

Zr₂(Cu,Ni) at the central joint region induced substantially low joint strengths below 200 MPa, but the joints without such segregation exhibited the strong joints more than the bulk strength (~530MPa) of Zircaloy-4 base metal (Fig. 3 (c)).

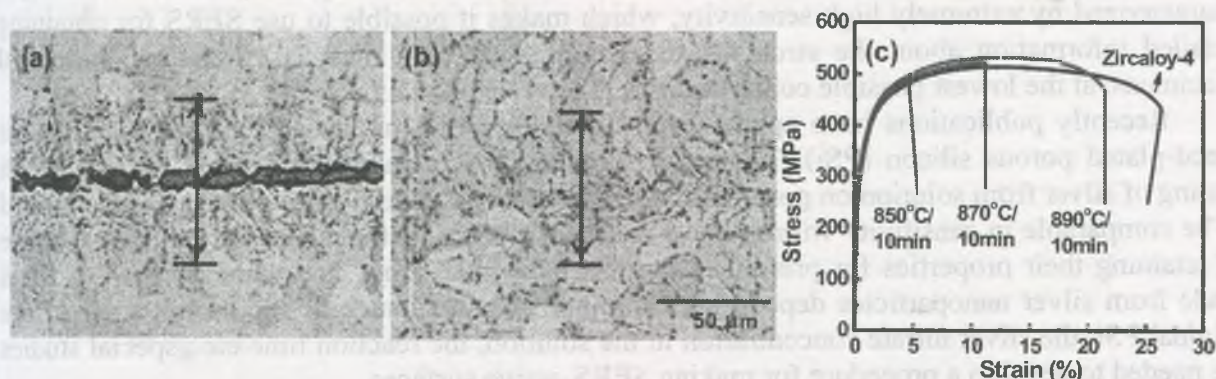


Fig. 3 - Cross-sectional SEM images for the Zircaloy-4 joints brazed at (a) 850°C, 10 min, (b) 890°C, 10 min, and (c) stress-strain curves obtained by a room temperature tensile test.

4. Conclusions

In this study, two different amorphous alloys based on the multi-component eutectic composition, i.e. Zr-Ti-Ni-Cu-Be and Zr-Ti-Ni-Cu were introduced as the fillers to braze the pure Ti Gr. 2 and Zircaloy-4. By using these amorphous alloy fillers, both the Ti and Zircaloy-4 were successfully brazed at low temperatures, e.g., ~820 °C for the Ti and ~890 °C for Zircaloy-4. Through the control of diffusion brazing, highly reliable joints were obtained with the formation of predominantly grown α -Ti and α -Zr grains by the isothermal solidification, which were almost comparable to the base metal structures. Such joints exhibited remarkably high strengths exceeding those of the base metals.

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PLASMONIC STRUCTURES FOR SURFACE-ENHANCED RAMAN SCATTERING BASED ON SILVERED POROUS SILICON

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The interaction of light with metal nanoarrays at dielectric interface leads to a collective oscillation of electrons known as the surface plasmon resonance (SPR) at specific frequencies. By varying the parameters of plasmonic structure and surrounding media the wavelength of the SPRs can be efficiently tuned giving rise to many successful applications. In particular, surface-enhanced Raman scattering (SERS) is a plasmonics-based process. SERS takes place for analyte molecules adsorbed on rough metallic surfaces - SERS-active substrates at spatial

domains, so-called "hot spots", where local light field strength can exceed the incident field by many orders of magnitude [1]. SERS spectroscopy, having all the advantages inherent to conventional Raman scattering (specificity or selectivity, characteristic spectra, noninvasiveness), is characterized by extremely high sensitivity, which makes it possible to use SERS for obtaining detailed information about the structure and composition of a material, including biological specimens, at the lowest possible concentrations [2].

Recently publications have appeared on obtaining SERS-active nanostructures based on metal-plated porous silicon (PSi). The active surfaces are rather easily formed by immersion plating of silver from solution on porous silicon substrates [3]. These solid-state materials proved to be comparable in sensitivity with the best colloidal silver substrates, and in this case capable of retaining their properties for prolonged periods. However, since the characteristics of films made from silver nanoparticles depend on a number of factors such as the morphology of the original PSi, the silver nitrate concentration in the solution, the reaction time etc., special studies are needed to develop a procedure for making SERS-active surfaces.

Here we present the results of studies of the plasmonic structures formed on the porous surface of PSi. Nanostructured silver films have been characterized by scanning electron microscopy. SERS-activity of the substrates was tested by comparing intensities in the spectra of rhodamine 6G and several tetrapyrrolic molecules, which are of great interest due to their biophysical, biochemical and biomedical applications.

The starting wafers for preparation of the PSi plates were p-type, boron-doped, $10 \Omega \cdot \text{cm}$ resistivity, (111) orientation silicon crystals. Porous silicon was prepared by electrochemical anodization in 3:1 mixture of HF and ethanol. An anodic current density and time of anodization were 20 mA/cm^2 and 30 min, correspondingly. Silver deposition was carried out employing the immersion plating method from the water solution of AgNO_3 .

The process of preparation of Ag nanostructured films on PSi depends on a number of factors, where the major ones are the concentration of silver ions Ag^+ and the reaction time. In order to determine the optimal conditions for preparation of substrates with maximum parameters for enhancement of the SERS signal, we obtained Ag-PSi samples under different reaction conditions: we varied the silver nitrate concentration and the soaking time of the PSi wafers in solution, where the temperature of the solution remained unchanged.

Fig. 1 shows the dependence of the SERS signal intensity on the soaking time for wafers of porous silicon in aqueous silver nitrate solutions of three different concentrations. The intensity of the 1650 cm^{-1} band in the SERS spectrum of rhodamine 6G was used as a standard to evaluate the sensitivity of the substrates as a function of the silver immersion plating conditions. For a low AgNO_3 concentration (1 mM), the intensity of the SERS signal gradually increases when the silver deposition time increases. However, the signal level remains rather weak even for prolonged metal deposition (up to 60 min). For a medium concentration (10 mM), the dependence of the SERS signal on reaction time is bell-shaped with a maximum in the 10–15 min range. Further increase in the silver deposition time leads to a fall-off of the SERS signal. Finally, when the PS substrates are held in a solution with a 100 mM AgNO_3 concentration, after 1 min a rather high level of SERS signal is already observed. On increase of the deposition time, the SERS intensity of rhodamine 6G drastically decreases. In a solution with a 10 mM Ag^+ concentration, the silver particles show a $100 \pm 40 \text{ nm}$ diameter, which corresponds to the optimal particle sizes published in the literature (10–150 nm) for SERS-active substrates. Furthermore, silver particles are closely packed on the PS surface: this helps the maximum SERS enhancement to be obtained, since in this case there are an abundance of vacancies for hot spots, i.e. the scattering cross section of the analyte molecules drastically increases.

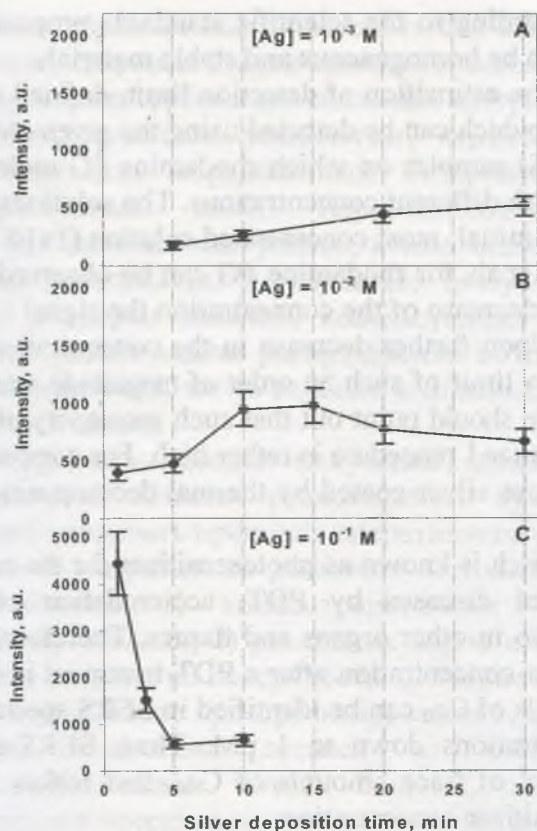


Figure 1- Dependence of the intensity of the 1650 cm^{-1} band in the SERS spectrum of rhodamine 6G on the silver deposition time, $\lambda_{\text{ex}} = 532\text{ nm}$, $[\text{Ag}] = 1\text{ mM}$ (A), 10 mM (B), 100 mM (c).

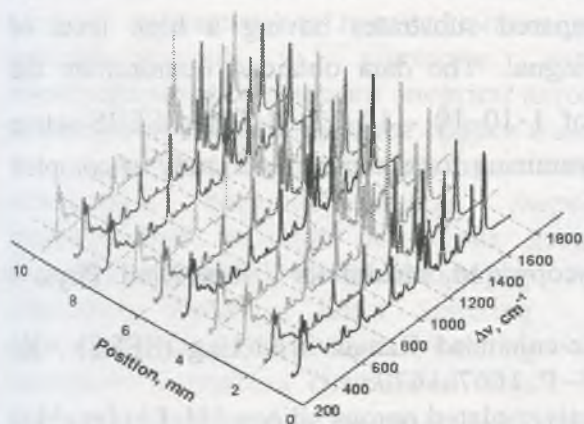


Figure 2- A set of SERS spectra of ZnTMPy4 deposited from a $1\ \mu\text{M}$ solution, obtained at various places of the Ag-PSi substrate. $\lambda_{\text{ex}} = 457.9\text{ nm}$.

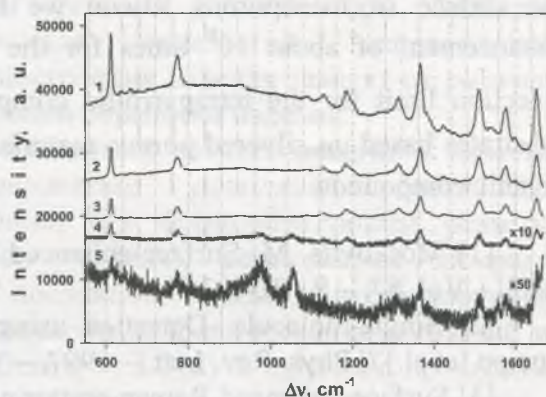


Figure 3- SERS spectra of rhodamine 6G ($1 \cdot 10^{-6}$ (1), $1 \cdot 10^{-7}$ (2), $1 \cdot 10^{-8}$ (3), $1 \cdot 10^{-9}$ (4), and $1 \cdot 10^{-10}$ M (5)), $\lambda_{\text{ex}} = 514.5\text{ nm}$

Very important characteristics of SERS-active substrates for the potential practical application are stability and reproducibility. Fig. 2 shows SERS spectra of ZnTMPy4 obtained by a surface scanning of a $15 \times 15\text{ mm}$ Ag-PSi plate by steps of 1 mm . We used a cylindrical lens to focus the excitation radiation over the sample surface (the size of the laser spot at the sample was $0.5 \times 6\text{ mm}$). No significant variation in SERS intensity over the sample surface can readily be observed. For this data set, a standard deviation of integrated spectral area is evaluated as less than 10%. To study the substrate stability we fabricated three Ag-PSi plates under similar conditions. One of them was impregnated by ZnTMPy4 immediately after preparation, and the other two let aged during 1 month in the air. Comparison of SERS spectra normalized to the standard band intensity shows that the Ag-PSi stored for 1 month does not yield any significant

change (less than 20%) in its effectiveness. According to the scientific standards proposed by Natan [4] our P*Si*-based SERS substrate appears to be homogeneous and stable materials.

We carried out a series of experiments on the estimation of detection limit, defined as the minimum concentration of the analyte compound which can be detected using the given method. SERS spectra were measured for a row of Ag-P*Si* samples on which rhodamine 6G molecules were adsorbed over a 2 h period from solutions with different concentrations. The solutions were prepared by successive dilution, starting from the initial, most concentrated solution (1×10^{-6} M). As can be seen from Fig. 3 good quality SERS signals for rhodamine 6G can be observed with concentrations as low as 100 pM. Upon a further decrease of the concentration the signal / noise ratio was practically too low to be exploitable. Upon further decrease in the concentration, we observed only the background signal. A detection limit of such an order of magnitude was also achieved when using CuT*Mpy*P4 as the analyte. We should point out that such sensitivity of Ag-P*Si* substrates we prepared according to the optimized procedure is rather high. For comparison, the detection limit of rhodamine 6G on P*Si* substrates silver-coated by thermal decomposition of silver [5] is two orders of magnitude worse.

Also we studied by SERS the chlorin e_6 , which is known as photosensitizer for the cancer treatment. During the treatment of oncological diseases by PDT, accumulation of the photosensitizer not only occurs in tumors, but also in other organs and tissues. Therefore, it is important to be able to monitor the photosensitizer concentration after a PDT treatment in order to minimize the damage to the organism. The bands of Ce_6 can be identified in SERS spectra for samples soaked in analyte solutions at concentrations down to 1 pM. Thus, SERS-active substrates Ag-P*Si* are promising for the detection of trace amounts of Ce_6 , that makes them possible to be used for the control of the photosensitizer concentration.

As a result of optimization of the procedure for the formation of nanostructured silver films on the surface of mesoporous silicon we have prepared substrates having a high level of enhancement of about 10^8 times for the SERS signal. The data obtained demonstrate the detection limit for the tetrapyrrolic compounds of $1 \cdot 10^{-10}$ – 10^{-12} M. Thus SERS-active substrates based on silvered porous materials are promising for detection and study of complex organic compounds.

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ЛИСТОВОЙ РАСКРОЙ И СБОРКА ПОТОКАМИ ЭНЕРГИИ ПО ТЕХНОЛОГИИ ПОСЛОЙНОГО СИНТЕЗА ИЗДЕЛИЙ

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Изготовление масштабных макетов, легко разрушаемых прототипов и заготовок деталей машин из композиционных материалов с рабочими поверхностями сложного