MICROSTRUCTURAL CHARACTERISATION OF ION-IMPLANTED SI_3N_4 BASED CERAMICS

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Abstract - Si_3N_4 based ceramics made by hot isostatic press, were implanted with N^+ ions at a fluence of 10^{17} ion/cm^2 and an energy of 500 keV. This paper deals with the investigation of the microstructure changes, which occur at the implantation in the surface layer. The implantation resulted in an amorphous and a cellular layer, near the surface, what was proved with transmission electron microscopy (TEM-EDS) and electron diffraction measurement. Due to these microstructural changes the tribological behaviour of the investigated ceramics can be improved.

1. INTRODUCTION

The mechanical- and tribological properties of ceramics are very surface sensitive. Accordingly the ion-implantation is a possible tool for improving these properties of ceramics. Many papers deal with the effect of implantation on the tribological properties of ceramics [1, 2, 3]. However, for the better understanding of the physical- and chemical mechanism under the wearing of ceramics, it is important to know the microstructural changes in the course of implantation. In our previous experiments it was shown, that in the surface layer of N^+-implanted Si_3N_4 based ceramics an amorphous layer originated, which depth and thickness are dependent on the applied flux and energy [4].

2. EXPERIMENTAL DETAILS

The starting material for the experiments was Si_3N_4 based ceramic, which was made by sinter-HIP method. Si_3N_4 (UBE SN-ESP), Y_2O_3 (C. Starck) and Al_2O_3 (Grade Al6, Alcoa) powders were used as sintering powders. The composition (in wt %) was Si_3N_4: 90 %, Y_2O_3: 6 % and Al_2O_3: 4 % [7]. The powders were milled in ethanol in a planetary type alumina ball mill. After compacting, the rectangular bars were sintered in an ABRA made HIP equipment in 99.999 % purity nitrogen atmosphere at 1690-1730 °C under 1-2 MPa pressure in the first stage and 10-20 MPa in the second. The dimensions of the samples after sintering were 5x4.5x50 mm.

For affect the wearing behaviour the samples were implanted with N+ ions at the fluence of 10^{17} ion/cm^2 and at the energy of 0.5 MeV. Before the implantation the surface preparation of samples were made by automata polishing equipment, the finally grain size was 0.25 μm. The probable N+ distribution was estimated with the Stopping and Range of Ions in Matter (SRIM) software [5] (Fig. 1.).

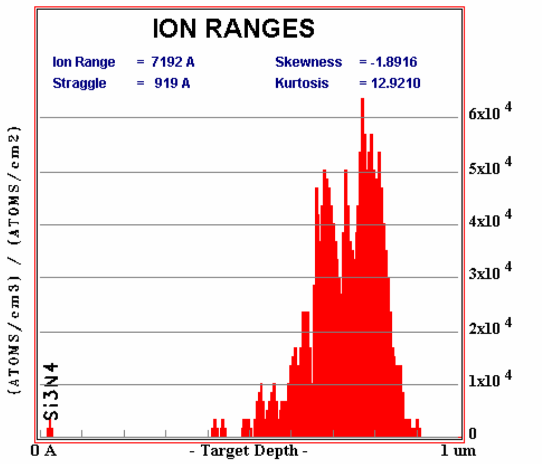


Fig. 1. *Estimation of the penetration depth of N^+ with TRIM*

3. RESULTS AND DISCUSSION

The samples contain ß-Si_3N_4 grains and glassy phase on the grain boundaries in accordance with the original composition. (Fig. 2.). The TEM image shows the microstructure, constituted by the light gray needle type ß-Si_3N_4 and between the grains, in the triple point the dark gray glassy phase.

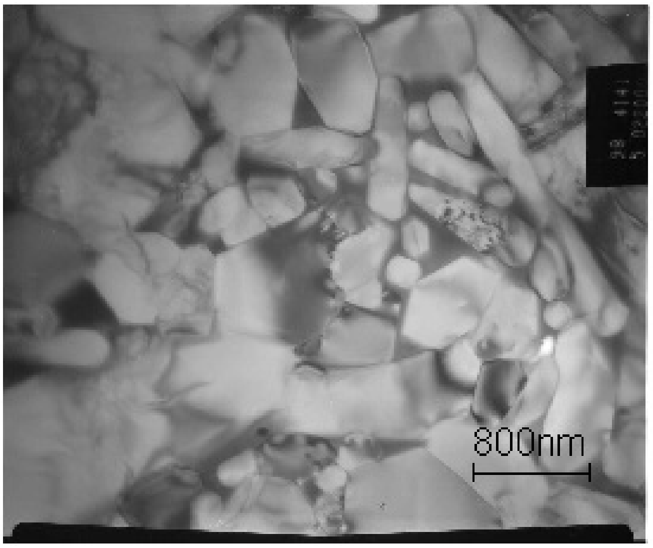
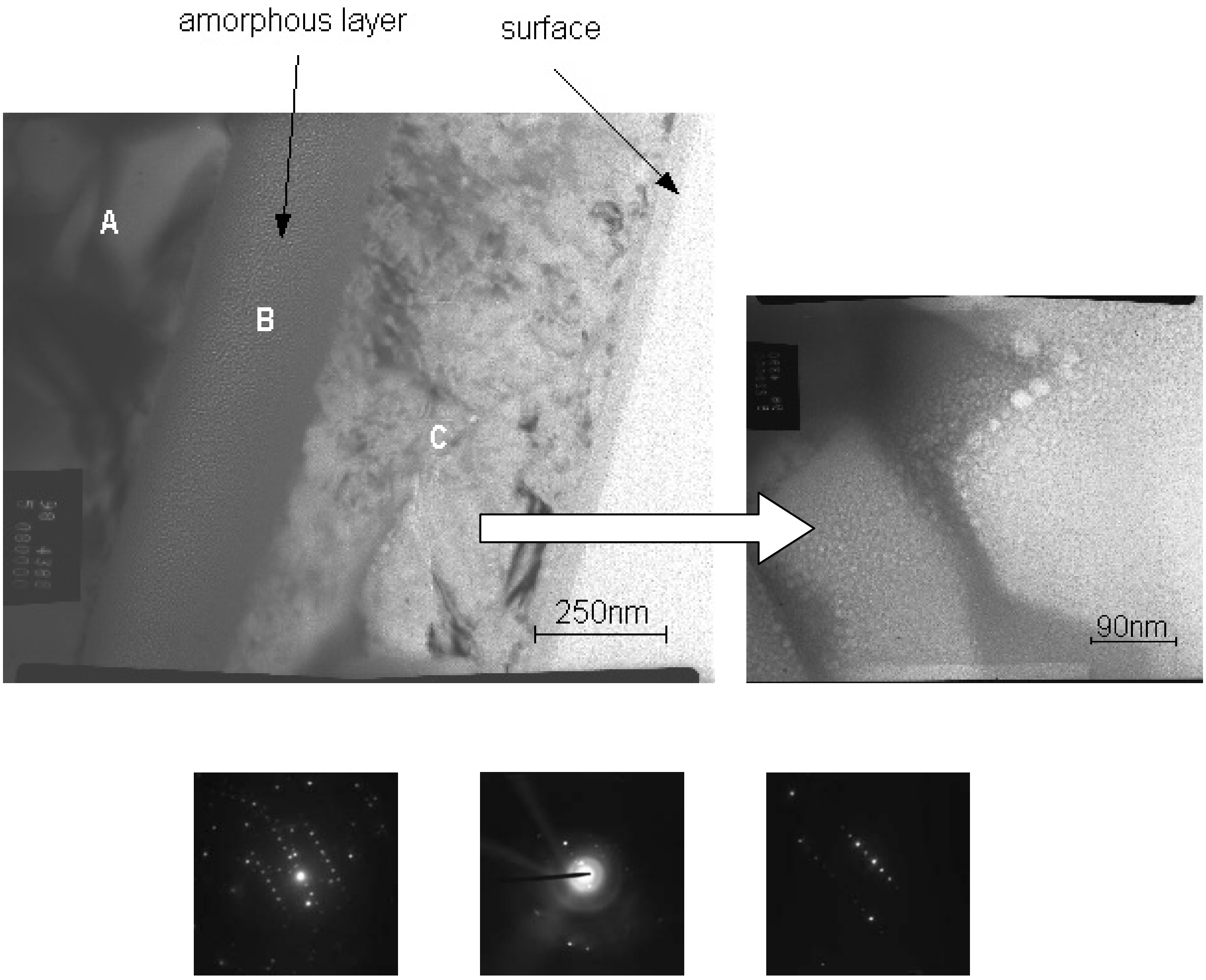


Fig. 2. *TEM image of the original microstructure of Si_3N_4 based ceramic*

The cross sectional TEM image of the N^+ implanted Si_3N_4 based ceramics shown in Fig. 3. On Fig. 3. three different areas under the surface of implanted sample in different depth can be seen. The electron diffraction patterns in the figure are from the locations indicated by **A B** and **C**. The area **A** and **C** show the characteristic crystal structure of the original material, whereas the electron diffraction pattern accomplished in the area **B** is broad fringes, which indicate the amorphous phase. The distance of the amorphous layer from the surface is 550 nm, the thickness is 300 nm, what is in good agreement with the ion-implanted region, estimated by TRIM (Fig. 1.).

The most important observation from these investigations is that in the surface layer, above the amorphous layer the crystalline structure was retained after the N^+ implantation, although one part of the passed ions was built up into the microstructure. The amorphisation takes place just in certain depth, forming a layer under the surface.



A **B** **C**

Fig. 3. *TEM and electron diffraction results of the N^+ implanted Si_3N_4 based ceramics*

Further experiments showed, that in the surface layer (area **C**) nano sized “bubbles” on the boundaries of Si_3N_4 grains were developed due to the implantation, which is not typical of the amorphous layer. The composition measurement (was performed in the three different area (area **A**, **B** and **C**)) is also in keeping with the TRIM estimation, according to the largest quantity of the nitrogen in the amorphous layer. Furthermore, the nitrogen concentration was also increased in the **C** surface layer, compared to the based composition and the composition of the unmodified area (**A**), respectively. Table 1. contains the composition of the samples (in weight %), meased in different depth from the surface. In each case minimum and maximum values of at least four measurements are given. In the amorphous layer the nitrogen is presented in double quantity than in the bulk material and also the surface layer consists 10% more nitrogen, which means, that either the “bubbles” contain N or the excess was built up in the original microstructure. It is necessary to carry out further experiments to explore these microstructural changes.

Table 1. *Results of TEM-EDS measurement in different depth, which contains the atomic composition of implanted ceramics in wt. %.*

Investigated area		Atomic composition [wt. %]			
		N	Si	Al	Y
A	min.	21,2	70,5	2,5	0,6
	max.	25,7	72,5	6,3	1,2
B	min.	37,2	54,2	1,2	0,7
	max.	44,0	59,6	2,8	1,7
C	min.	30,9	48,2	1,7	1,1
	max.	35,3	61,9	3,4	17,4

The explanation of the highest Y content in region **C** is that the detector were received the signal from the Si_3N_4 grain boundary glassy phase, which contains mainly $Y_2Si_2O_7$ phase [6].

Surface amorphisation of Si_3N_4 based ceramics by ion-implantation has been reported by some researchers [7, 8, 9, 10], from these papers it is evident that the implantation takes effect also on the mechanical- and chemical properties of ceramics. Oblas et al. [10] and Nakamura et al. [11] also have observed cellular structure in the surface layer of implanted ceramics.

4. CONCLUSIONS

Investigations on the N^+ implanted Si_3N_4 based ceramics were showed, that:

(1) In the surface layer of ceramics were developed an amorphous layer affected by ion-implantation, which was 300 nm thick in 550 nm depth using a fluence of 10^{17} ion/cm^2 and an energy of 500 keV.

(2) The developed profile of N^+ concentration during the implantation is in good agreement with the result of the TRIM simulation.

(3) The surface layer, above the amorphous layer remained crystalline after the N^+ implantation, although one part of the passed ions was built up into the microstructure.

(4) Nano sized "bubbles were developed" on the boundaries of Si_3N_4 grains of the surface layer due to the built up N^+ ions.

ACKNOWLEDGEMENT

The authors express their thanks to Dr. P. Arató (Research Institute for Technical Physics and Materials Science of the Hungarian Academy of Sciences) for the sample, to Dr. N. Wanderka (Hahn-Meitner Institute, Berlin) for the TEM measurements, J. Opitz (Hahn-Meitner Institute, Berlin) for ion-implantation and to Prof. H. Schubert (Technische Universität, Berlin) for the professional consultation.

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