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Study of chemical interaction at Al–ZERODUR interface

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Abstract

Effect of thermal annealing on bulk and interface properties of ZERODUR glass ceramics was investigated by Raman and X-ray spectroscopy as well as secondary ion mass spectrometry. For this purpose thin aluminium films were deposited onto the surface of ZERODUR samples prepared by mechanical polishing. Internal stresses in the bulk of investigated samples were revealed using modulation–polarization technique. The ability of chemical reactions in Al–ZERODUR system is briefly analyzed to explain experimental data. Contribution of amorphous and crystalline phases of ZERODUR to observed phenomena is discussed.
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1. Introduction

ZERODUR is glass ceramic widely used in different branches of industry and science. For example, it has decisive advantages for application in modern LCD lithography. Chemically ZERODUR consists of oxides Li_2O–SiO_2–Al_2O_3. It is synthesized at the temperatures 700–1000 °C. In order to stimulate formation of nucleating center titanium oxide is added to the starting charge. This ceramics has both crystalline and amorphous phases. The last one is represented by crystallites of nanometer sizes (d = 50–70 nm). The crystalline phase has a negative linear thermal expansion while that of the amorphous phase has positive. This results in zero thermal expansion coefficient in the wide temperature range −40 to +100 °C. Among other important advantages of this material besides zero thermal expansion coefficient, is good processability. Thus, very low surface roughness can be achieved.

ZERODUR serves as the mirror substrate material for large-scale telescopes. Currently the world's largest and most powerful telescope has four main mirrors made of ZERODUR glass ceramic, each with a surface of over 50 square meters and a diameter of 8.2 m. Very large mirrors and other systems may be composed of many components made of ZERODUR. So, assembly of these components is important engineering task. Different devices made of ZERODUR often include metal-to-glass ceramics interfaces. Typically, such parts are processed at elevated temperatures and then cooled to room temperature, so significant thermo-mechanical stress may arise and result in different failures that degrade performance of devices. Also, residual stresses may exist in samples of ZERODUR as a result of mechanical treatment. Components of devices made of ZERODUR can be connected together by diffusion welding using aluminium film of 100 nm thickness previously deposited on the surface in a vacuum chamber and then annealed at temperatures 400 − 600 °C. The performance of such connection depends on chemical and physical phenomena occurred at the aluminium–ZERODUR interface. The aim of this work is to investigate these phenomena by different experimental techniques as well as to clarify their nature.

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2. Experimental results and discussion

2.1. Raman spectra

Raman spectroscopy is known as excellent tool to study the local order and its perturbation in both crystalline and amorphous materials. The short-range order in amorphous material is the same as in crystalline, so their Raman spectra are expected to be similar. However, Raman spectroscopy does not allow to clear whether bond angle or bond length fluctuations are predominant. In the present investigation Raman scattering has been measured on samples of ZERODUR ceramics at room temperature. Argon laser ($\lambda = 514.5$ nm, $P \approx 100$ mW) was used for excitation of Raman spectra. Experimental spectra were recorded in a photons counting mode.

The modeling of the amorphous network in ZERODUR is rather difficult due to microstructure of this material composed of crystalline and amorphous phases is not known exactly. However, interpretation of Raman spectrum for one of these phases is possible if there is information about the vibration spectrum of another phase. Taking this into account, the vibration spectrum of SiO_2 film grown on a sapphire substrate was measured first of all. The necessity of such measurements is based on assumption, that the characteristic spectral lines corresponding to chemical bonds of SiO_2 should be observed also in ZERODUR ceramic.

The glassy SiO_2 represents the amorphous network from silicon atoms tetrahedrally surrounded by oxygen atoms. The tetrahedrons are bounded with each other by means of oxygen atoms, so Si–O–Si bridges with the angle between bonds close to 150° is formed. In other words, in the amorphous network each of Si atom is surrounded by four oxygen atoms and each atom of oxygen is surrounded by two atoms of Si. Vibration spectrum of such SiO_2 structure was calculated earlier.[1] It has been established that moving of oxygen atoms in directions perpendicular to planes of Si–O–Si triangle results in vibration with frequency of 458 cm^{-1}.

Raman spectrum of SiO_2 film grown on a sapphire substrate is shown in Fig. 1. This spectrum was obtained at 90° geometry of light scattering. An excitation of vibrations has been performed by laser beam sliding along the film surface. The vibration peaks

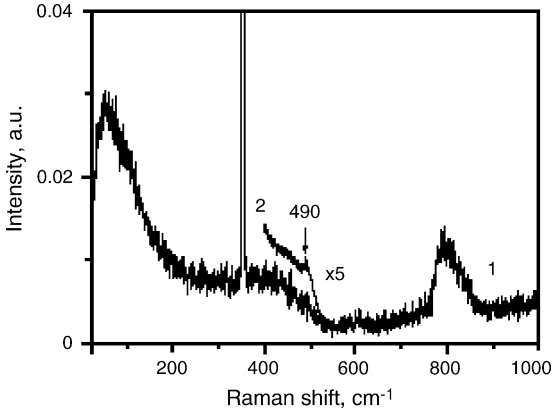

Fig. 1. Raman spectra of amorphous film of SiO_2 (curve 1) and the same film annealed at $T = 500$ °C during 15 min.

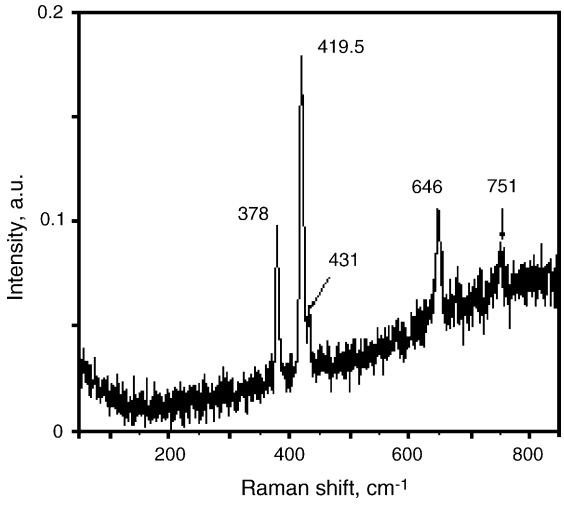

Fig. 2. Raman spectra of sapphire (α-Al_2O_3).

with frequencies around 800 and 100 cm^{-1} are shown. The peak at 400 cm^{-1} can be attributed to Si–O rocking vibrations of SiO_2 tetrahedron, and that one at 800 cm^{-1} is due to vibration of chemical bonds of Si–O–Si bridge.[2] The intensive narrow peak at 378 cm^{-1} is due to radiation of Ar plasma.

Curve 2 in Fig. 1 represents Raman spectrum of the same film after thermal annealing in nitrogen atmosphere during 15 min at $T = 400$ °C. It is seen that weak peak occurs at the frequency of 490 cm^{-1}. It has been shown in[3] that thermal annealing of SiO_2 films results in composition transformation

$$2SiO_x \rightarrow xSiO_2 + (2 - x)Si, \quad (1)$$

For example, in those parts of SiO_2 film where stoichiometry is broken, elementary silicon can arise at high temperatures. It has been shown earlier[4] that high temperature annealing of SiO_2 non-stoichiometric films results in a broad peak with maximum centered at 490 cm^{-1}, which may be attributed to Si–Si bonds. This means that clusters of amorphous silicon can be formed in annealed SiO_2 films.

To obtain information about vibrations in Al_2O_3, depolarized Raman spectrum of sapphire was measured, Fig. 2. As seen, three peaks at 419, 646 and 751 cm^{-1} are clearly observed in the spectrum. The peak at 378 cm^{-1} is also observed in the spectrum of SiO_2. Since the scattering property of sapphire is less than the film of SiO_2, this peak in Fig. 2 is less intensive. It is possible to suppose that in the case of amorphous films of Al_2O_3 measured spectrum should agree qualitatively with that one shown in Fig. 2, but expected peaks should be more wide.

Raman spectra of the specially prepared samples of ZERODUR ceramic were measured. Samples were cut in a form of parallelepiped with dimensions of 15 mm × 15 mm × 40 mm. Their lateral faces were polished. One of them was covered by thin aluminium film thermally evaporated in a vacuum system. Then prepared samples were annealed at temperatures 400 or 600 °C within 15 min. After annealing the metallic layer was removed from the one part of the covered surface while the trace of Al was saved in another part.

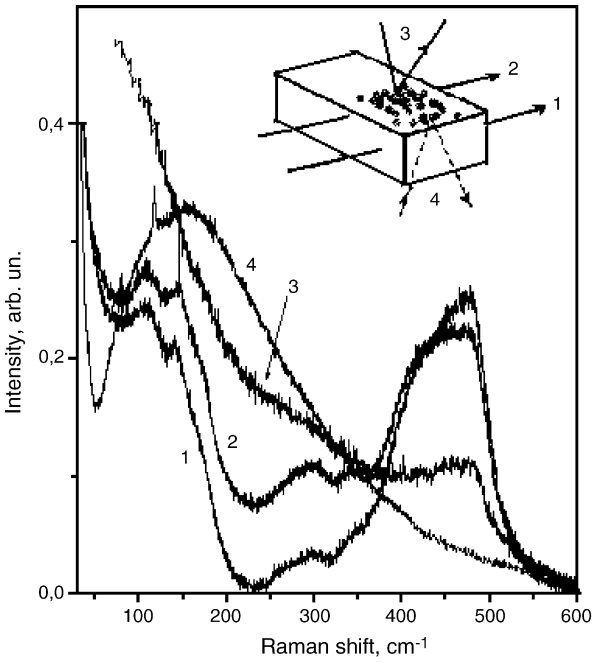

Fig. 3. Raman spectra of ZERODUR. Four specific directions of Raman spectra excitation are shown.

Fig. 3 shows Raman spectra measured from two parts of a sample. The geometry of measurements is shown in the insert. The spectra 1 and 2 were recorded using standard 90° technique. Two broad peaks are observed in two spectral ranges 400–500 cm^{-1} and 100–200 cm^{-1} in the spectrum obtained at the bulk excitation. The edge of the first peak at frequencies less than 50 cm^{-1} represents the decline of Rayleigh line. From the comparison of this spectrum with Raman spectra of SiO_2 and Al_2O_3 (Figs. 1 and 2) one can suppose that peaks in the spectral ranges 100–200 cm^{-1} and 400–500 cm^{-1} can be attributed to SiO_2 and Al_2O_3, respectively. It is well known that aluminium occupies position with octahedral surrounding of oxygen in the crystalline corundum γ-Al_2O_3 or sapphire α-Al_2O_3. In amorphous phase it has the same nearest surrounding. However, little changes of angles and lengths of chemical bonds can occur in amorphous network giving rise to change of frequencies of appropriate vibrations of elementary octahedron. This may be regarded as possible cause of large broadening of observed spectral peaks.

It is well known that reactivity of Al is higher in comparison with Si. So, it may be reasonably assumed that the diffusion of Al into ZERODUR is accompanied by substitution reaction

$$4Al + 3SiO_2 = 2Al_2O_3 + 3Si \quad (2)$$

Note that energy of chemical bonds in Al_2O_3 is approximately 20% higher than in SiO_2. So, reaction (2) is possible at the high temperature. This can be assumed as additional proof that exchange reaction is carried out at 400 °C. However, the problem arises concerning possible positions of Al in the investigated ceramics. In the crystal lattice of SiO_2 aluminium can occupy both substitutional and interstitial positions. The replacement of Si by Al in tetrahedral structures of SiO_2 can take place because

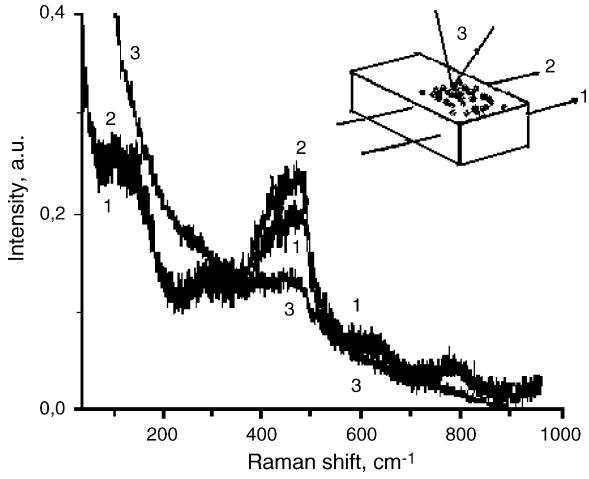

Fig. 4. Raman spectra of annealed at 600 °C sample of ZERODUR measured at three specific directions of excitation.

Al has smaller radius. If this is the case appropriate spectral peaks shift towards higher frequencies. Curve 4 in Fig. 3 represents Raman spectrum measured at the part of the surface where this process is the most probable. This result qualitatively confirms the above speculations. On the other hand, Al can substitute Si in amorphous phase too. In this case clusters of amorphous Si may be formed. The Raman spectrum shown in Fig. 3 (curve 3) was measured from the surface that has been previously covered by Al. The weak peak at 490 cm^{-1} can be attributed to Si–Si bonds. Furthermore the behavior of experimental curve in the spectral range 400–500 cm^{-1} qualitatively coincides with curve 2 in Fig. 1, which corresponds to amorphous clusters of silicon in SiO_2.

The Raman spectra of a ZERODUR sample covered with aluminium film and annealed at 600 °C are shown in Fig. 4. The annealing was carried out in a vacuum chamber at overpressure of Ar to prevent re-evaporation of Al atoms. Numbering of spectral curves correspond to the parts of a sample shown in the insert where measurements were made. The spectra 1, 2 were obtained at 90° geometry of Raman spectra registration. It is seen, these spectra agree well to those ones shown in Fig. 3. However, in the spectral region of 600 and 800 cm^{-1} the small intensity bands are observed. These peaks well correspond to peaks observed for SiO_x ($1 < x \leq 2$) film deposited on silicon and annealed at the high temperature.[5] As was shown in this investigation, the peak at 800 cm^{-1} is caused by deviation from the stoichiometry in SiO_x films, as well as the peak at 600 cm^{-1} belongs to silicon and is combined phonon state. The cause of deviation from stoichiometry in silicon oxide matrix may be the above substitution reaction (2).

Therefore, from measurements of Raman spectra one can conclude that usage of Al film for joining of ZERODUR plates with subsequent annealing at temperatures 400–600 °C can form silicon nanoclusters in a glass ceramic matrix.

It is necessary to note that the existence of amorphous phase of alumina Al_2O_3 should not be excluded in glass ZERODUR. The structure of amorphous network is not known exactly. If to assume that broken chemical bonds are not present in amor-

phous phase, it is possible to suppose that the structural unit of net should be AlO_3. In this case each atom of Al is bonded with three atoms of oxygen, and each atom of oxygen is bonded with two atoms of aluminium through a bridge Al–O–Al. Investigation of Raman spectra in $Pr_xNd_{1-x}AlO_3$ crystals[6] which contain the AlO_3 as structure units shows that AlO_3 has vibration frequencies in the spectral ranges 50, 150, 270 and 480 cm^{-1}. These frequencies are in good agreement with measured spectra shown in Figs. 3 and 4 (curve 1 and 2).

2.2. X-ray diffraction spectra

X-ray researches were executed to check whether phase transformation has place in glass ceramic ZERODUR. X-ray diffraction measurements were carried out using DRON-3M (Russia) diffractometer ($\lambda = 1.542$ Å). Experimental setup was equipped with a Bragg-Bretano focusing system. For this purpose, LiF curved crystal was mounted before a detector. In order to limit vertical and horizontal divergence of the incident beam a set of slits were used. Standard sample of powdered α-quartz was used for periodic calibration of diffractometer.

Fig. 5 shows typical diffraction pattern from a sample of ZERODUR before (curve 1) and after (curve 2) annealing at temperature of 600 °C. The observed peaks are caused by crystalline phases of ZERODUR. Experimental data shown in Fig. 5 can be explained by presence of SiO_2 and Al_2O_3 crystallites of different polytypes. At the same time, several peaks in the diffraction angle region 60–95° cannot be attributed to hexagonal or cubic phases of both SiO_2 and Al_2O_3. Note that these peaks are more intensive and narrow in an annealed sample. This means that annealing results in more perfect crystalline phases.

At the same time increase of background scattering at low angles is clearly observed in the annealed sample in comparison with the non-annealed one. This may be attributed to increase of relative portion of amorphous phase caused by thermal annealing. It is well known that amorphous phase causes increase of background scattering of X-rays at low angles. This result may be regarded as indirect proof of formation of silicon amorphous phase in annealed samples.

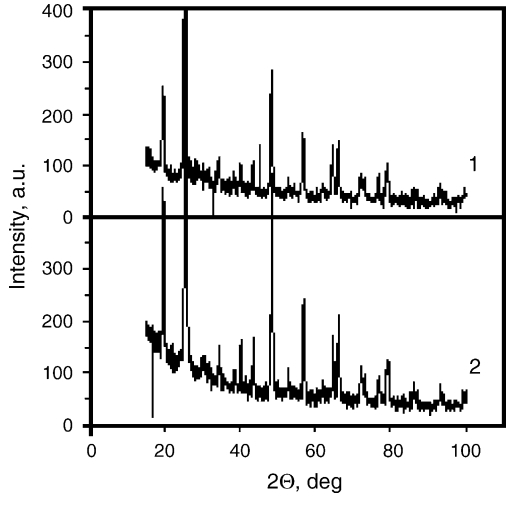

Fig. 5. X-ray diffraction pattern of a sample of ZERODUR before (curve 1) and after (curve 2) annealing at 600 °C.

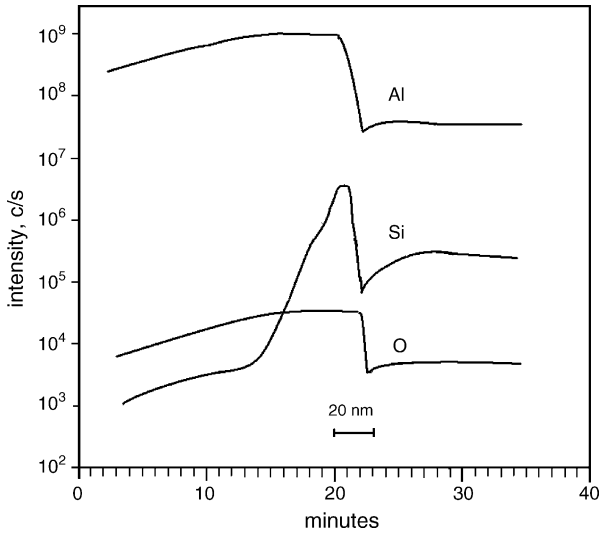

Fig. 6. SIMS profiles of Si, Al, and O measured at the interface Al–ZERODUR in a sample covered by aluminum layer and annealed at 400 °C during 15 min.

2.3. SIMS profiles

In order to clarify physical properties of Al–ZERODUR interface the secondary ion mass spectrometry (SIMS) measurements have been carried out. The SIMS profile measurements were obtained with IMS-4F ("Cameca") spectrometer. To sputter a sample surface Ar^+ primary beam with energy 4–10 keV was used. The SIMS profiles were measured before and after thermal annealing. The curves of count-rate versus time were recorded for three monitored species Al, Si and O, Fig. 6. The sputtering rate was determined by measuring the SIMS crater depth with a surface profilometer Alpha-Step 200 (Tencor Instruments). In non-annealed samples no peculiarities have been observed and all species were smoothly distributed under the surface of a sample. However, their distribution was drastically changed after the metal deposition and annealing at $T = 400$ or 600 °C, Fig. 6. As seen, the aluminium overlayer is enriched with silicon. This effect may be caused by several reasons, such as outdiffusion of silicon from the bulk or chemical substitution reaction at the interface. Taking into account results of Raman scattering measurements described above the substitution reaction (2) seems to be the most important reason for observed effect. The additional silicon may be in form of interstitial ions or silicon clusters.

2.4. Internal stresses

Internal stresses in samples of ZERODUR may be caused by several reasons such as slicing of the starting material, mechanical polishing and thermal annealing. In order to test possible stresses experimental measurements were made on a number of samples. Measurements were based on a method of modulation–polarization spectroscopy. Optical schema of experimental setup is shown in Fig. 7.[7] Laser radiation LG-126

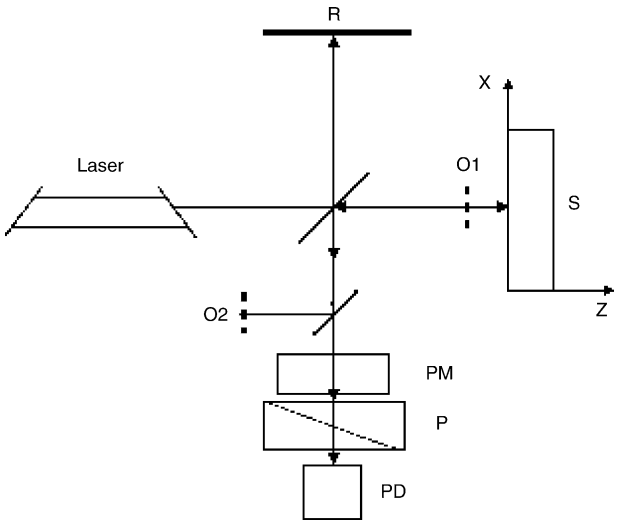

Fig. 7. Optical schema of setup for investigation of stresses in solids.

($\lambda = 0.63$ or 1.15 μm) polarized at the angle of 45° is divided by the splitter Sp on two beams with equal intensities. One of them is directed on the anisotropic reflector R (a quarter-wave plate) and another on a sample S. After reflection both beams are converged together and passed through the polarization modulator PM and the polarizer P. Their intensities are detected by the photodiode PD. When this setup is operated in a transmission mode additional mirror is mounted after a sample.

As the laser radiation is polarized at the angle of 45° its propagation through the sample can be considered as a result of propagation of two orthogonally polarized waves E_x and E_v. If there is no internal stresses in a sample both waves at the output of a sample will have equal phases. This means that input and output beams are polarized in the same plane. If polarization plane of the polarizer P is orthogonal to polarization plane of laser radiation, there is no signal from the photodetector. However, the signal may arise due to anisotropy of optical elements of the schema caused by their imperfection. Turning the reflector R around its axis the signal can be compensated and the initial condition of polarization state is established. If the internal stress is presented, the radiation reflected from the sample will not be linearly polarized. It will be elliptically polarized in the common case. The form of the polarization ellipse and its spatial orientation is completely defined by magnitude and direction of internal stresses.

The elliptic polarization is known to be a mix of linearly and circular polarized light. The intensity of a circular component is proportional to the stress magnitude. The polarization modulator PM used in the setup allows one to register separately intensities of both components. Thus, by scanning a sample by a laser beam and detecting the intensity of circular polarized light, it is possible to measure the distribution of stresses along the scan trace.

The spatial resolution of the setup is defined by a diameter of a laser beam, which falls onto a sample. Therefore, to increase the spatial resolution the micro-objective O_1 is mounted in front of a sample. Micro-objective allows laser radiation to focus on the surface of a sample. The laser beam spot with diameter of a several micrometers can be achieved. The visual inspection of the spot size and its location on the surface of a sample is carried out through an eyepiece O_2.

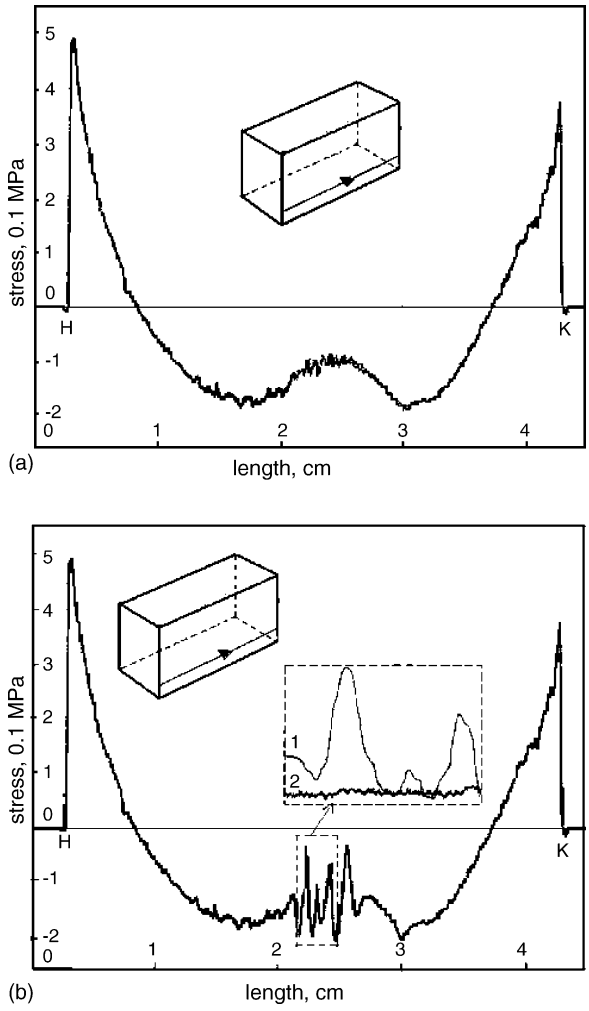

Fig. 8. Distribution of internal stresses in ZERODUR glass ceramic before (a) and after annealing at 600 °C (b). Insert: 1, distribution of stress and 2, intensity of reflected light.

The distribution of the investigated stresses along a scan trace is shown in Fig. 8. The measured sample was prepared in a form of rectangular parallelepiped with thickness of 1 cm and length of 4 cm. The aluminium film was deposited on the bottom face of the sample, as it is shown in figure and then the sample was annealed at temperature 400 or 600 °C during 15 min. The scanning was carried out at the distance of 1–1.5 mm from the aluminium film in direction indicated by arrow. The edges of a sample are designated by capital letters H and K. The setup has been previously calibrated. For this purpose the known external pressure was applied to the investigated sample. The calibration allows us to measure stresses along the trace in absolute value. It is seen from Fig. 8(a) that there are tensile strain at both edges of the sample and compressive strain at the centre.

The distribution of stresses in the same sample after annealing at the temperature 600 °C is shown in Fig. 8(b). The scanning was executed in the same direction and approximately in the same place of the sample. The comparison of curves in Fig. 8(a)

and (b) shows, that the general picture of stresses distribution has not changed. However, there is a group of separate lines in the central part of the sample pointing out the presence of local stresses. Despite of the small absolute value of stresses, it must be pointed out the fact of their presence. The stresses distribution selected with a dotted line is shown in larger scale in the insert. The fact, that observable heterogeneities have appeared as a result of high-temperature annealing, testifies the formation of other phase having another thermal-expansion coefficient. The presence of this phase causes the appropriate stresses.

In the insert of Fig. 8 selected with a dotted line, curves 1 and 2 show the distribution of stresses and intensity of reflected light, accordingly, along the same trace. The comparison of curves 1 and 2 indicates that peaks observed on curve 1 are just caused by internal stress because curve 2 does not show any features which should be attributed to the light scattering on bulk inhomogeneties or surface defects. As the stresses cause the refractive index changes, the question can arise about absence of the light scattering. The answer lies in the fact that the scattering reflects a change of the refractive index at a level of 10^{-4}–10^{-5}, whereas the polarization–modulation method is sensitive to changes at a level of 10^{-9}–10^{-10}. As seen from Fig. 8, the measured stresses have rather low magnitude and they could hardly be detected in the light scattering experiment. However, they are sufficient to be detected by the modulation–polarization technique.

3. Conclusions

Mechanical properties of metal–ZERODUR joint may depend on chemical processes at the interface, which occur during their manufacture and storage. Chemical reactions may include interdiffusion of metal and components of ZERODUR, formation of mixture phases and new chemical compounds. Beside this, the possible out-diffusion of components (Si, Li) into the metal can modify its physical properties. Naturally, the diffusion processes at the interface depend on temperature. In this case temperature is important parameter not only from the point of view of diffusion velocity but also the activation energy of possible chemical reactions. For example, the exchange reaction (2) seems to be the most simple type of possible chemical reactions at the interface.

The high-temperature annealing of ZERODUR ceramic at the presence of aluminum can result in forming amorphous or crystalline silicon phase as clusters or nanocrystals. This process can result in occurrence of local internal stresses.

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