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LETTERS
TO THE EDITOR

Synthesis of Single-Domain Chromium Dioxide Nanoparticles with High Coercivity

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Chromium dioxide is among the best known and widely used magnetic materials. Its ferromagnetism, half-metallic conductivity, and giant magnetic resistivity attract the scientific interest to this material.

The mentioned properties of CrO_2 depend on its particles size. The introduction of modifiers during hydrothermal synthesis of chromium dioxide allows changing the particles size and, hence, magnetic properties of the final product. In view of that, the study of CrO_2 formation is of dual interest. Firstly, it leads to elucidation of the mechanism of influence of small amount of additives on crystallization of ultradisperse particles from the solution; secondly, it allows the modification of magnetic properties of a material widely utilized in magnetic recording media.

The development of materials for hard drives with high information density is the most promising modern application of chromium dioxide. Such materials are special due to the high coercive force.

It is known that the highest coercivity is typical of magnetic materials consisting of single-domain particles. Therefore, this work aimed at the preparation of the single-domain CrO_2 nanoparticles with high coercivity via hydrothermal synthesis in the presence of stannic acid and tellurium compounds as modifiers.

The tin-containing modifier was introduced in the form of the pre-hydrated oxide. The SnO_2 nanoparticles act as the crystal nucleating agent if their size does not exceed 5 nm : the modifier activity depends on both the ratio of Sn and Te compounds and on the specific surface area (SSA) of tin dioxide [1]. The application of an additional iron-based modifier results in a change of many properties of the powder product : the average particles length and thickness, monodispersity, crystal lattice parameters, the phase composition, H_C, the specific magnetization σ_M, and the Curie temperature.

We prepared and studied a series of products at the Sn : Te : Fe : Cr molar ratio of 2 : 1.75 : z : 1000, z being varied in the 0–125 range and α-Fe_2O_3 with SSA of 9 m^2/g acting as the iron source. We observed a steady decrease in the chromium dioxide SSA from 34 to 13 m^2/g upon increase of z in the given range. The average thickness of needle-shaped particles as estimated from SSA coincided with the XRD coherent domain size at $0 \le z \le 75$. The SSA changes were accompanied by an increase in the structure parameter a, the c parameter being constant. Simultaneously the σ_M value decreased, and H_C increased from 522 (z 0) to 761 Oe (z 75) and further smoothly decreased to 622 Oe. The observed changes of structure parameters and σ_M coincided with the data reported in [2] and were assigned to the formation of the a $Cr_{1-x}Fe_xO_2$ solid solution, the electroneutrality being maintained by chromium transformation in the Cr(V) state [2] or by the appearance of oxygen vacancies, the Fe(III) magnetic moment being antiparallel to that of CrO_2. Moreover, part of Fe(III) atoms was present in the prepared powder in the form of $(Cr_{1-x}Fe_x)_2O_3$ solid solution, its formation being confirmed by X-ray diffraction and nuclear gamma resonance spectroscopy [3]. Such solid solution should possess the σ_M value [4] by two orders of magnitude lower than that of CrO_2; its fraction at z = 125 increased to 14.5 vol %. As discussed in [3], it was a ballast phase having no

influence on the powder H_C value. Hence, the increase in H_C was exclusively due to the formation of the $Cr_{1-x}Fe_xO_2$ solid solution. The H_C value of single-domain powder is generally determined either by magnetic crystallographic anisotropy or by the shape anisotropy. According to the data reported in [5], one of the factors plays the decisive role in determination of the H_C value at the experiment temperature. Since in the case of the single-domain CrO_2 powder the H_C changed in the same direction as σ_M over the whole temperature range studied (0–300 K) and was independent of the particular H_C value [6–9], the shape anisotropy should be considered as the only factor governing H_C.

Basing on the obtained data on H_C as a function of the anisotropic particles thickness [10], the experimentally determined H_C can be considered as a sum of the purely dimensional part and the contribution from modification with iron. It was found that the second part was the highest (347 Oe) at z = 75, being of 324–316 Oe at higher z. The hysteresis squareness loop was simultaneously decreased from 0.46 to 0.43; in other words, despite the higher thickness the particles were single-domain. Iron-free CrO_2 particles with the similar SSA (17–13 m^2/g) were not single-domain [10] and showed the hysteresis loop with lower squareness. That result was likely due to the composition of surface magnetic layer based on the $Cr_{1-x}Fe_xO_2$ solid solution, its high magnetic crystallographic anisotropy preventing magnetization reversal of the particles and uniting the polycrystalline and potentially multi-domain particle into a single-domain one. The comparison of the data on change of H_C of CrO_2 particles with their thickness [10], similar results of the γ-Fe_2O_3 powder studies [11], and the above-mentioned results permit a conclusion that the single-domain CrO_2 particles were magnetically switched primarily incoherent/fanning model. The presence of iron atoms turned the magnetic reversal mechanism to the coherent one, allowing preparation of the powders with H_C over 900 Oe.

Chromium dioxide nanoparticles were prepared via hydrothermal route at 330°C from CrO_3, tin dioxide, and metatelluric acid in stainless steel autoclave as described elsewhere [1, 10, 12, 13]. The product was removed from the ampule, ground with a knife mill, washed with distilled water, and dried in an oven. Phase composition and morphology of the samples were studied by a set of independent methods: X-ray diffraction analysis, transmission electron microscopy, and BET measurement of specific surface area.

X-ray diffraction analysis was performed using a compact Difrei 401 device (Nauchnye pribory, Russia). The diffraction patterns were recorded at room temperature using Cr-K_α radiation, 2θ of 20º–140º. The curved position-selective detector was used. The average size of XRD coherent domain size was calculated from physical broadening of the X-ray peaks using the Selyakov-Scherrar and the Selivanov–Smyslov methods. Parameters of magnetic hysteresis loop were studied at room temperature at Resource Center of St. Petersburg State University "Innovative technologies of composite nanomaterials" using a Lake Shore 7410 vibration magnitometer.

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