Preparation of special-purity scandium for designing plastic and breakable materials based on the metal

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Abstract. The development of advanced technologies is related to the preparation and application of rare-earth metals. The tendency of development of rare-earth metal (REM) industry in Russia consists in tending to shed its dependence on the importation of REMs, to organize their production and products based on them in the required quantities, and to find new application fields for REMs. The aim of the present study is to elaborate the purification technologies of scandium and scandium hydride and to approbate its application as breakable additions to powder mixtures for the preparation of Nd-Fe-B permanent magnets. It is demonstrated the possibility to control the grains size of the 2-14-1 phase in Nd-Fe-B with the ScH$_2$ addition. Moreover, our systematic studies are aimed at the development of corrosion-resistant Ag-free Pd-based REM-containing alloys with the high hydrogen permeability for the separation of high-purity hydrogen from hydrogen-containing mixtures. In the present study, the hydrogen permeability and mechanical properties of Pd-Sc thin foils prepared with special-purity scandium are discussed.

1. Introduction

From the viewpoint of development of advanced technologies, the production and application of rare-earth elements remain the focus of much research, which indicate the state of branches of economical activity, in particular, in the field of manufacturing the high-technology products in the power engineering, such as catalysts for the decomposition of organic fuels and preparation of high-purity hydrogen and permanent magnets for wind-energy and defense industries (navigation systems, guidance systems, radars, etc). The tendency of the development of rare-earth industry in Russia exhibits the trend to be free from the importation of rare-earth metals (REMs) and to organize the production of REM-based materials at the required levels. The preparation of high-purity rare-earth metals is the natural and reasonable course of the economy development, without which the creation of chains REM – permanent magnets, REM – electronics, and REM – fuel cells is impossible.

In accordance with [1], three grades of rare-earth metals (REMs) can be assigned; these are (1) ultrapure, (2) routine metals prepared under laboratory conditions, and (3) commercial. The purity of high pure REMs is $>99.0$ at % with respect to all elements of the Periodic Table. The purity of metals prepared under laboratory conditions is 99% with allowance for all elements. The content of base metal in commercial REMs is $<98$ at %. The transition from the commercial-purity metal to the metal corresponding to the next purity grade leads to about tenfold increases in the metal cost.
The aim of the present study is to prepare special-purity scandium, to study the impurity distribution, and to demonstrate possible applications of scandium for engineering the optimum structure of Nd-Fe-B-based permanent magnets, in which a scandium-based compound plays role of breakable component, and for designing Pd-based foils, in which scandium plays role of both plastic and strengthening component, as well as the component increasing the hydrogen permeability of Pd-based foil membranes.

2. Experimental
The purification technology of scandium by vacuum sublimation and optimum regimes of the purification have been elaborated at the Baikov Institute of Metallurgy and Materials Science [2]. The purification is performed at a residual pressure of $10^{-4} - 10^{-5}$ Pa in a resistor furnace equipped with a graphite heater. The preliminary degassing scandium for 0.5 h is performed to remove volatile impurities, in particular, calcium. The REM is evaporated from a tantalum crucible and deposited on a water-cooled copper condenser in the form of a druse (~150 g) of small crystals growing together. The evaporation process is realized for 6 h at a temperature of $\sim 100°C$ below the melting temperature of scandium. The purity of sublimed scandium is $\sim 99.956$ wt.%; the sum of controlled impurities (without allowance for H,C,N,O) is $\sim 0.044$ wt.%. The contents of gas-forming impurities, oxygen, carbon, nitrogen are 200, $<90$, and $<7$ ppm, respectively. Thus, we can state that the prepared metal corresponds to the high-purity grade.

The further purification of scandium and homogenization of its impurity composition was performed using zone melting in high-purity helium atmosphere. The metal was melted in an arc furnace using a nonconsumable tungsten electrode and water-cooled copper bottom having a horseshoe-shaped hole 420 mm long and 25 mm width (see figure 1) (the original structure of the horseshoe-shaped hole was designed at the Baikov Institute of Metallurgy and Materials Science, Russian Academy of Sciences). The molten metal zone 20 mm in width passes along the ingot at a rate of 100 mm/min. After clockwise-anticlockwise passes, the ingot was turned and, anticlockwise-clockwise passes were realized. After that, the ingot again was turned of and clockwise-anticlockwise passes were realized. Contents of impurities were determined by laser mass-spectrometry. Results of the analysis are presented as average geometrical ratios, which characterize the average factor of variations of the impurity contents for selected sections of the ingot.

Scandium, with the composition homogenized in such a manner, was used as the alloying element for Pd-based alloys intended for the preparation of thin foils by cold rolling. The Pd-Sc alloys were prepared using high purity metals, namely, palladium of 99.95 wt % purity and special-purity scandium. The melting was performed in a protective atmosphere using an arc furnace, a water-cold bottom, and a nonconsumable tungsten electrode. Foil membranes 100 µm thick were fabricated by cold rolling using a four-roll mill and intermediate vacuum annealings at 900–950°C for 30–90 min in accordance with the blank thickness. The preparation process of foils is described in detail in [3].

![Figure 1. (a) Appearance of the horseshoe-shaped scandium ingot; (b) schematic diagram of sections 1-6 analyzed for the impurity contents.](image-url)
The use of sublimed scandium for alloying Nd-Fe-B magnet compositions is based on the role of scandium as an element, which can restrict the grain growth of the main Nd$_2$Fe$_{14}$B (2-14-1) phase. The effect of scandium is similar to that of Ti, Nb, Mo, and V. Scandium is added to the powder mixture in the form of breakable (brittle) composition scandium hydride (ScH$_2$). The ScH$_2$ compound was prepared by direct reaction of Sc with hydrogen using a Sieverts apparatus. The scandium hydride can be milled together with Nd-Fe-B alloy powder to a micron-sized powder and can be homogeneously (at the macro level) distributed in the powder for manufacturing permanent magnets.

The base alloy having the composition (wt.%) Nd-24.0, Pr-6.5, Dy-0.5, B-1.0, Al-0.2, Fe-balance was prepared by strip-casting technique and subjected to hydrogen decrepitation during heating to 270 °C in a hydrogen flow at a pressure of 0.1 MPa and subsequent 1 h dwell at this temperature. The scandium hydride (0.5 and 1 wt.%) and hydrogen-decrepitated strip-cast alloy were mixed and subjected to fine milling for 40 minutes till reaching an average particle size of 3 μm using a vibratory mill and isopropyl alcohol medium. After wet compaction of the pulp in a transverse magnetic field of 1500 kA/m, blanks of magnets were sintered at 1080 °C for 2 h and subjected to the optimum heat treatment (HT) at 500 °C for 2 h. The high-resolution field emission gun-scanning electron microscope QUANTA 450 FEG equipped with an EDX APOLLO X microprobe was used for the investigation of microstructure and chemical composition of the magnets. The grain size of Nd(R)$_2$Fe$_{14}$B phase was evaluated using the automatic image analysis, when the ferret max of grains was measured.

The specific hydrogen permeability of Pd-Sc foil was measured on an experimental stand using a high-temperature working cell; the method of filling of calibrated volume was realized. The diameter of working surface of membrane is 20 mm; the range of working temperatures is 20-700°C. The range of working pressures before (over) and after (under) the membrane is varied from 0.1 to 2.5 MPa and from 0.02 to 1.0 MPa, respectively.

The mechanical characteristics of foils were estimated using Instron testing machines.

3. Results and discussion

3.1. Impurity composition of scandium

Results of the analysis of scandium subjected to zone-melting purification and homogenization are given in figure 2(a, b, c) in the form of impurity distributions along the ingot length. In the course of zone melting, the movement of impurities along the Sc ingot is realized in accordance with their equilibrium distribution coefficient $K_0$ [4], which characterizes the isothermal ratio of impurity contents in liquid and solid phases being in thermodynamic equilibrium upon solidification of the melt. As is known, the equilibrium distribution coefficient of a binary system is less than unity (<1) when an impurity element concentrates in the melt and moves with the molten zone (moves towards the end of ingot). Such a behaviour is typical of metallic impurities and carbon. In the case of $K_0 > 1$, the impurity remains in the solid and shifts to the beginning of ingot. The distribution coefficients were estimated in [4] in accordance with the atomic numbers of elements. The data [1] indicate that the equilibrium distribution coefficients of metallic impurities in Sc is <1; it should be noted that the equilibrium coefficients for Fe and Co in Sc are 0.096 and 0.02, whereas that for rare-earth metals are in a range of 0.53-0.74. (0.21 for La). The very low value of the coefficient for Co can explain its concentration for section 4. The depletion of ingot of volatile and light element is noted; the existence of specific distribution of elements for section 3 is observed, which is likely to be related to the use of clockwise-anticlockwise passes.
Figure 2. (a, b, c) Distribution of impurity elements along the scandium ingot prepared by zone melting with a horseshoe-shaped hole.
3.2. Application of scandium hydride in Nd-Fe-B sintered magnets

Figures 3a and b show the microstructure of the sintered magnets prepared from the powder mixture with 0.5 and 1 wt.% of ScH$_2$ compound, respectively (the analyzed phases are indicated). It is assumed that the scandium hydride decomposes during sintering [5] and active fine Sc powder reacts with the powder mixture components. The stoichiometric composition of matrix grains in the both samples is close to that of the Nd(R)$_2$Fe$_{14}$B phase (phase 1 in figure 3). The several intergranular Nd-rich phases at multiple 2-14-1 grain junctions, which contained ~58 to 71 wt.% Nd and ~19 to 23 wt.% Pr (phase 2), were observed. The scandium content in these phases was variable. Other found phases in the structure of both magnets were REM-(Fe)-based oxides between grains (phases 3 and 5). The higher content of ScH$_2$ addition led to the formation of the plate-shaped Sc-Nb-(B) particles (phases 4 and 6). The increased content of Sc was observed only at the intergranular phases, i.e. no significant diffusion of Sc to matrix 2-14-1 grains was realized during the sintering and subsequent heat treatment despite of the fact that the atomic radius of scandium is less than that of Nd and other REMs comprised the magnet (Pr, Dy) [6].

![Figure 3](image.png)

**Figure 3.** The microstructure of Nd-Fe-B sintered magnet prepared from the powder mixture with (a) 0.5 and (b) 1 wt. % of ScH$_2$ addition and marked analyzed phases.

Figure 4 shows the X-ray elemental mapping of Sc in matrix grains and in the intergranular phases of Nd-Fe-B sintered magnet prepared from the powder mixture with (a) 0.5 and (b) 1 wt.% of ScH$_2$ addition.
Figure 4. X-ray elemental mapping of Sc in matrix grains and in the intergranular phases of Nd-Fe-B sintered magnets prepared from the powder mixtures with 0.5 wt.% of ScH$_2$ addition.

The effect of Sc on the microstructure of sintered magnets is analogous to that of Ti, Nb, Mo, which form borides at grain boundaries [7]. Scandium effectively restricts the grain growth during sintering and heat treatment, which can favour the high coercivity. The grain size distribution in the sintered magnets prepared from powder mixture with 0.5 and 1 wt.% ScH$_2$ is shown in figure 5. The mean grain size of both sintered magnets was nearly identical and achieved the value of 7 ± 3 µm. However, the major difference in the microstructure of both magnets consisted in the grain size distribution. The higher content of ScH$_2$ results in the fact that the proportion of small grains (≤ 4 µm) is two-times higher and the size distribution became more uniform [8].

Figure 5. The grain size distribution in the sintered magnets prepared from powder mixtures with (a) 0.5 wt.% and (b) 1 wt.% of ScH$_2$ addition.
3.3 Pd-Sc foils for membrane separation of hydrogen

The preparation of Pd-Sc alloys for the membrane separation of high-purity is due to (1) the need to alloys with the high hydrogen permeability at low temperatures (to 350°C), which is typical of Pd-REM compositions and (2) the high corrosion resistance of Sc as compared to that of the other REMs.

When preparing qualitative thin films, it is of importance the purity of palladium with respect to gas-forming impurities and the purity of alloying components. Since palladium is characterized by internal oxidation and formation of complex impurity inclusions in the crystal lattice, the chemical purity of alloy component along with maintaining the purity in a final product, which is determined by the preparation technology of the foil, is of importance. Palladium alloys melted in the high-vacuum atmosphere, which are pure with respect to interstitial impurities, must exhibit the adequate plasticity in order to be subjected to cold rolling (with intermediate annealings) to thin foils. It is assumed that the maximum specific hydrogen permeability corresponds to the compositions with 4-5 wt. % Sc.

Special-purity scandium was used to prepare Pd-Sc alloy with 3.8 wt.% Sc; the composition corresponds to the solid-solution region in the Pd-Sc phase diagram [9].

Foils 50 µm thick were prepared by cold rolling and their mechanical properties and hydrogen permeability were studied. According to data given in figure 6, the hardness, strength, and relative elongation of the Pd-Sc foils are comparable with those of the other Pd-REM alloys.

![Figure 6. Mechanical properties Pd-REM alloys.](image)

The specific hydrogen permeability of the Pd-3.8 wt.% Sc alloy is 3.2 m³/m²h·MPa⁰.⁵ at 350°C and is two-times higher than that of the industrial Pd-23% Ag alloy.

Conclusions

1. Possibilities of the sublimation and zone-melting methods for the preparation high-purity and special purity scandium are demonstrated.
2. The detailed investigation of the microstructure of Nd-Fe-B sintered magnets prepared from the powder mixtures with 0.5 and 1 wt.% of ScH₂ showed the presence of scandium-boron inclusions at grain boundaries of the main magnetic 2-14-1 phase; the effect of scandium on grain growth restriction was demonstrated.
3. With allowance for the adequate corrosion resistance of the Pd-Sc alloys and their high hydrogen permeability at low temperatures, the alloys show promise as materials for designing membrane elements for the industrial separation of high-purity hydrogen for fuel cells.
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