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Effect of Grain Size on Mechanical Properties of Irradiated Mono- and Polycrystalline $MgAl_2O_4$

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The influence of the size of crystalline regions on mechanical properties of irradiated oxides has been studied using a magnesium aluminate spinel $MgAl_2O_4$. The samples characterized by different dimensions of crystalline domains, varying from sintered ceramics with grains of few micrometers in size up to single crystals, were used in the experiments. The samples were irradiated at room temperature with 320 keV Ar^{2+} ions up to fluences reaching 5×10^{16} cm^{-2}. Nanomechanical properties (nanohardness and Young's modulus) were measured by using a nanoindentation technique and the resistance to crack formation by measurement of the total crack lengths made by the Vickers indenter. The results revealed several effects: correlation of nanohardness evolution with the level of accumulated damage, radiation-induced hardness increase in grain-boundary region and significant improvement of material resistance to crack formation. This last effect is especially surprising as the typical depth of cracks formed by Vickers indenter in unirradiated material exceeds several tens of micrometers, i.e. is more than hundred times larger than the thickness of the modified layer.

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1. Introduction

The ever increasing amount of plutonium originating from nuclear reactors and dismounted nuclear weapons represents a serious threat to international security. Today about 1400 tons of plutonium exists worldwide; about 300 tons in military installations, 200 tons have been used for fabrication of mixed oxides (MOX) nuclear fuel and about 900 tons is stored in power plants [1]. Taking into account that the fabrication of a nuclear warhead requires less than 10 kg of plutonium and that one 1000 MW reactor produces something like 200 kg of ^{239}Pu per year it becomes clear that the problem of excess plutonium must be rapidly solved. Two strategies are currently envisaged; (i) the use of ^{239}Pu as a nuclear fuel in new generations of reactors and (ii) direct disposal of spent nuclear fuel (SNF) in geological repositories [1–3]. In the first case fissile isotopes have to be embedded in a special material, called inert matrix fuel (IMF), in the second scenario SNF must be transformed into a stable form which can be permanently disposed. For both purposes special materials must be developed to fulfill very tough safety requirements imposed by nuclear engineering rules and international non-proliferation treaties. Among them one can list: ability to incorporate fission products and neutron absorbers, possibility of remote synthesis, chemical durability and resistance to radiation damage. This last condition covers large spectrum of properties; persistence of crystalline structure, absence of swelling, lack of atom's release from material and, finally, preservation of material mechanical resistance upon irradiation.

The main aim of this work is to analyze mechanical properties of irradiated magnesium–aluminate spinel, one of the oxides envisaged to be used in manufacturing of inert matrix fuel. Although the material is recognized for its radiation resistance, most of the experiments were performed on single crystals and little is known about the effects of irradiation on mechanical strength of this material in polycrystalline form. A detailed objective of the study is thus to understand the differences in material response upon irradiation caused by its mesoscopic organization which has been varied from single crystals to sintered ceramics characterized by small-sized (few micrometers range) grains.

2. Experimental

Four types of samples have been used in the experiments: ⟨100⟩ oriented single crystals and three sintered ceramics characterized by different grain size. In the

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first ceramics the grains have 1–5 μm, in the second one 3–10 μm and in the last one 10–30 μm. All samples were one-side polished to mirror finish and annealed in 1500 °C during one hour to remove damage caused by the polishing process. The samples were irradiated with 320 keV Ar^{2+} ions at fluences varying from 10^{14} cm^{-2} up to 5×10^{16} cm^{-2}. The irradiations were performed using limited beam current density to keep the sample temperature below 50 °C. Accordingly to calculations made with a SRIM code the projected range of 320 keV Ar ions in $MgAl_2O_4$ corresponds to 210 nm and the projected range to 52 nm [4]. The amount of damage created by irradiating ions was measured in single crystals by using the Rutherford backscattering/channeling (RBS/C) method [5]. Nanomechanical properties of the samples (nanohardness and the Young modulus) were analyzed using an atomic force microscope (AFM) coupled with a Hysitron® head. Berkovitch-shaped diamond indenter has been used for both nanomechanical measurements and AFM surface scans. Each measurement has been repeated 3–6 times. The indents were made by using a 5 mN maximum load which corresponds to about 100 nm of maximum penetration depth, i.e. less than half of the thickness of the modified layer. In such conditions the hardness values are generally not influenced by the unmodified bulk material [6]. The load/unload curves were fitted using the Oliver–Pharr method [7]. The resistance on crack formation was studied by using a standard method consisting in the measurement of the length of cracks forming at the corners of the indent made by Vickers indenter [8]. Because of the low thickness of the modified layer in these experiments only the lowest possible load of 0.5 N was used.

3. Results and discussion

A tremendous advantage of the experiments performed on single crystals is the possibility to directly measure various characteristic describing the material studied, for instance damage level (via RBS/C method) and nanomechanical properties. Such a combination constitutes a very useful guideline to study the correlations between structural and functional properties.

An example is shown in Fig. 1 presenting the results of damage, stress and nanohardness measurements performed on spinel crystals. One may note that at the beginning of the irradiation process the stress level increases very rapidly. When the stress level becomes high enough to destabilize the initial defect structure a structural transformation takes place leading to the fast increase of damage level f_D and, simultaneously, to the stress release. Dashed line represents the variations of nanohardness upon irradiation. Taking into account that compressive stress leads to hardness increase, it is not surprising to observe the correlation between stress and hardness. The sequence of processes occurring during low-energy irradiation can be accounted for in the frames of multi-step damage accumulation model [9, 10]. The solid line shown in Fig. 1 is the fit to the experimental data made using this model.

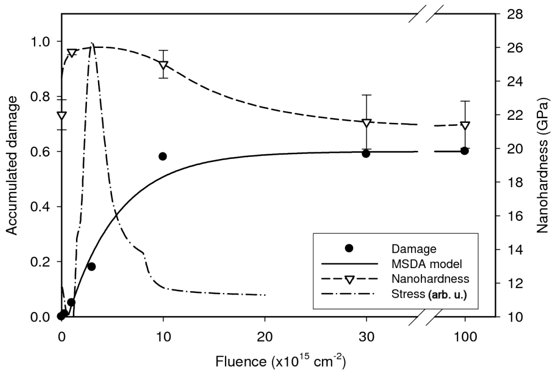

Fig. 1. Accumulated damage (f_D), nanohardness and stress evolution versus irradiation fluence measured for a $MgAl_2O_4$ single crystal.

Next part of the experiments was devoted to the analysis of nanohardness changes in polycrystalline samples irradiated with increasing fluences of Ar ions. The results are shown in Fig. 2. The general trend in hardness variation in polycrystals is similar to that measured for single crystals (full circles in Fig. 2), i.e. an increase at a low-fluence range followed by stabilization at values close to those measured for unirradiated material and finally decrease up to 18–21 GPa. This last effect is likely due to formation of argon precipitates in the irradiated spinel. An interesting observation is the fact that the fluence range in which a hardness increase is observed decreases with decreasing size of grains. The most likely explanation of this result is the accelerated stress release in samples composed of small grains. This, in turn, indicates that defect transformation from point defects typical for early stages of damage build-up to dislocations or dislocation loops characteristic for intermediate stages [11, 12] in sintered ceramics occurs at lower irradiation fluences than in bulk single crystals.

It is well known that in polycrystalline materials the mechanical resistance is to the large extent defined by properties of grain boundaries. AFM coupled with Hysitron head offers an unrivalled opportunity to measure the mechanical properties in selected areas of the sample. It is thus possible to measure nanohardness in the center of grains and in the vicinity of grain boundary. The results of such a measurement are shown in Fig. 3 presenting the dependence of nanohardness measured in the center of the grains (open triangles) and in the vicinity of grain boundary (full triangles) for a sample characterized by small size of grains. One may note the huge differences in the hardness measured in grains and grain boundaries in virgin samples (23 and 17 GPa, respectively), these differences rapidly decrease with the irradiation fluence. Simultaneously, the hardness increases with the irradiation fluence. At 1×10^{15} cm^{-2} hardness in grain centers and in grain boundaries reaches 26

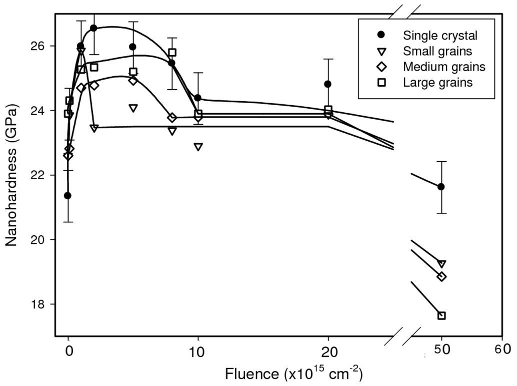

Fig. 2. Nanohardness versus irradiation fluence measured for single crystals (full circles) and for polycrystals inside ≈ 2 μm sized grains (open triangles), ≈ 5 μm sized grains (open diamonds) and > 10 μm sized grains (open squares). The lines serve only the purpose to guide the eye. For the sake of clarity error bars are shown only for the single crystal.

and 25 GPa, respectively, and differs by only 1 GPa. At high irradiation fluences (above 1×10^{16} cm^{-2}) the hardness measured at grain boundaries may even exceed the value obtained for grain body. Several mechanisms can be evoked to explain this effect. Among them ion beam mixing of neighboring grains leading to the reinforcement of the bonds between them is the most likely possibility. Another possibility is the stress-induced hardening effect.

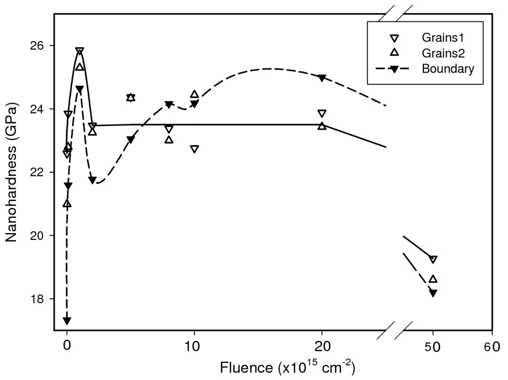

Fig. 3. Nanohardness versus irradiation fluence measured inside grains (open triangles) and in the vicinity of grain boundaries (full triangles) for ≈ 2 μm sized grains. Top and down triangles represent two different series of measurements. The lines serve only the purpose to guide the eye.

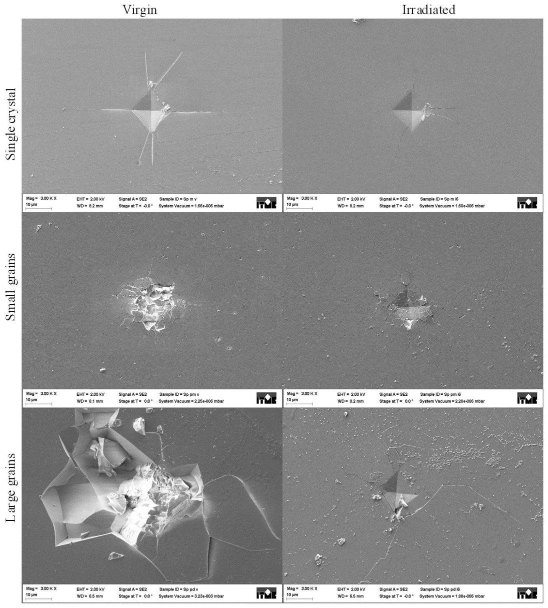

Fig. 4. SEM pictures taken in the vicinity of indents made with the Vickers indenter on the surface of MgAl$_2$O$_4$ samples. Left column: virgin samples. Right column: samples irradiated up to 5×10^{16} cm^{-2}. From top to bottom: single crystals, ceramics composed of small-sized grains and ceramics composed of large-sized grains.

The last part of the experiments was focused on the analysis of irradiation on crack formation in spinel. Ceramics are brittle materials, hence its resistance for cracking has a crucial importance for the safety issues. An interesting question is thus how the radiation damage will influence the susceptibility for cracking in materials used in nuclear industry. Figure 4 gives the first insight into this problem presenting the scanning electron microscopy (SEM) images of the indents made with the Vickers indenter on the surface of magnesium aluminate spinel samples. The left column contains pictures taken for virgin samples, the right one the images of samples irradiated up to a fluence of 5×10^{16} cm^{-2}. It is obvious that the crack propagation in irradiated samples is to the large extent reduced when compared to the virgin ones. To the best of our knowledge it is the first demonstration of the possibility to increase the resistance for crack formation in ceramics.

4. Conclusions

The results presented in this paper may be summarized in the main conclusion that the experiments performed on single crystals provide very useful information that may apply also to their polycrystalline counterparts. Sintered ceramics are at least as irradiation-resistant as their single crystalline analogs; nanohardness evolution upon irradiation suggests that the structural transformations from point defects to more extended complex defects occur at much lower irradiation fluences than in single crystals. Mechanical resistance of sintered spinel ceramics seems even to improve upon irradiation. First the hardness of grains remains close to the virgin samples, secondly the hardness of grain boundaries and resistance for crack formation significantly increases. Several mechanisms can be evoked to explain these results: ion beam mixing of neighboring grains, increased plasticity of irradiated material and compressive stress in the surface layer are the most likely ones.

Acknowledgments

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References

[1] R.C. Ewing, W.J. Weber, J. Lian, *J. Appl. Phys.* **95**, 5949 (2004).

[2] M. Bunn, J.P. Holdren, *Ann. Rev. Energy Environ.* **22**, 403 (1997).

[3] W. Stoll, *Mater. Res. Bull.* **23**, 6 (1998).

[4] J.F. Ziegler, J.P. Biersack, U. Littmark, *The Stopping and Range of Ions in Solids*, Pergamon, New York 1985 (`http://www.srim.org/`).

[5] *Handbook of Modern Ion Beam Materials Analysis*, Eds. J.R. Tesmer, M. Nastasi, Materials Research Society, Pittsburgh PA, USA 1995.

[6] A.A. Pelegri, X. Huang, *Comp. Sci. Technol.* **68**, 147 (2008).

[7] C. Oliver, G.M. Pharr, *J. Mater. Res.* **7**, 1564 (1992).

[8] G.R. Anstis, P. Chantikul, B.R. Lawn, D.B. Marshall, *J. Amer. Cer. Soc.* **64**, 533 (1981).

[9] J. Jagielski, L. Thomé, *Vacuum* **81**, 1352 (2007).

[10] J. Jagielski, L. Thomé, *Appl. Phys. A* **97**, 147 (2009).

[11] S. Moll, L. Thomé, G. Sattonnay, A. Debelle, F. Garrido, L. Vincent, J. Jagielski, *J. Appl. Phys.* **106**, 073509 (2009).

[12] J. Jagielski, L. Thomé, *Nucl. Instrum. Methods Phys. Res. B* **266**, 1212 (2008).