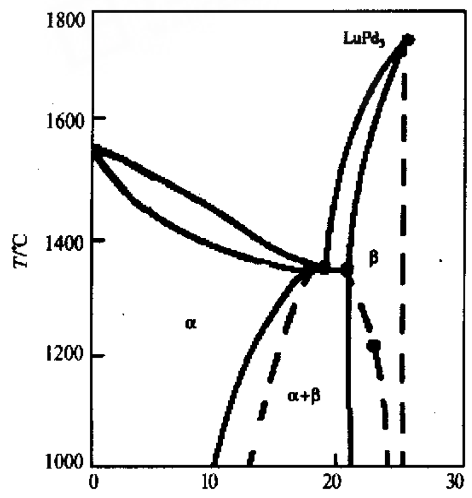

Fig. 4 Portion of the Pd-Lu phase diagram designed on the basis of DTA data (shown by dashed lines) and X-ray diffraction data (solid lines)
α—lutetium solid solution in Pd; β—palladium solid solution in Pd_3Lu

The preparation of the metals in the high-purity state allows one to study their true magnetic, electrical, absorption, thermal, etc. properties, to find distinctive features of their characteristics, and subsequently to use in developing new alloys and materials based on them.

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