Wettability of carbon and silicon carbide ceramics induced by their surface alloying with Zr and Cu elements using high intensity pulsed plasma beams

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Abstract. Joining of metals with ceramics is very difficult, because properties of these materials are very different. One of the methods of improving mechanical strength of the obtained joints is the introduction of an additional interlayer to the joining area. This paper presents the Zr and Cu-rich layers in C and SiC substrates obtained using the high intensity pulsed plasma beams method. The results of Zr plasma modifications were beneficial and similar to the results obtained in previous works with Ti. The measured contact angles were below 90°. The results with Cu plasma were unfavourable with contact angles close to 180°. Apart from the sessile-drop test and to extend the range of analysis, the investigated samples were examined by stereoscopic optical microscopy (OM), scanning electron microscopy (SEM), energy-dispersive X-ray spectroscopy (EDXS), grazing angle X-ray diffraction (GXRD), and Rutherford back scattering (RBS) measurements.

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Introduction

Ceramic materials, such as: oxides, nitrides, borides, carbides and carbon are widely applied in modern constructions and devices [10, 17]. Their advantages are: low density, high mechanical strength and corrosion resistance at high temperature as well as a favourable high performance/weight relationship. However, application of these materials in joints or in composites with metals is very difficult, because usually ceramics is non-wettable by liquid metals. There are various approaches aimed at mitigation of this problem [14, 19, 22, 24].

Interaction of a liquid metal with a ceramic substrate plays a key role in the creation of a proper joint or composite [18]. This is difficult in the case of Cu-carbon system because the solubility of carbon in copper does not exceed 0.02 at.% [5] and additionally, since the "d" shell of copper is fully occupied, Cu is not a carbide forming element [12, 23]. An increase in the strength of the interfacial interaction in such a system is possible in two ways, i.e. by an increase in the solubility of one phase in another or by inducing a reaction between the components as a result of the introduction of a new chemical element to the system (e.g. Fe forming Fe_3C carbide) [4, 13].

In the case of silicon carbide, the maximum solubility of Si in Cu amounts to 11.25 at.% at a temperature of 842°C. Copper with silicon creates stable silicides, which may be incorporated into the interlayers between the bonded materials [15]. This is promoted by a comparatively easy decomposition of SiC [7, 16].

The introduction of additional chemical elements to the Cu-SiC system, such as titanium, iron, molybdenum, chromium, tungsten and nickel may promote the creation of an interlayer and thus increase the durability of the created joints. In the case of carbide forming elements (Ti, Fe, Mo, Cr, W), a reactive layer is formed, while in the case of Ni, the layer is of a diffusive type [8, 11].

In the present attempt, we tried to modify C and SiC substrates before their joining with copper using high intensity pulsed plasma beams (HIPPB). In our previous works [2, 3] we reported the results obtained for titanium incorporated into carbon and silicon carbide to induce the wettability. The process was conducted in three versions:
1. "50 mono" – i.e. 50 Ti pulses of energy density equal to 7 J/cm^2,
2. "50 multi" – i.e. 5, 10, 15 and 20 Ti pulses of energy density of 7, 5, 3 and 1 J/cm^2, respectively,
3. "200 multi" – i.e. 20, 40, 60 and 80 Ti pulses of energy density of 7, 5, 3 and 1 J/cm^2, respectively.

The best results were obtained for "200 multi" type process while the worst – for "50 mono" type process. In the present work, we show the results of using HIPPB technique for the incorporation of Zr and Cu into the near surface layer of carbon and silicon carbide substrates. The aim of these investigations was to check the effectiveness of HIPPB in inducing wetting of these material surfaces by liquid copper in two cited above extreme cases, i.e. "200 multi" and "50 mono". Additionally, the paper includes selected previous results for Ti for a simple comparison.

Calculations

The experiments were preceded by numerical computation of thermal evolution in substrates and thermodynamical considerations.

Thermal evolution

The numerical computation of thermal evolution in substrates subjected to pulse irradiation were applied in order to estimate the dependence of surface temperature, melting depth and liquid phase duration on the duration and energy density of the pulse.

The program applied in the investigations on modelling the thermal evolution of a surface layer of material exposed to the action of intense plasma pulses was based on a finite element method, used at the National Centre for Nuclear Research in Otwock (Poland), and referred to as ETLIT (energy transport in laser irradiated targets), developed by W. Szyszko [20, 21]. Actually, the code applies to a solid material absorbing a pulse of energy momentarily transforming into the thermal one at the surface and as such may be easily adopted to plasma pulse conditions.

Figure 1 summarizes the results of modelling and presents a maximum temperature at the surface of the modified material, a melting depth and duration of the molten phase as functions of pulse length and a pulse energy density for C and SiC substrates. The plots of relations were obtained by extracting the specific values generated by successive runs of the program of time evolution. The arrangement of particular relationships and the scales of plots were chosen to make their direct comparison possible.

By comparing the plots, it is easy to notice considerable differences in the physical properties of C and SiC. The maximum temperature on the surface of SiC is approximately 50% higher than the maximum temperature on the surface of graphite. This results from a lower thermal conductivity of carbide. The greater surface plateau of the melting point values of carbon in comparison to SiC is due to an approximately seven-fold difference between the heat of fusion value for carbon and silicon carbide.

In order to induce melting of carbon, one should apply pulses with duration in the region of tenth of μs and an energy density value above 4 J/cm^2, while for melting SiC, it is sufficient to apply pulses several times longer and with lower energy density.

For the same values of pulse length and energy, the depth of melting is several times greater for silicon carbide. The same applies to the duration of the molten phase and results in better homogenizing of the molten material.

A non-monotonous course of the plots, particularly visible for calculations of the duration of the molten phase, may be due to the rounding up of the calculations introduced by the program [1].

Thermodynamical considerations

Thermodynamical considerations relate to possible reactions between the components of the incorporated dopant elements, the substrates and the working gas. The following processes can be expected:
– dissociation of SiC with silicon precipitation at higher temperature,
– formation of Ti and Zr carbides.

The design and operation of a rod plasma injector makes it possible to synthesize the alloys and chemical compounds in non-stationary conditions using three sources of components, i.e. the working gas, the material of electrodes and the material of modified substrates.

Figure 2 shows the results of thermodynamic predictions of possible reactions for a substrate materials (C and SiC), the material of electrodes (Ti, Zr and Cu) and the working gas (N$_2$). The results are presented in the form of Ellingham graphs. The tabulated data available in Ref. [9] were used in calculations. The calculations were carried out using spreadsheet type computer programs.

The values of Gibbs free energy are plotted as functions of the reaction temperature. In all cases, the values of ΔG change with temperature rise, the slope of changes being individual for each reaction. Reactions with positive Gibbs free energy should not occur in the system.
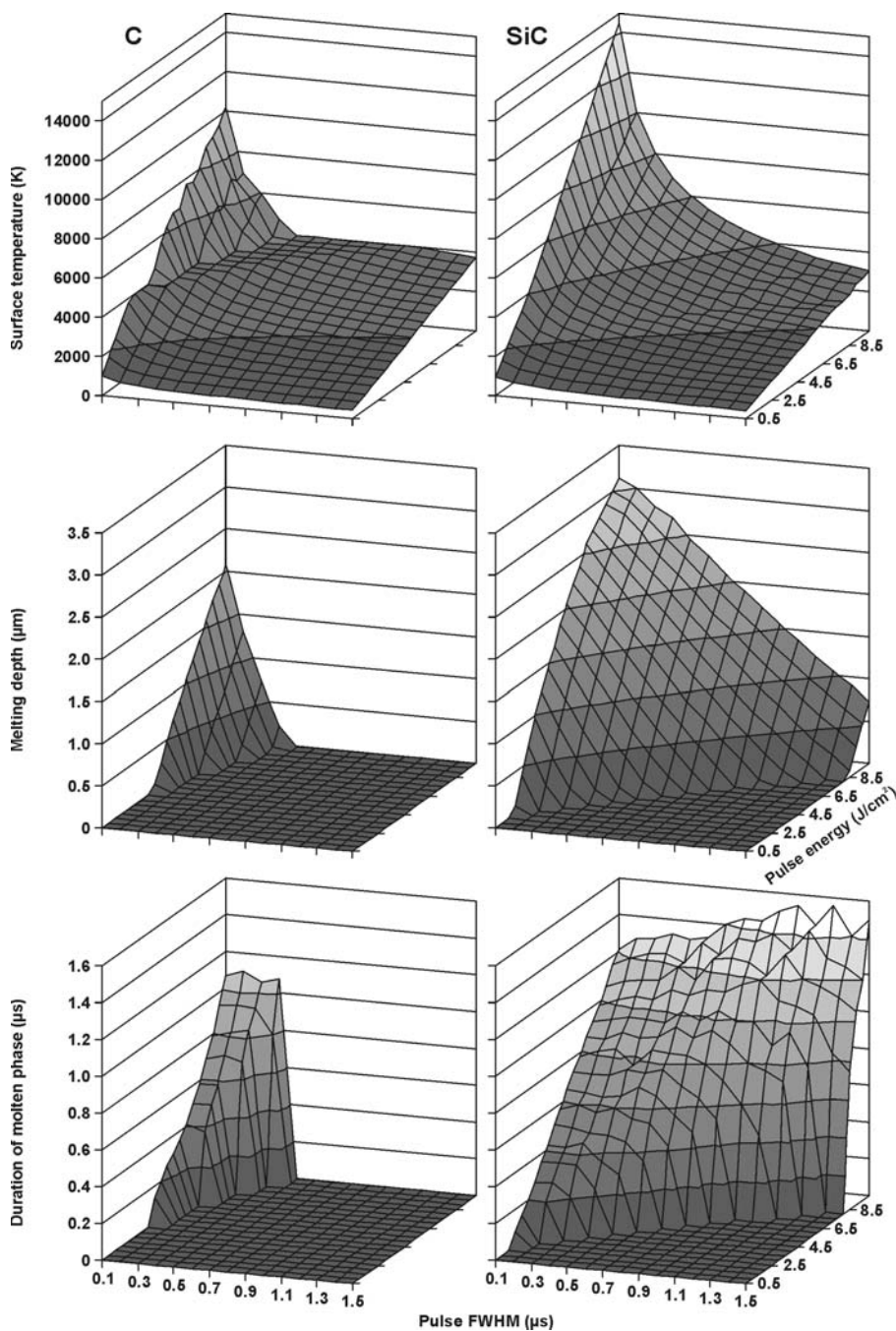
Fig. 1. The results of modelling of surface temperature, melting depth and melt duration depending on pulse FWHM and pulse energy.

As may be noticed, the majority of chemical reactions may occur during substrate modifications with zirconium and titanium. In these cases there exists a strong probability of creating carbides and nitrides of these metals.

Experimental

Samples

The samples were cut of the commercial pyrolytic graphite (Cp), glassy carbon (Cg), carbon-carbon composite (C/C) and silicon carbide (SiC) in the form of coupons of 10×5 mm^2 in size. The thickness of samples was 0.2,

1.0, 1.6 and 2.0 mm for Cp, Cg, C/C and SiC, respectively. Before processing, the samples were washed in high purity acetone under ultrasonic agitation.

Processing

The samples were irradiated with pulsed plasma beams generated in a rod plasma injector (RPI) type of accelerator (IBIS), described in detail in Ref. [1]. The main parameters of plasma pulses generated by IBIS are as follows: power density – 1...10 MW/cm^2, pulse duration – about 1 μs, energy density – 1...7 J/cm^2, number of pulses – 50 or 200, mode of RPI – deposition by pulse erosion (DPE).
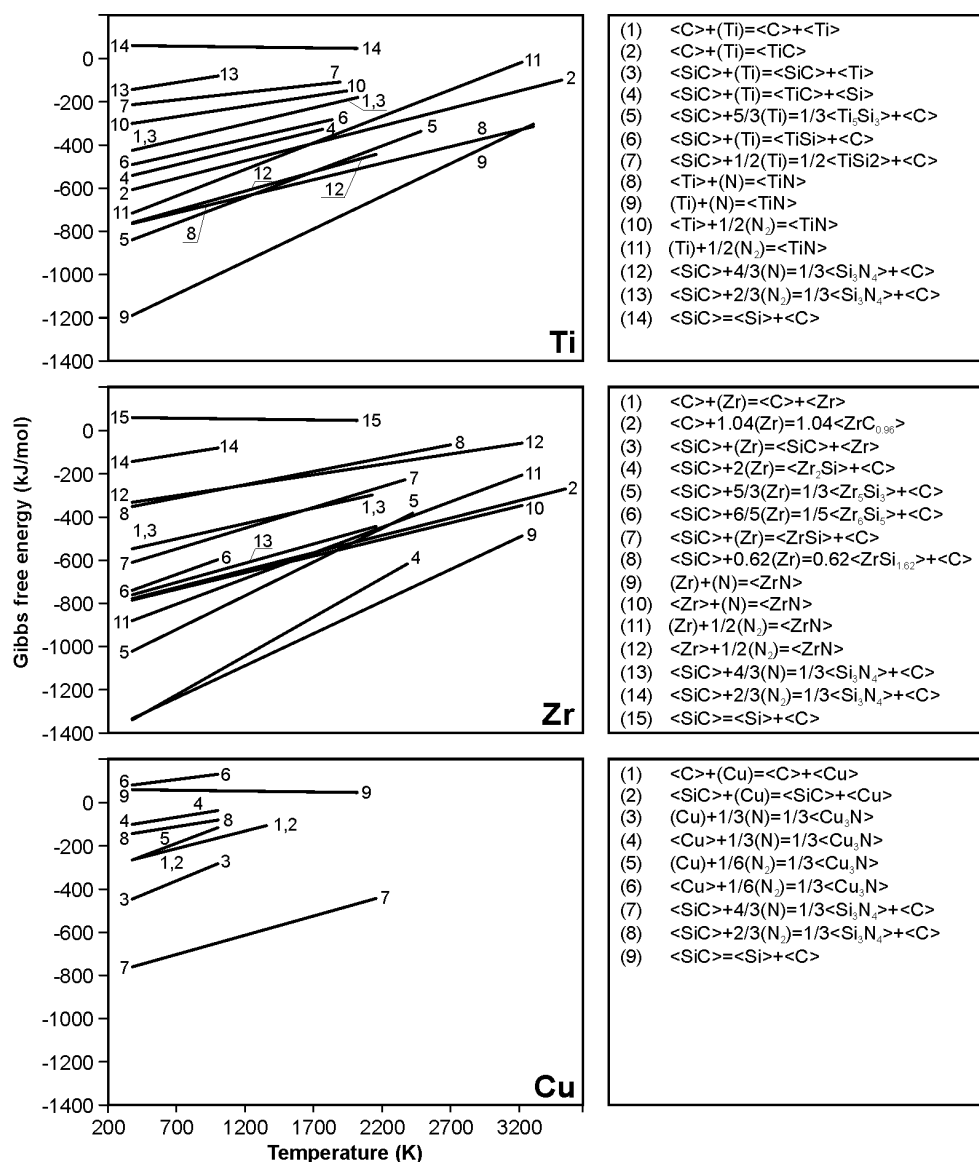
Fig. 2. The results of thermodynamic calculations of possible reactions for substrate material (C and SiC), electrode material (Ti, Zr and Cu) and operating gas (N_2).

The process was conducted in two versions:
1. "50 mono", i.e. 50 Zr or Cu pulses of energy density equal to 7 J/cm^2,
2. "200 multi", i.e. 20, 40, 60 and 80 Zr or Cu pulses of energy density 7, 5, 3 and 1 J/cm^2, respectively.

Characterization

The prepared samples were investigated by sessile--drop tests, stereoscopic optical microscopy (OM) and scanning electron microscopy (SEM) observations, energy-dispersive X-ray spectroscopy (EDXS), grazing angle X-ray diffraction (GXRD) and Rutherford back scattering (RBS) measurements. The significance of the first four analytical methods is fairly obvious and is discussed below. The RBS measurements, performed using H^+ or He^+ beam of energy of few MeV, supply reliable and absolute information on the chemical composition and element distribution of the surface layer up to a thickness of about 1 μm. Therefore, they are an indispensable tool in examining all types of modified surface layers.

To check the wettability the sessile-drop examination was performed on all samples. After the test, the samples were examined and photographed and the wetting angle was determined using a home-made computer-supported sessile drop tester.

The quality of the surface of oxidized samples was examined with the use of a stereoscopic optical microscope. Scanning electron microscopy was used to detect changes of the processed and oxidized sample morphology with magnification ranging from 100 to 5000 times. Energy dispersive X-ray spectrometry was used for quantitative surface elemental analysis.

The RBS spectra were recorded using 1.7 MeV He^+ ion beam at a normal incidence to the sample. The back scattered particles were detected at an angle of 170° using a Si(Li) detector with a 15 keV energy resolution. The RBS spectra were analyzed using SIMNRA computer code [6].

Prior to further tests, virgin, pretreated and oxidized samples were examined by the XRD method using Cu-K_α radiation and grazing angle geometry (1°).

Results and discussion

Figure 3 shows the results of sessile-drop tests for virgin, "50 mono" and "200 multi" series along with SEM observations. It is obvious that such a preparation of carbon ceramic surfaces in the "50 mono" case does not lead to improvement of their wettability with liquid copper except for the case of SiC modified by Zr. In the "200 multi" case Zr fulfils the requirement of good wettability in all cases. This situation is very similar to the case of Ti modifications. Unfortunately copper practically fails in all cases.

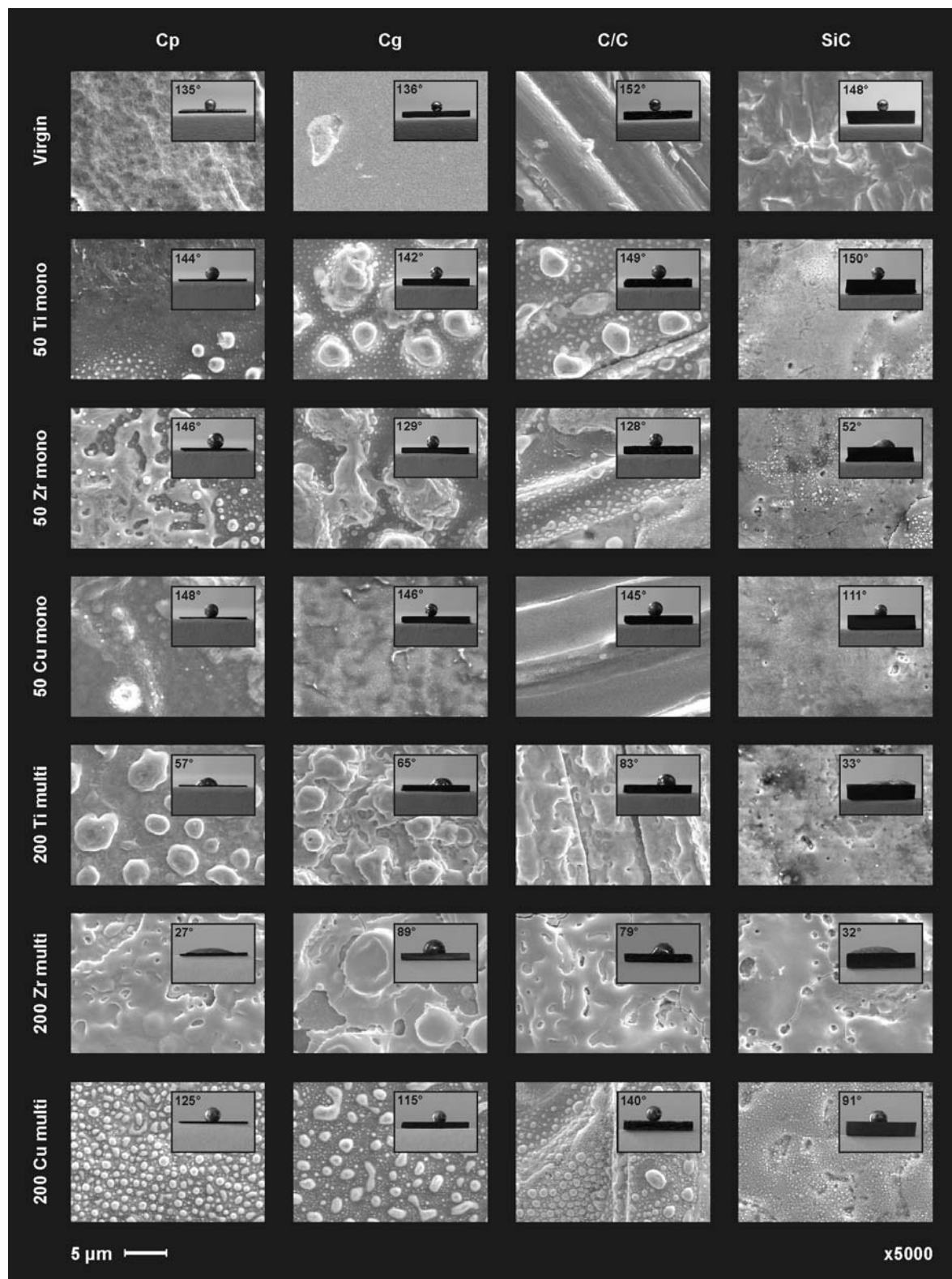Figure 4 presents the results of concentration analysis performed by the EDX method. It is worth-

Fig. 3. The results of SEM microscopic observations of Cp, Cg, C/C and SiC substrates for different kinds of modification process with superimposed results of wetting tests.
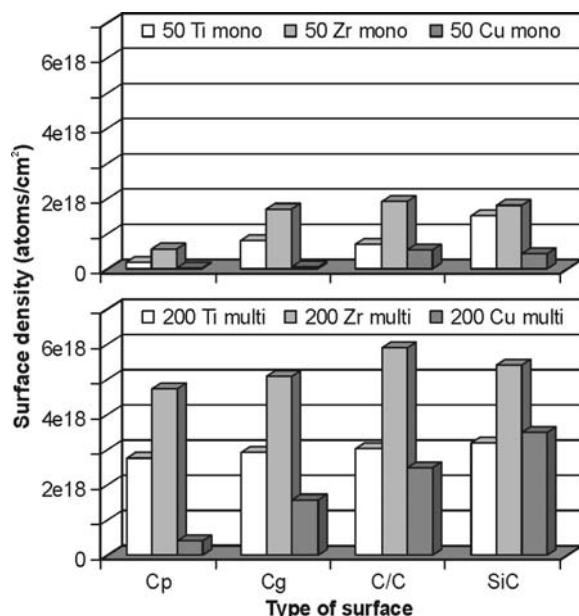
Fig. 4. The results of concentration analysis performed by EDXS method.

while noting that for the same processing conditions the deposition is most effective for SiC substrate. The largest concentration of doped elements are obtained for "200 Zr multi" case. This concentration is about 2 times higher than for Ti in the same process. Only in one case, for "200 Cu multi" and for SiC substrate, copper concentration is higher than Ti concentration.

Figure 5 shows the RBS spectra of SiC along with the depth profiles of elements deduced from SIMNRA code analysis. The results of HIPPB of Zr and Cu are compared with previous results of Ti. In the case of a "50 mono" series, the surface concentrations are at the level of 20 at.%, whereas for "200 multi" they are among 60 to 90 at.%. In all cases the concentration of elements gradually decreases with depth without a sharp step just beneath the surface.

An inspection of Fig. 5 suggests that a successful wetting requires several factors to be satisfied at the same time. These are:
a) appropriate alloyed element concentration at the surface (200 multi vs. 50 mono),
b) appropriate "grading" of the layer (at least through the first 500 nm of the layer),
c) appropriate chemistry between the alloy component and the substrate (Ti and Zr vs. Cu).

Figure 6 presents the GXRD patterns for the virgin and "50 mono" modified surfaces of SiC. The precipitation of Zr carbides is observed, like in the case of Ti modifications. In all cases the line of precipitated silicon is also present which was predicted by thermodynamical calculations. The first peak on the left-hand side of the spectrum, marked as "?" does not originate from SiC.
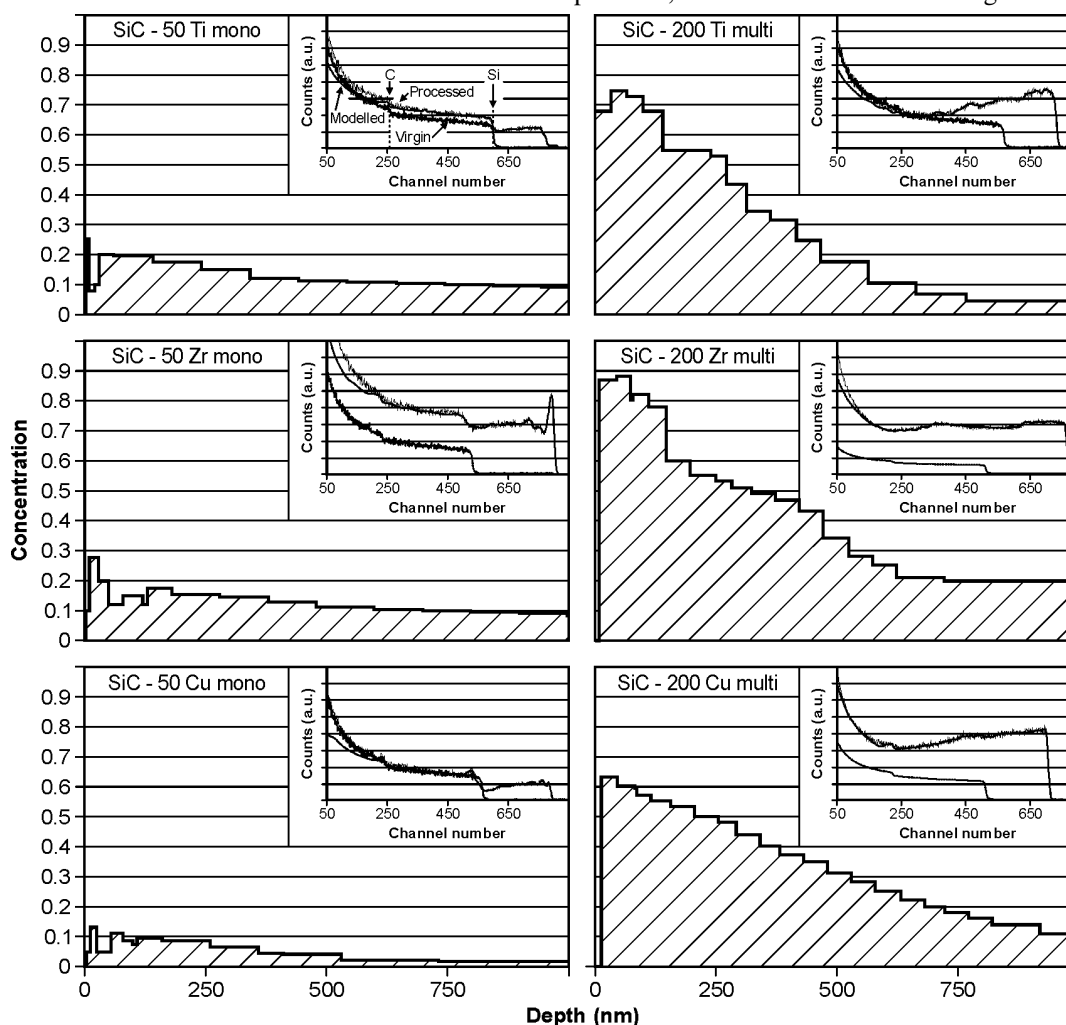

Fig. 5. RBS spectra along with depth profiles of elements deduced from SIMNRA code analysis.
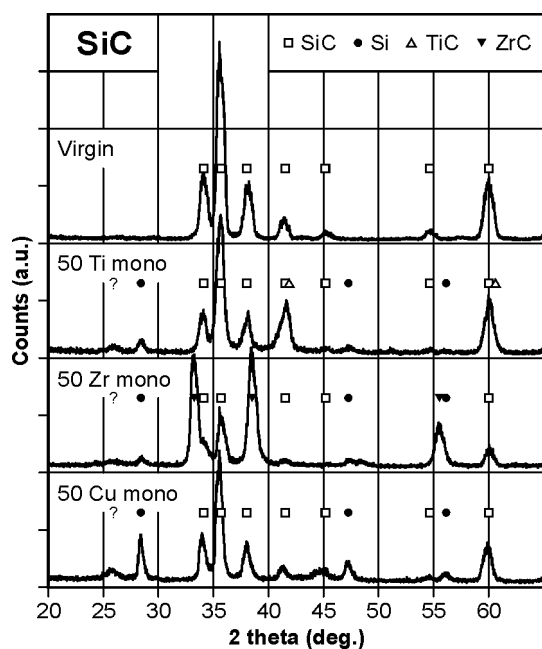
Fig. 6. GXRD patterns for the virgin and the "50 mono" modified surfaces of SiC.

Its width indicates a small size of the precipitates of a new phase. Identification of this phase is difficult in view of the presence of only one line in the pattern. The results obtained for the "200 multi" series and for the carbon substrate were very similar (of course without SiC dissociation).

Conclusions

The conclusions which can be drawn from the results obtained can be summarized as follows:
1. The version "50 mono" does not results in an improvement of wettability.
2. The version "200 multi" leads to beneficial results for Zr, but not for Cu.
3. Among all substrates, the best results were obtained for SiC due to its best cohesion and the best ability to absorb the modifying elements.
4. It is concluded that a good wettability in SiC requires an appropriate alloy element, present at the surface with a close to 100% concentration, and developing an extended graded profile.

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