

Behavior of amorphous metal alloy mirrors under ion bombardment

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The reflectance of mirrors fabricated from amorphous metal alloys and the inhomogeneities seen on their surfaces are investigated as a function of ion fluence for exposure to deuterium and argon plasma ions. In the case of deuterium plasmas, the uptake of deuterium as function of ion energy was estimated. The effects of long term sputtering with argon ions on the reflectance and surface state of amorphous and crystallized mirrors were studied.

Key words: mirrors of amorphous alloys, reflectance, ion bombardment, sputtering, surface inhomogeneities

1. Introduction

One possible reason for the degradation of plasma facing mirrors (first mirrors, FM) in ITER is the development of surface microrelief due to the impact of charge exchange atoms (CXA). The use of single crystal mirrors prevents the appearance of a step structure due to long-term CXA bombardment. However, because of the gradual accumulation of defects in the near-surface layer, such a mirror can lose the advantage of the single crystal structure with a corresponding deterioration of reflectance. Mirrors fabricated from amorphous materials may have better prospects for maintaining a smooth surface following long-term sputtering, as they have only nano-scale order. This idea was first proposed in a paper published by the authors, Ref. [1]. Now, with development of many different bulk amorphous alloys (BAA) [2,3], there is the possibility of providing experimental verification of this idea.

In the paper we present results which demonstrate the ability of amorphous mirror to maintain their optical properties even following the removal of $\sim 13.4 \mu\text{m}$ due to sputtering with argon ions.

2. Samples

The experiments were carried out with mirror specimens fabricated of amorphous materials prepared by:

- 1) Liquidmetal Technology Corporation (LTC) in the USA,
- 2) Institute of Solid State Physics, Materials Science and Technologies of National Science Center "Kharkov Institute of Physics and Technology" (ISSPMT), and
- 3) Hahn-Meitner-Institute (HMI) in Berlin, Germany.

The elemental composition of the LTC and ISSPMT samples is -

Zr(41.2)Ti(13.8)Cu(12.5)Ni(10)Be(22.5), and of the HMI samples is - Zr(46.8)Ti(8.2)Cu(7.5)Ni(10)Be(27.5).

Due to difference in technological processes, in spite of similarity of composition, the mirror samples from LTC and ISSPMT were found to have different kinds of inhomogeneities and a little different value of reflectance, as will be shown below.

All samples were disk-shaped with thickness ~ 2.5 mm and diameter 22 mm (LTC and ISSMT samples) or 5 mm (HMI samples). The samples were polished to the mirror quality with gradually decreasing abrasive particles, then washed in acetone and stored in air. Before exposing the samples to deuterium or argon plasmas to see the effect of ion bombardment, the surface of every sample was first cleaned with low energy (50-60 eV) ions from a deuterium plasma (typical fluence $1 \cdot 10^{19}$ ion/cm²) to take off the organic film that appears due to washing in acetone. The reflectance values measured after plasma cleaning were taken as the initial values of reflectance for all mirror samples.

The plasma-exposure experiments were performed in the DSM-2 facility [4], with parameters of ECR discharge plasma: $n_e \sim 10^{10} \text{ cm}^{-3}$ and $T_e \leq 5 \text{ eV}$. Samples could be biased to produce more energetic incident ions.

3. Initial surface characteristics and optical properties

The polishing procedures exposed the existence of a number of inhomogeneities on the surface of the amorphous materials which could be seen by both optical microscope and by scanning electron microscope (SEM). In Fig.1a a SEM photo obtained with secondary electrons shows a group of inhomogeneities on the surface of a LTC mirror sample. Altogether, these inhomogeneities occupy only a small part of the sample surface (1-2 %).

They were raised a little above the matrix surface, but did not noticeably affect the reflectance at normal incidence (measurements were done in the wavelength range 220–650 nm). The SEM photos of such inhomogeneities made with elastically backscattered electrons (Fig.1b) indicate the predominance of elements with lower atomic number in comparison with the matrix composition; this result was supported by the results of microanalysis shown in Table 1.

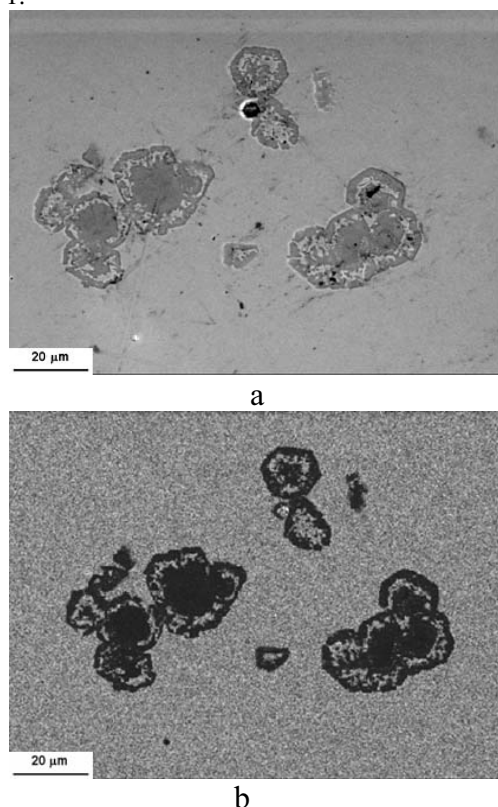


Fig.1 SEM photos with secondary (a) and backscattered electrons (b) of inhomogeneities on the LTC sample surface.

Table 1. Elemental composition of the LTC mirror material: nominal (2nd column) and measured by means of microprobe method in the matrix and in the inhomogeneity (without taking into account Be). Data in brackets – ratios to the Zr content.

Element	Nominal composition, from LTC (at. %)	Matrix composition (at. %)	Inhomogeneity composition (at. %)
Zr	41.2 (100%)	52.8 (100%)	43.0 (100%)
Ti	13.8 (33.2%)	17.4 (33%)	12.0 (28%)
Cu	12.5 (30%)	15.2 (28.8%)	24.3 (56.5%)
Ni	10 (24%)	14.6 (27.7%)	20.7 (43%)
Be	22.5 (54.9)		

The irregularities on the surfaces of ISSPMT samples were very different, being shallow pits (~60 nm in depth) with rather flat lower surfaces. Also, they were distributed

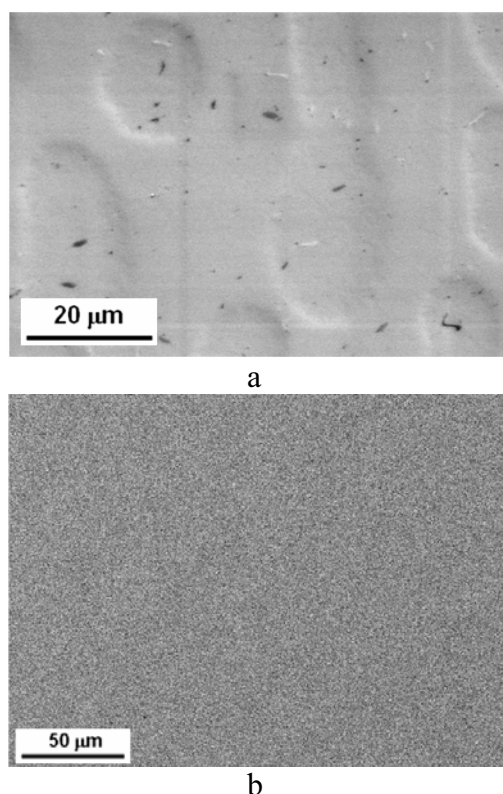


Fig.2 SEM photos with secondary (a) and backscattered electrons (b) of the shallow pits observed on the ISSPMT sample surface.

more-or-less uniformly over the surface of samples, Fig.2a). In contrast to the LTC samples, these pits were invisible in SEM photos made with backscattered electrons (Fig.2b), indicating that the composition of the material is uniform, and thus, these irregularities are located only at the surface. At present we do not have a satisfactory explanation for the appearance of these pits; possibly they are the result of the polishing procedures.

Inhomogeneities also appear on the surface of the HMI samples, see Fig.3a. The majority of these surface features appear to have a “star-like structure” but are not oriented in the plane of surface and therefore are only partly seen. On one occasion, the full structure of such an inhomogeneity was revealed after bombardment with argon ions, Fig.3b. Its shape is very similar to that of the crystals described in Ref. [5].

The initial reflectance, R , of the different amorphous mirrors does not differ significantly, but is strongly dependent on wavelength in the range of measurements, Fig.4. For wavelengths exceeding ~350–400 nm the reflectance of the BAA mirror samples is close to the reflectance of tungsten.

4. Experimental results and discussion

4.1. Uptake of deuterium

In the plasma exposure experiments, samples were exposed to deuterium or argon ions without mass separation of the ion flux. In the case of deuterium plasmas, a small amount of water and nitrogen were

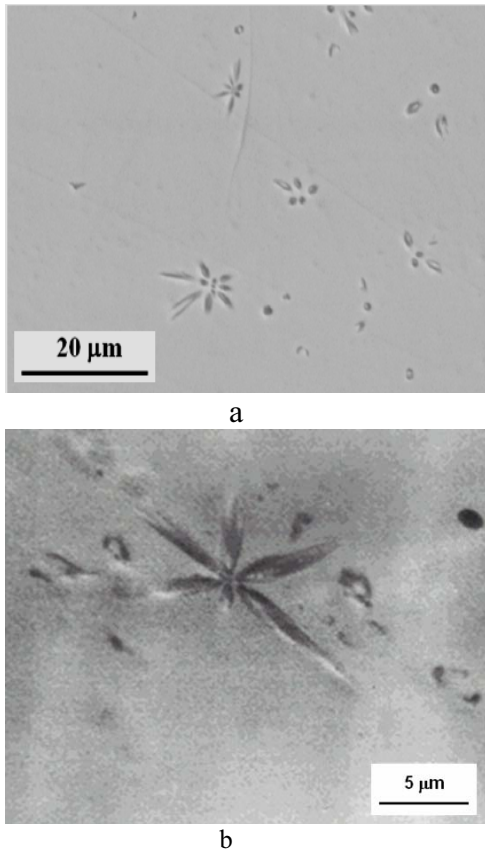


Fig.3 SEM photos of the polished mirror surface of a HMI sample after exposure to ions of deuterium plasma with energy 60 eV (a), and after sputtering with argon ions of the layer $\sim 5 \mu\text{m}$ in thickness (b).

registered by a vacuum analyzer, but with argon as the working gas only traces of these components were observed. The water-cooled mirror holder was negatively biased to accelerate ions either to fixed energy (20-1000 eV) or to an energy variable with time (with frequency 50 Hz) in the range 50-1500 eV [4].

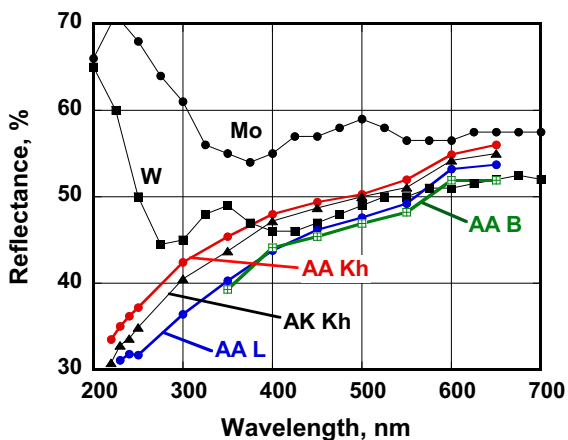


Fig.4 The spectral reflectance of the amorphous mirror samples in comparison with the reflectance of Mo and W mirrors [6]. Abbreviations near curves mean: AAL – LMT sample, AAKh – ISSPMT sample, AAB – HMI sample, AK Kh – crystallized ISSPMT sample.

It was found that mirror samples of all materials absorb large amounts of deuterium when the mirror specimens were bombarded with ions of a deuterium plasma. As measured by the laser ablation technique, deuterium was found at depths much larger than the calculated D^+ ion range [7] following exposure of the LTC specimen to a fluence of $5.9 \cdot 10^{20} \text{ ion/cm}^2$. Because of deuterium absorption, a weight gain was observed for ion energies below 1000 eV, even when there was a clear indication of sputter erosion.

The fraction of retained deuterium was estimated for low ion energies (20-100 eV) where the ion sputter erosion was thought to be negligible. In doing this estimation, we did not take into account that in the SHF discharge there are D_2^+ and D_3^+ ions as well as D^+ (e.g., [8]), therefore the total atom flux will be somewhat larger than the ion flux. Fig.5 shows the rise of the portion of trapped deuterium with ion energy over this energy range.

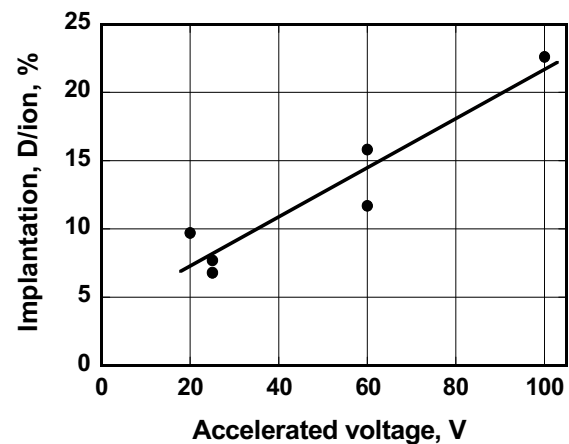


Fig.5 Energy dependence of the amount of deuterium retained by one of the LTC mirror samples for an incident ion fluence of $5.9 \cdot 10^{20} \text{ ion/cm}^2$.

The sputtering yield was estimated by measuring the depth of the hole which appeared following bombardment through an 8 mm aperture or through a nickel metal grid. The yield was somewhat higher than the sputter yield of pure zirconium - the heaviest component of the alloy.

4.2. Effect of ion bombardment on reflectance

The bombardment of samples with keV deuterium ions results in a sharp drop of reflectance even after quite short exposure times, with the extent of the decrement depending on the wavelength: the shorter the wavelength the deeper the drop. Results of an experiment where a LTC mirror was in series exposed to ions with a wide energy distributed or to low energy ions (60 eV) are shown in Fig.6. Here the reflectance at three wavelengths is plotted as a function of the total ion fluence (fluence of wide energy distribution ions + fluence of low energy ions). The blue points (dotted curves) were obtained after exposure to ions with a wide energy distribution and the red points (solid curves) after exposure to the low energy

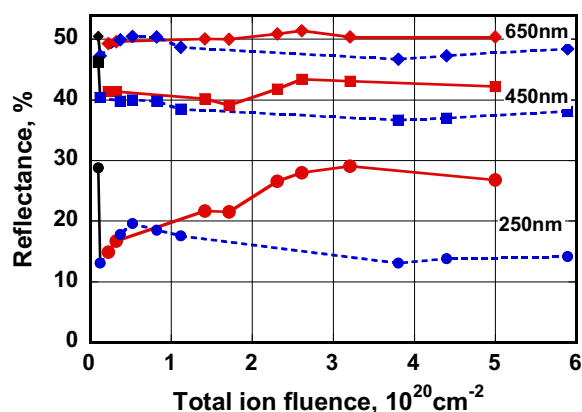


Fig.6 Dependence of reflectance on the total ion fluence at the indicated wavelengths for LTC sample. The total fluence is the sum of fluences of wide energy distribution ions and 60 eV ions. The data for exposures to wide energy distribution ions – dotted curves, and to 60 eV ions – solid curves.

ions. The first point for every curve represents the initial reflectance (after short cleaning with 60 eV ions).

A short exposure to the wide energy distribution ions resulted in a significant drop of reflectance (second point on every curve after the initial point). However, it is seen that after an initial transient (up to $\sim 0.8 \cdot 10^{20}$ ion/cm²), the long-term exposures to low energy ions (solid lines) leads to gradual increase of reflectance almost to the initial level (at fluences $\sim 3.2 \cdot 10^{20}$ ion/cm² and $\sim 5 \cdot 10^{20}$ ion/cm²). The followed exposures to the more energetic ions (at fluences $\sim 3.8 \cdot 10^{20}$ ion/cm² and $\sim 5.9 \cdot 10^{20}$ ion/cm²) again brought reflectance to low values (similar to the level of the first drop).

Qualitatively similar reflectance behavior was observed for ISSPMT mirror samples when they were subjected to deuterium plasma ions of ~ 1 keV energy and then to ions with 60 eV energy.

The ability to restore the reflectance of BAA mirror samples may indicate that the deterioration of reflectance under energetic ion impact is not due to the development of surface roughness, but due to some chemical processes on the surface.

A similar restoration of reflectance due to exposure to low energy deuterium ions following high energy ion bombardment was observed in similar experiments with Be mirrors [9]. In that paper it was hypothesized that when the beryllium surface is exposed to deuterium ions in an atmosphere contaminated with water vapor, the normal BeO surface layer can be partially transformed into the Be(OD)₂ with corresponding decrease in reflectance. Because the current BAA mirror samples contain a significant portion of beryllium (22.5 and 27.5 %), it would not be surprising to have a similar effect take place with these samples.

4.3. Modification of the surface

For the deuterium plasma-exposed LTC specimens (experiments of Fig.6), the thickness of sputter eroded layer at the end of the experiment was estimated to be ~ 2 μ m [7]. Most of the surface area remained smooth, but the inhomogeneities shown in Fig.1 were transformed into shallow pits with a depth of 0.2-0.3 μ m as measured with an interference microscope, Fig.7.

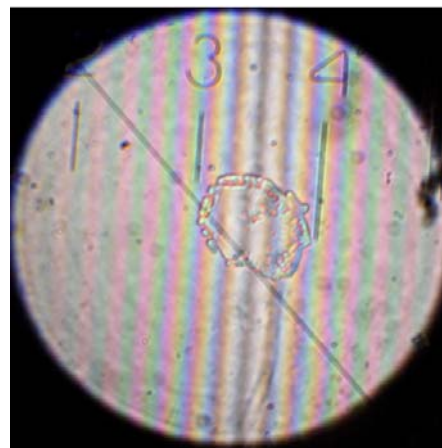


Fig.7 The interferogram of one of the pits appeared after LTC sample was sputtered to the depth ~ 2 μ m by a deuterium plasma. It is seen that the pit is about 0.25 μ m in depth and has a flat bottom.

The fact that the rate of sputtering of the inhomogeneities is higher than for the matrix is in good qualitative agreement with the results of microanalysis showing that the elemental composition inside these inhomogeneities has a lowered portion of zirconium and increased portions of copper and nickel (Table 1). Higher sputtering yields are expected for the lower mass elements.

In addition, part of the LTC specimen surface ($\sim 15\%$) bombarded with 300 eV deuterium ions developed 'blister-like surface features' with diameter from a few μ m up to ~ 60 μ m, Figs. 8 [10]. Such artifacts were not found on the surface of other LTC samples after exposure to the same or other ion energies. We thus suggest that possibly the part of the LTC samples where the blister-like surface features appeared, had some unique peculiarity in the structure of the material. These artifacts strongly differ from the "classical" blisters observed in [11,12] when metal glasses were bombarded with high energy He⁺ and H⁺ ions. Namely, it was found [10] that independently of size, the 'blister-like surface features' are plane or have the plane pedestal with thin cupola-like roof, have annular groove and no one was found to be burst.

4.4. Comparison of the reflectance behavior of amorphous and crystallized mirrors

To avoid the problems which appear to be related to chemical processes on the mirror surface and to shorten the total exposure time, experiments directed to checking

the idea of [1] were performed on ISSMT mirror samples with argon ions.

The experiment was performed with mirror samples fabricated of the same material but with different structure: amorphous and crystalline.

Three ISSMT disk samples were cut approximately in equal halves, with one half of each disk left amorphous while the second half was annealed at 773° K for 1 hour.

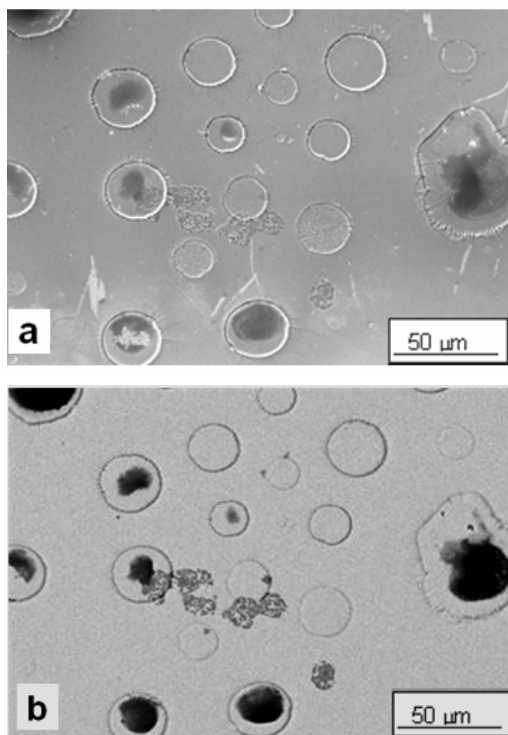


Fig.8 SEM photos with secondary (a) and backscattered electrons (b) of blister-like surface features on the LTC sample surface after bombardment with 300 eV deuterium ions.

The annealed samples developed a crystalline structure, as demonstrated in Fig.9.

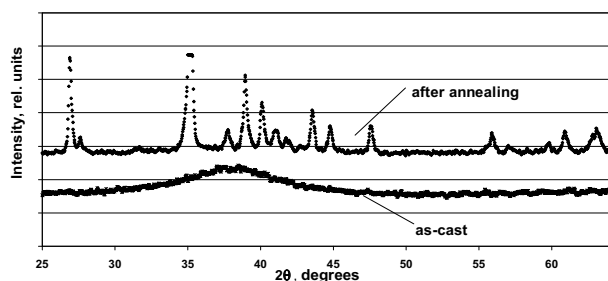
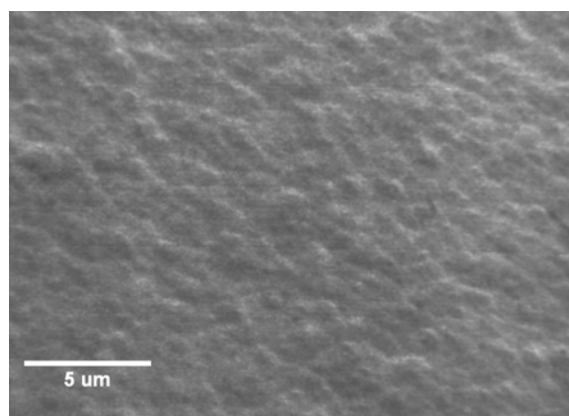
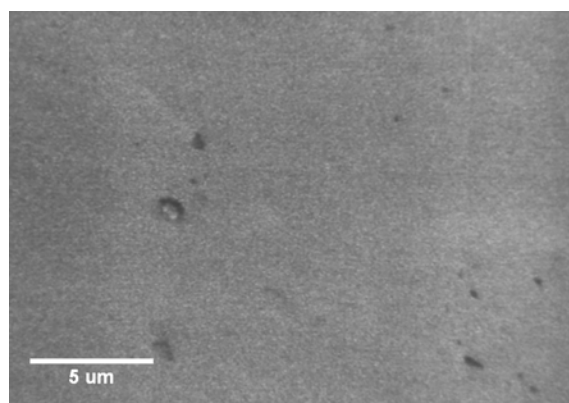


Fig.9 Results of x-ray diffraction measurements obtained with mirrors fabricated of two halves of the same ISSMT sample: the un-annealed amorphous sample and the sample annealed at 773° K for 1 hour.

Both mirrors were repeatedly exposed to argon plasmas under similar experimental conditions, with ion energies ranging from 100-1350 eV.



a



b

Fig.10. SEM photos of the surface of ZrTiCuNiBe crystallized (a) and amorphous (b) mirror samples (ISSPMT) after long term bombardment with Ar^+ ions under similar experimental conditions.

After the first series of plasma exposures, the crystallized specimen weight-loss corresponded to an eroded layer thickness of about 8.9 μm in comparison to 6.8 μm for the amorphous specimen. In addition, the surface of the crystallized mirror developed a surface roughness that was variable along the specimen surface. At the same time, the surface of amorphous specimen continued to be smooth; even the pits (Fig.2) became much shallower than seen initially. Fig.10a, shows the part of crystallized specimen surface with high roughness, while Fig.10b is typical of any part of the amorphous specimen surface.

Further exposures to 1 keV argon ions was carried out with a total sputtering of the crystallized sample by $\sim 21 \mu\text{m}$ and of the amorphous sample $\sim 13.5 \mu\text{m}$. For both samples no significant change in the surface roughness was observed, in comparison with that shown in Fig.10. The reflectance of crystallized sample significantly decreased after this second series of exposures but the amorphous mirror maintained its initial reflectance without any measurable change.

When bombarded with 1 keV deuterium ions, a weight loss was observed for the crystallized mirror, in contrast to its amorphous counterpart half, which showed no measurable weight change, presumably due to deuterium uptake. A preliminary estimation, based on the

supposition of equal ion sputtering rates for both mirrors, gives a deuterium retention rate of about 30% for the amorphous mirror.

5. Conclusion

All amorphous samples absorbed large fractions of deuterium when bombarded with deuterium plasma ions, with the fraction absorbed increasing with increasing ion energy in the range 20-100 eV (for LTC samples).

On the surface of one LTC sample, blister-like artifacts were found which differ strongly from the “classical” blisters and which have not been observed for other materials [10].

Under bombardment with deuterium ions, the reflectance behavior of the mirrors is qualitatively similar to the behavior of Be mirror samples, probably due to similar chemical processes on the surface, i.e., the partial transformation of beryllium oxide into beryllium hydroxide.

Following long term sputtering with Ar^+ ions, the amorphous mirror samples demonstrate the ability to maintain the good optical properties in contrast to crystallized mirror samples of the same material, thus supporting the assumption made in [1].

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References

1. V.S.Voitsenya *et al.*, Rev. Scient. Instrum. **70**, 790 (1999).
2. W.L.Johnson. JOM Journal of the Minerals, Metals and Materials Society (March 2002) 40.
3. A.Inoue and A.Takeuchi. Material Science and Engineer. **A 375-377**, 16 (2004).
4. A.F.Bardamid *et al.*, Surf. Coatings Technol. **103-104**, 365 (1998).
5. N.Wanderka *et al.*, Mater. Sci. Forum **312-314**, 365 (1999).
6. E.D. Palik (Editor), Handbook of Optical Constants of Solids (Academic Press, 1985).
7. A.F.Bardamid *et al.*, Physica Scripta **T123**, 89 (2006).
8. K.S. Golovanivsky *et al.*, Soviet J. Plasma Phys. **7**, 324 (1981).
9. V.S. Voitsenya *et al.*, J. Nucl. Mater. **329-333**, 1476 (2004).
10. A.F. Bardamid *et al.*, J. Nucl. Mater. **376**, 125 (2008).
11. A.K.Tayagi and R.V.Nandedkar. J. Nucl. Mater. **132**, 62 (1985).
12. A.K.Tayagi and R.V.Nandedkar. J. Nucl. Mater. **148**, 22 (1987).