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Deposition of the amorphous metal coating onto hollow glass microspheres

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Amorphous metal Pt−Zr coatings micron in thickness, as well as crystalline ones, were obtained on the surfaces of hollow thin−wall glass microspheres using direct current magnetron sputtering at the deposition rate of 0.1 nm/s. Being in the range of 1−1.5 nm, the roughness of the obtained amorphous coatings is essentially lower than that of crystalline coatings of the same composition.

Keywords: metal glasses, amorphous metal films, platinum, zirconium, magnetron sputtering, glass microspheres, inertial confinement fusion targets.

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Obtaining metal coatings on spherical and other−shape particles with sizes ranging from microns to millimeters is demanded in developing coatings absorbing electromagnetic radiation, in powder metallurgy, and in catalysis. The strictest requirements are imposed on the characteristics of coatings on glass spheres which are sometimes used in fabricating targets for the inertial confinement fusion (ICF) [1]. To satisfy those requirements, the methods for fabricating ICF targets are being continuously improved (for instance, by involving ultrasound in galvanic deposition to reduce the roughness [2] or by using ion assistance in magnetron sputtering to increase the density [3]). There is known a contactless technique for retaining light−weight microspheres in plasma during the sputter deposition of a coating, due to which the number of surface defects is reduced [4]. The obtained coatings have a columnar crystal structure. The roughness and permeability of amorphous metal (AM) coatings on large flat substrates may be considerably lower than those of films with the granular crystal structure [5–7]. It is possible to assume that the AM coating on a sphere will also be superior to the crystalline analogues in these parameters. Study [7] has established that the conditions for obtaining an amorphous alloy by magnetron sputtering in the Pd−Zr system are limited to the low substrate temperature range (below 90°C). Higher temperatures promote formation of crystalline films in this system. Geometric parameters of hollow glass microspheres make it difficult to maintain the temperature at a low level during the sputter deposition of metal on them; therefore, the possibility of obtaining an AM coating on such spheres is not obvious. The goal of this work is to demonstrate the possibility of depositing the AM coating on hollow spheres with diameters of about the size of the inner shell of the ICF double−shell target.

Estimation of the microsphere stationary temperature under the influence of the heat flow getting onto the sphere in certain operating modes of the employed magnetron sputter was performed preliminary. The sphere−cuvette contact area was regarded as negligible. The heat loss due to radiative heat exchange between the small−size sphere and large−size cooled chamber was considered. The reduced emissivity for the two−body system was assumed to be 0.05 (polished platinum). The value of the heat flow density necessary for estimation was measured in a preliminary experiment by using a thermal probe. The measurement procedure and probe design used in that experiment were almost the same as in [8]. The target and chamber walls were cooled with water, the argon pressure was 0.4 Pa, the probe−target distance was 8 cm. The flow density measured at the discharge power values of 50 and 140 W appeared to be 0.2 and 0.7 kW/m^2, respectively. As per the obtained estimates, these values corresponded to the microsphere stationary temperatures of 190 and 320°C, respectively. Notice that the used procedure can provide somewhat underestimated values of the heat flow and sphere temperature, since it does not take into account the revealed in [9] difference in the cooling rates at the switched-on and switched-off magnetron, which is most important in the case of a relatively high discharge power. Based on the estimation results, the binary Pt−Zr system was chosen for preparing AM films on microspheres, in which the adatom mobility was lower and devitrification temperature was higher than those in the Pd−Zr system [10]. First the Pt−Zr films were obtained and studied on smooth wafers $0.4 \times 20 \times 20$ mm in size at different temperatures ranging from 60 to 380°C. The results allowed us to refine the details of the necessary setup outfit and to deposite the Pt−Zr AM films on the hollow glass spheres 400−1000 μm in diameter and 1−3 μm in wall thickness.

The coatings were applied using a planar magnetron sputter having an unbalanced magnetic system and equipped with a mosaic target [7]. As the target, a

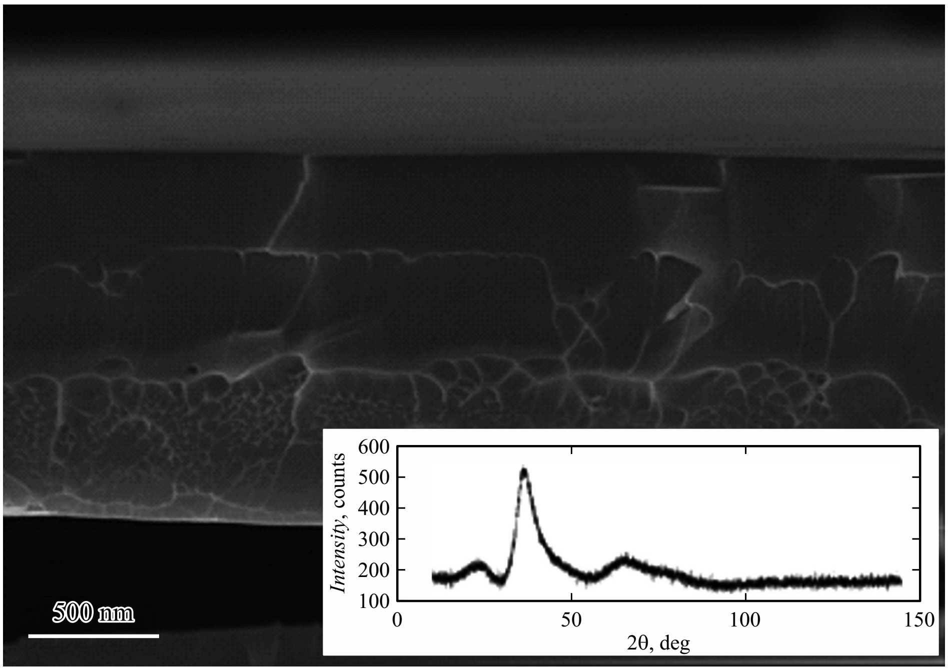

Figure 1. The surface and transverse fracture of the Pt : Zr = 1 : 4 amorphous film applied on a flat substrate, and its diffraction pattern (in the inset).

100 mm–in–diameter wafer made from zirconium and having platinum inserts in the regions under sputtering was used. When the coating was deposited on flat substrates, the sputter discharge power was 480 W; in depositing on microspheres, the power was varied from experiment to experiment in the range of 50–480 W. In both cases, the argon pressure of 0.4 Pa and the target–substrate distance of 8 cm matched the values used in the preliminary calorimetric measurements. The flat glass and silicon substrates were mounted on a fixed holder. To vary the temperature, the substrate–holder thermal contact was adjusted with spacers. During the deposition, the spherical microsubstrates were moved so as to make uniform the deposition of coatings on their surfaces. For this purpose, they were placed into a moving massive cuvette with a flat bottom. This cuvette was set in vibration from the outside of the vacuum chamber. This vibration made the bottom periodically inclining with respect to the horizontal plane, which caused rolling of the spheres over the cuvette bottom. Slow displacements were periodically followed by the cuvette shock shaking. The cuvette with microspheres and motionless substrate holder were electrically isolated from the discharge electrodes. Concurrently with the films on microspheres, films on the flat cuvette surface were growing. Structures of those films were also studied. The coatings were studied with field–emission scanning electron microscope SUPRA 40 with attachment INCA for the X-ray spectral analysis. The X-ray diffraction patterns of large samples were recorded with the spectrometer based of a diffractometer with the Cu$K\alpha$-radiation source. The coating roughness was measured with atomic force microscope AIST-NT SPM (model SmartSPM-1000) and optical profile meter Profilm3D.

At the flat wafers, films Pt : Zr = 1 : 4 were fabricated at the growth rate of 2.5 nm/s. The crystalline phases were found only in the films obtained at the temperature of 350–380°C. Fig. 1 presents the images of the surface and transverse fracture typical of the films grown at the substrate temperatures of 60–320°C. Destruction of the film top parts is of the shear character typical of metal glasses. The „vein–like“ shape of the fracture lower part is also characteristic of metal glasses. The remaining part of the fracture surface, as well as the film outer surface, is smooth and free of any signs of graininess in the scale of several nanometers to hundreds of nanometers. The Fig. 1 inset presents the diffraction pattern of the demonstrated film. It exhibits halos characteristic of metal glasses (with the maxima at 36 and 65°). The small–angle halo corresponds to the substrate glass. The films grown on the flat surface of the moving cuvette demonstrate a similar structure.

Contrary to this, the same–composition coatings on microspheres obtained at the sputter discharge power of 75–480 W had the columnar structure typical of crystals. Films on the spheres which, according to the fracture type, correspond to metal glasses, were obtained only at the minimal discharge power of 50 W matching the minimal microsphere temperature. Fig. 2 presents with different magnification the image of the fracture of the film obtained on the sphere; the film exhibits characteristic signs of the metal glass destruction. For comparison, Fig. 2, *b* presents a fragment of the same–composition crystalline film obtained on the microsphere at a high

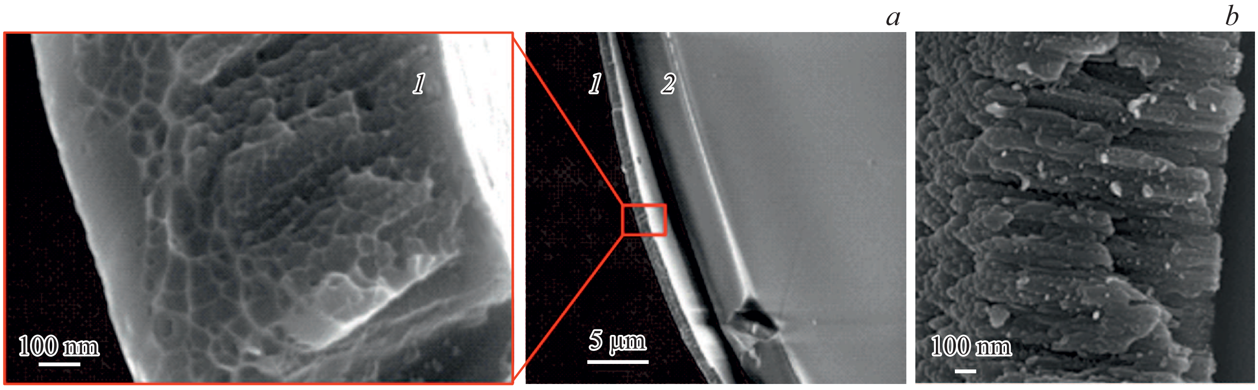

Figure 2. The fracture images of the amorphous metal film (*a*) and crystalline film of the same composition (*b*) on the spheres 0.5 mm in diameter. *1* — film fracture, *2* — spherical substrate fracture.

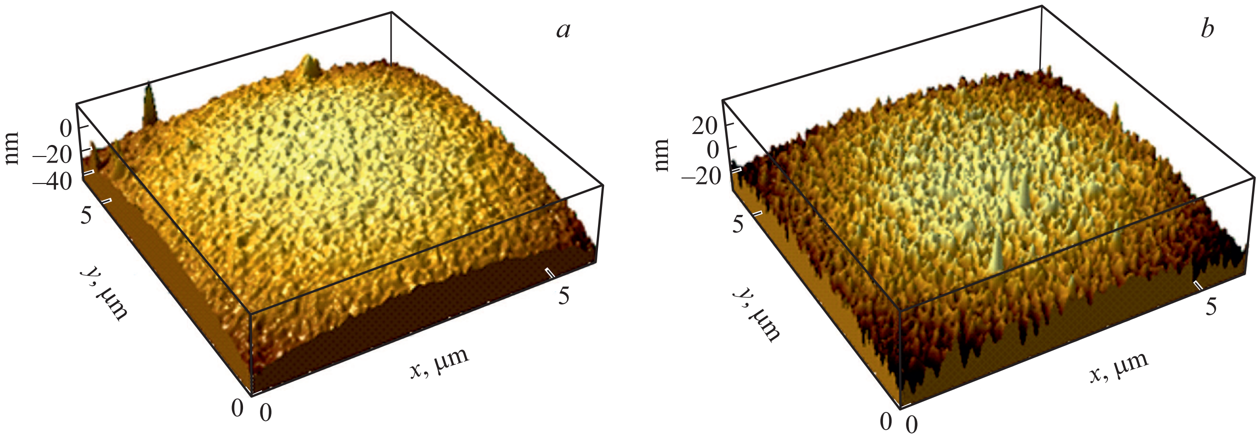

Figure 3. Surface reliefs of the films obtained on microspheres at different discharge powers: *a* — 50 W (amorphous), *b* — 140 W (crystalline).

discharge power. Comparison of these results with those obtained in depositing films on flat surfaces, in combination with estimates of the microsphere temperatures, and also the Pt : Zr = 1 : 4 characteristic composition, allowed us to state that the film shown in Fig. 2, *a* has the amorphous structure. The relief of films grown on microspheres is shown in Fig. 3. As per data acquired with the atomic force microscope and optical profile meter, the AM film roughness ranges from 1 to 1.5 nm, which is much lower than in the case of the same−composition crystalline coating (5−7 nm). The occurring defects may be eliminated by properly preparing the initial microsphere surfaces and equipping the operating chamber. Contrary to the case of crystalline films, the increase of the AM film roughness with increasing film thickness is not a mandatory attribute [11]. In this experiment, the rate of depositing the AM coatings on microspheres was limited by the necessity of maintaining low temperature and equaled 0.1 nm/s. Such a rate is typical of the process of obtaining crystalline shells of the ICF targets up to 0.1 mm thick by magnetron sputtering [1,3]. However, the problem of increasing the deposition rate in order to obtain thick coatings remains topical. In our case, we propose to solve this problem by increasing the discharge power with retaining the value of the heat flow to the substrate due to using a better−balanced magnetic system of the sputter [12]. This makes it possible to obtain on the spheres thicker AM coatings meeting the requirements for the ICF target shells.

Thus, this study has established the possibility and conditions of depositing amorphous metal coatings on thin−wall spheres with diameters belonging to the range of the inner shell size of the ICF double−shell target.

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Conflict of interests

The authors declare that they have no conflict of interests.

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