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AFM and AUGER investigations of as-deposited and heat treated copper coatings on glassy carbon surfaces with titanium intermediate layers

E. Neubauer[a,b,*], C. Eisenmenger-Sittner[a], H. Bangert[a], G. Korb[b]

[a] *Institute of Solid State Physics, Vienna University of Technology, A-1040 Wien, Austria*
[b] *Department of Materials and Production Engineering, ARC Seibersdorf Research, A-2444 Seibersdorf, Austria*

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Abstract

Copper carbon composites are a prospective material for application as heat sink material in thermal management applications. One of the main drawbacks of this material combination is the lack of adhesion between copper and carbon. In order to improve the interfacial properties in this system a basic investigation on carbon substrates was done, where the influence of an adhesion promoting intermediate layer was investigated. Besides the study of the influence of a Ti intermediate layer on the growth mode and surface topography of a copper coating, the diffusion of Ti after a heat treatment was analysed by using Auger electron spectroscopy.

Keywords: Interface; PVD coating; AES; AFM; Surface topography

1. Introduction

As known from various references the wetting of carbon by copper is very poor [1–6]. This results in a poor mechanical and thermal interface in composite materials, where a copper matrix is reinforced with carbon fibres. An advanced method for the preparation of such composites is the coating of fibres with matrix material followed by a consolidation process [7,8]. For the deposition of the copper matrix in general electrochemical coating methods are used. Nevertheless, vacuum technologies would have advantages because of the possibility to tailor the interface between the coating and the matrix.

One of the big advantages vacuum technologies offer is the possibility to apply plasma pre-treatment before the coating with the matrix material or to pre-coat the substrate with a thin adhesion promoting intermediate layer. In addition, such methods allow to modify the microstructure of coatings by a variation of the deposition parameters. In this research study we investigate the influence of Ti intermediate layers on the adhesion of a copper coating on carbon. The investigations include the characterization of the surface topography and roughness of the Ti-interlayer and the Cu coating as well as the

*Corresponding author. Tel.: +43-50-550-3345; fax: +43-50-550-3366.
E-mail address: erich.neubauer@arcs.ac.at (E. Neubauer).

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chemical analysis of the surface of the copper coating before and after a heat treatment. Titanium was chosen in this research study as a candidate material because it was already investigated in previous studies for its ability to improve the wetting behaviour of liquid copper on carbon substrates [1–5].

2. Experimental

By using a model system (a plane carbon substrate, instead of a carbon fibre as a substrate) PVD coating experiments were performed in order to investigate mechanisms which allow to tailor the interface and therefore to improve the properties of the material combination.

To study the microstructure of copper coatings on carbon, a special type of carbon material was used. SIGRADUR G is a so-called glassy carbon with an amorphous structure and a very smooth surface, which is characterized by a high purity and physical and chemical isotropy. This material is prepared at 2.200°C [9].

In order to get an information about the surface morphology of this type of material chemically pre-cleaned substrates were used. The area roughness value of the substrate material (area roughness of a $1.5 \times 1.5\,\mu m^2$ area) was determined by atomic force microscope (AFM, Topometrix Explorer). The used roughness parameter was R_a which is the arithmetic mean of the deviation of the height from the profile mean value. This value was found to be in the range 0.8–1 nm.

The films were prepared on cleaned glassy carbon substrates [10] by sputter deposition from two inclined targets [11]. The deposition was done at a pressure of 0.4 Pa using Ar as sputter gas. After the deposition of the intermediate titanium layer the substrate holder was rotated to the position of the copper target and a copper layer with a thickness of 800 nm was deposited. Sputter rates for Ti- and Cu-layers were 0.5 and 1 nm/s, respectively.

At the beginning of the investigations coated samples with different Ti intermediate layer thickness were prepared. The surface topography and roughness of these samples were investigated using an AFM.

In order to simulate the hot pressing process which is part of the manufacturing of the composite material, the deposition of the copper coating was followed by a temperature treatment at 800°C under vacuum (10^{-5} mbar) for 1 h. At such elevated temperatures diffusion between the layer systems and the substrate can take place and might have an influence on adhesion of the copper coating. Due to this step several changes in surface topography (e.g. by re-crystallization) were observed.

2.1. Microstructural investigations

2.1.1. Ti coatings on glassy carbon as-deposited

The untreated Ti coatings on the carbon substrate generally show weak adhesion. The Ti coating delaminates from the surface if the thickness exceeds 200 nm. The roughness (R_a value) determined by line scans of the Ti coatings is in the range between 1 and 1.5 nm. The surface morphology of thin (<25 nm) coatings does not differ from that of the substrate material. For larger coating thickness the grain size is in the order of approx. 50 nm (see Fig. 1a and b).

2.1.2. Ti coatings on glassy carbon after heat treatment

In the case of heat treated Ti samples the surface roughness increases up to a coating thickness of 15 nm and then stays constant at a level of 10–12 nm (Fig. 2). The surface morphology changes from a very fine grained structure (approx. 60 nm in diameter) to a grain size of about 300 nm (diameter) if the layer thickness increases from 0.75 to 100 nm (see Fig. 3a–c).

2.1.3. Cu–Ti-layer system on glassy carbon as-deposited

Topographical investigations of the copper layer on a Ti intermediate layer show a very smooth surface with a roughness of approx. 10 nm. There is no influence of the Ti-layer thickness on surface topography observable.

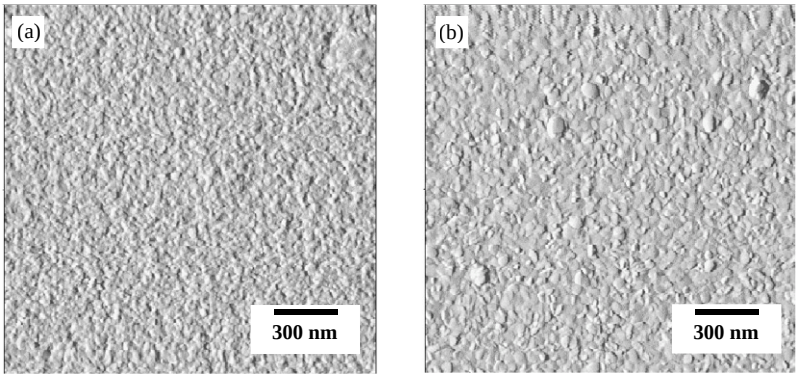

Fig. 1. (a) Surface topography of a Ti coating, 5 nm thick. (b) Surface topography of a Ti coating, 100 nm thick.

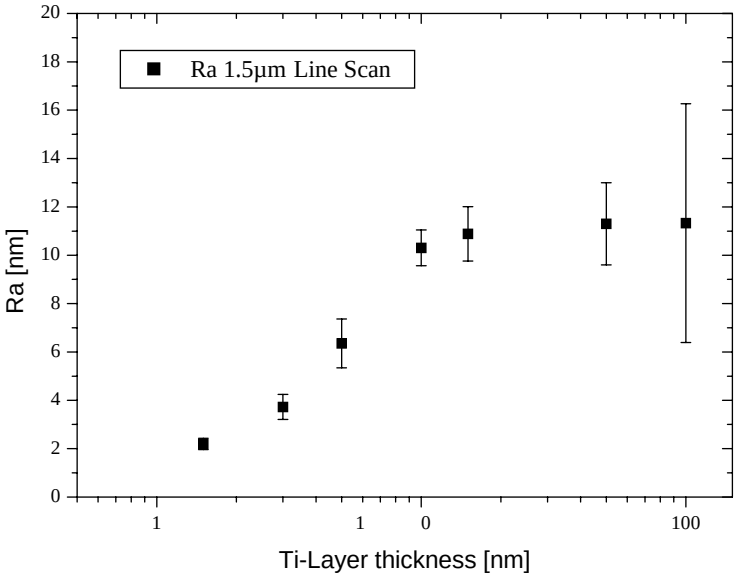

Fig. 2. Influence of Ti-layer thickness on surface roughness after heat treatment at 800°C.

2.1.4. Cu–Ti-layer system on glassy carbon after heat treatment

The heat treated Cu–Ti samples show different behaviour as a function of the Ti coating thickness. While in the case of very thin Ti intermediate layers (<5 nm) the fine grained structure is maintained, copper coatings on thicker Ti-layers show several grooves with a width in the range between 2 and 5 µm and a depth of approx. 300–500 nm (Fig. 4a–c). For the very thick Ti intermediate layers (>50 nm) we observe that there are no grooves any more. Instead there are sharp ridges at the grain boundaries with heights of 200–300 nm. The surface overall roughness of the Cu–Ti coatings is in the range between 60 and 120 nm.

2.2. Auger analysis

In order to obtain information on the diffusion of atoms from the film/substrate interface to the surface of the Cu coating, Auger analysis was used as a qualitative tool [12]. Two samples, one before and one after the heat treatment were investigated. The layer system consists of a 800 nm thick copper coating which was deposited on an intermediate layer of 5 nm of Ti.

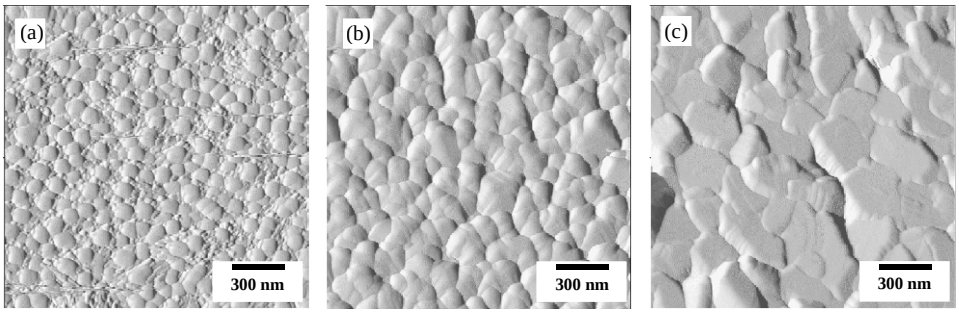

Fig. 3. (a) Surface topography of Ti after heat treatment with coating thickness of 5 nm. (b) Surface topography of Ti after heat treatment with coating thickness of 15 nm. (c) Surface topography of Ti after heat treatment with coating thickness of 100 nm.

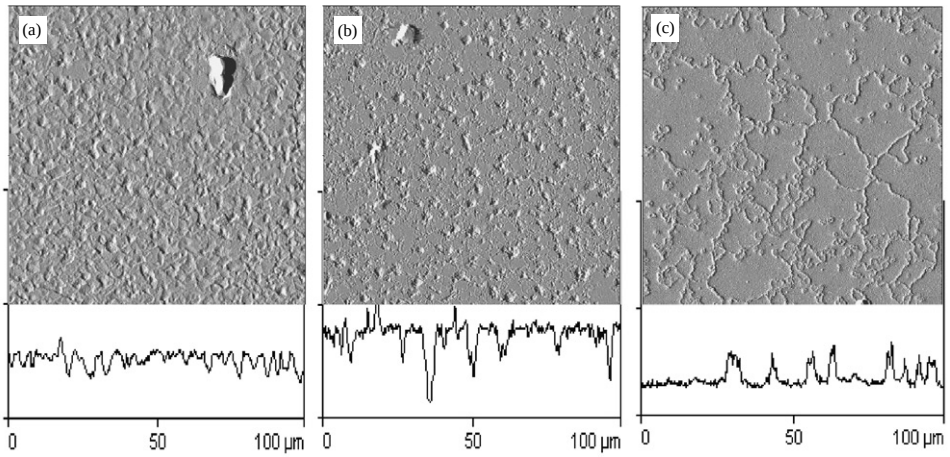

Fig. 4. (a) Topography of Cu–Ti-layers after heat treatment with a Ti coating thickness of 5 nm. (b) Topography of Cu–Ti-layers after heat treatment with a Ti coating thickness of 15 nm. (c) Topography of Cu–Ti-layers after heat treatment with a Ti coating thickness of 100 nm.

For AES analysis the samples were transferred into the UHV chamber with a background pressure of 2×10^{-10} mbar. During sputtering of the sample surface, the pressure increased up to approx. 3×10^{-8} mbar. The ion current varied between 80 and 120 nA on an area of approx. $5 \times 3\,\mu m^2$. In the case of the layer system before heat treatment, no Ti signal was observed on the surface. There were some contaminants (mainly C) at the surface but after some minutes of sputtering time they were totally removed and the outer copper coating was found to be pure.

On the heat treated sample we also detected C at the surface but as sputtering time increased the peak height lowered and after 14 min there was no C detectable (see Fig. 5). At the near-surface region (after 2 min) we detected Ti and O and a strong Cu signal. Ti and O exhibited a smaller peak after $\sim$30 min and completely vanished after $\sim$50 min. Therefore, we can conclude that Ti diffuses during the heat treatment from the interfacial area to the surface where it is oxidized. Although we cannot detect Ti in the bulk of the film, we cannot exclude its presence due to the detection limit of AES.

Beside the investigation of the surface of the copper layer we have also analysed the interface between the Cu–Ti-layer and the carbon substrate. Therefore, the coating was removed and the carbon surface was analysed. No Ti was found on the substrate material, which means the interfacial crack takes place between the Ti coating

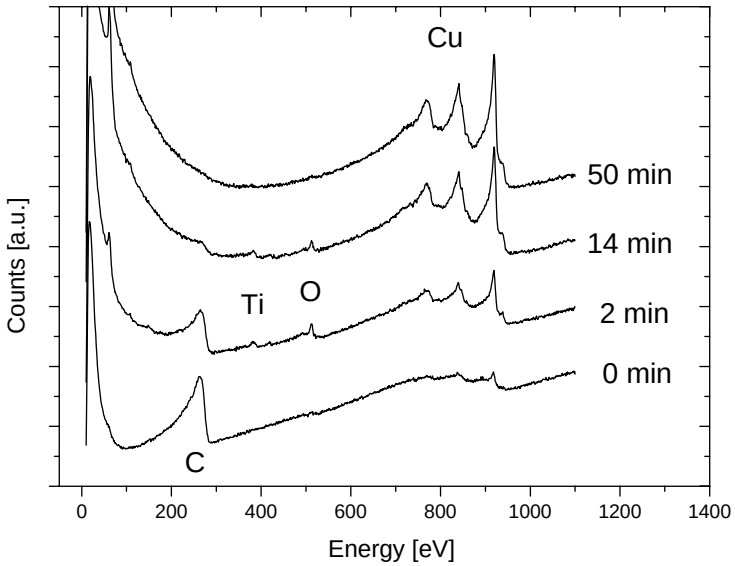

Fig. 5. Auger profile of a Cu–Ti-layer system (Ti-layer thickness 5 nm) on glassy carbon after heat treatment (800°C, in vacuum for 1 h) after various sputtering times.

and the carbon substrate. The back side of the removed coating was chemically analysed by energy dispersive X-ray analysis and Ti was detected which confirms that there is still Ti at the interfacial area. These results are comparable to the behaviour of Cr in the Cu–Cr–C system after heat treatment which was investigated by using SIMS methods [13].

3. Conclusion

In order to improve the interface adhesion in Cu–C metal matrix composites, Ti as a candidate material was tested in this work. Thin intermediate layers (<25 nm) improve the adhesion, although we observe fracture between Ti and the C substrate. Thick intermediate layers (100 nm) lead to a delamination of the copper coating because of the stresses which build up in the coating. The investigations performed in this work clearly show that Ti intermediate layers of different thicknesses influence the surface topography of copper coatings and the roughness of the coatings after heat treatments. From the surface topography as well as from the Auger analysis it was concluded that a diffusion of Ti from the interface to the top of the copper coating takes place after a heat treatment. Such a diffusion of Ti through copper, even if thin intermediate layers are used, might cause the degradation of thermal and electrical properties of a real composite material by dispersion of Ti atoms in the copper matrix. To confirm this future work will concentrate on the preparation and testing of composite materials by using of copper coated carbon fibres with a Ti intermediate layer.

Acknowledgements

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