Effect of Ti and Zr additions on wettability and work of adhesion in Ag/C system

Danuta Wójcik-Grzybek[1], Krystyna Frydman[1], Natalia Sobczak[2], Rafał Nowak[2], Anna Piątkowska[1], Katarzyna Pietrzak[1]

Wettability in the silver/carbon system was examined by the sessile drop method under vacuum at the temperature of 1243 K. Vitreous carbon, diamond and graphite were used as solid substrates. After wettability tests, the solidified Ag/C and Ag-X/C (X - 1 wt.% Ti or Zr) couples were subjected to structural characterization by SEM and EDX analysis. Liquid pure silver does not wet these substrates and shows week adhesion, regardless of the type of the carbon material used. The introduction of 1 wt.% carbide forming additions Ti or Zr into silver changes dramatically the interaction in the Ag/C system leading to the formation of continuous reaction product layers (TiC_x and ZrC_x, respectively) at the drop/substrate interface. These interfacial layers are responsible for good wetting and high work of adhesion between AgTi1 and AgZr1 alloys and all types of carbon materials examined in this study.

Key words: wettability, adhesion, contact angle, Ag/C system

Wpływ Ti i Zr na zwilżalność i pracę adhezji w układzie Ag/C

Przedstawiono wyniki badań zwilżalności w układzie srebro/węgiel wykonanych w atmosferze próżni, w temperaturze 1243 K. Pomiary kąta zwilżania wykonano metodą leżącej kropli na podłożach z węgla szklistego, diamentu i grafitu. Po testach zwilżalności wytworzone pary materiałów Ag/C i Ag-X/C (X - 1% wag. Ti lub Zr) poddano analizie strukturalnej metodami SEM i EDX. Ag/C jest układem niereaktywnym, w którym srebro nie zwilża węgla. Prezentowane badania wykazują, że dodatek 1% wag. Ti lub Zr do srebra powoduje obniżenie kątów zwilżania i wzrost wartości pracy adhezji w układzie Ag/C niezależnie od typu materiału węglowego. Jest to związane z powstawaniem na granicy kontaktu kropli z podłożem węglowym warstw przejściowych zawierających węgliki TiC_x lub ZrC_x.

Słowa kluczowe: zwilżalność, adhezja, kąt zwilżania, układ Ag/C

1. Introduction

In many fields of material engineering the studies on new, innovative technologies depend on our knowledge of the phenomena occurring at the interface. The knowledge of interfacial phenomena related to adhesion and spreading kinetics is necessary for the fabrication of metal-ceramic composites and layered structures as well as in joining dissimilar materials [1 - 4].

From a practical point of view, in many technological applications it is particularly important to obtain a good adhesion between two solid phases. Such a good adhesion is commonly believed to be closely related to solid/liquid adhesion in the same system. In a design of a new technological process of material bonding it is absolutely crucial to determine adhesion energy in a liquid/solid system, even if bonding with a liquid phase is not predicted.

The Ag/C system belongs to the extensively investigated metal/ceramic systems because of its high importance for the synthesis of composite materials, e.g. Ag-C composites containing 2 - 5 wt.% C that are widely used as low-voltage electrical contacts. Due to their unique properties, such as excellent resistance to welding as well as low and stable contact resistance, these composites are applied as contacts in current limiters (often used in asymmetric pairs), brush contacts, etc. [5]. Moreover, silver matrix composites containing carbon fibers offer highest thermal and electrical conductivity combined with

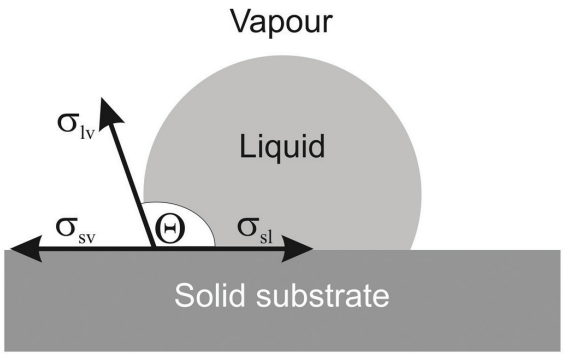


Fig. 1. Definition of the equilibrium contact angle θ: σ_{lv} – liquid/gas interfacial energy, σ_{sv} – solid/gas interfacial energy, σ_{sl} – solid/liquid interfacial energy.
Rys. 1. Równowagowy kąt zwilżania θ: σ_{lv} – energia powierzchniowa ciecz/gaz, σ_{sv} – energia powierzchniowa podłoże/gaz, σ_{sl} – energia powierzchniowa podłoże/ciecz.

[1] *Institute of Electronic Materials Technology*, 133 Wólczyńska Str., 01-919 Warsaw, Poland, e-mail: Danuta.Grzybek@itme.edu.pl
[2] *Center of High-Temperature Studies of Metals and Alloys, Foundry Research Institute,* 73 Zakopiańska Str., 30-418 Cracow, Poland

low coefficient of thermal expansion. Therefore, they are promising candidates to be used in thermal management applications [6].

Silver and carbon do not react with each other and are mutually insoluble. Liquid silver does not wet carbon forming high contact angle θ >> 90° (Fig. 1) [7 - 9] and thus low work of adhesion (W_A) calculated from Young-Dupré equation [1 - 4]:

$$W_A = \sigma_{lv} (1 + \cos\theta), \quad (1)$$

where:
σ_{lv} – liquid/gas interfacial energy,
θ – contact angle.

In non-reactive systems, such as Ag/C, van der Waals forces dominate at the liquid/solid interface. The value of these forces is directly proportional to the density of atoms on the contact surface and inversely proportional to their squared distance [6 - 9]. As a result, adhesion and wettability depend on atomic density on the contact surface and are related to crystallographic orientation of the substrate, which was confirmed experimentally and presented in Refs. [8 - 9]. Nogi et al. [9] studied the influence of substrate crystallographic orientation on wettability in non-reactive systems, like metal/C (diamond). In the case of diamond, the atomic density on the crystallographic planes decreases in the following order: (111)>(110)>(100). Among the metals that were the subject of studies (Bi, Pb, Sn, Ag, Au, Cu), the lowest contact angle and the highest work of adhesion were observed for the closest packed crystallographic plane of diamond, i.e. (111). The only exception was Ag, in the case of which the contact angle for the same plane was the highest of all planes, i.e. 147°, while the values for (110) and (100) planes were 103° and 135°, respectively. These measurements were carried out in hydrogen atmosphere at temperature 1273 K.

One way of improving the wettability and obtaining a good bonding in non-reactive metal/ceramic couples is to use an additive of an active element, exhibiting chemical affinity to the substrate. As a result, an non-reactive system can transform into a system, where interfacial chemical interactions are present. Ti, Zr, Cr and Si are often used as such active additives [10 - 13].

It should be highlighted that wettability in a metal/ceramic system is affected not only by its thermodynamic properties (mutual solubility, reactivity), but also by such external factors as: temperature and atmosphere of the process, impurities, surface roughness, crystallographic orientation, etc. [13 - 15].

2. Experimental procedure

The examination of wettability in the silver/carbon system was carried out using vitreous carbon (C_v), diamond (C_d) and graphite (C_g) as the substrates. The effect of active additives of Ti and Zr on the wetting behavior in the Ag/C system was studied. The wettability tests were performed for pure silver and silver alloys containing 1 wt.% of the active element, i.e. AgTi1 and AgZr1 alloys, respectively.

The contact angle was measured by the sessile drop method in which the images of a drop placed on a flat, smooth and leveled substrate were recorded vs time. A classic procedure of contact heating (CH) of a couple of examined materials was applied in the wettability tests. The measurements were carried out at the Center for High-Temperature Studies of the Foundry Research Institute in Cracow using high temperature facility described in details in Ref. [16].

Silver of high purity (99.999%) and the active additives of titanium (purity 99.99%) and zirconium (purity 99.95%) were used in the experiments. During the wettability tests silver alloys with the active additives were produced *in situ* directly in a vacuum chamber. Prior to placing the weighted metal portions into the vacuum chamber, their surfaces were cleaned ultrasonically in acetone and then in ethanol. A weighted portion of the reactive additive was slightly pressed into the silver sample and the whole assembly was placed onto the carbon substrate so that the additive remained at the top and did not have a contact with the substrate. During the heating, the process of melting the sample started from the top and ended at the time when a liquid drop was formed (Fig. 2).

Amorphous vitreous carbon, polycrystalline graphite and diamond obtained by CVD method were applied as substra-

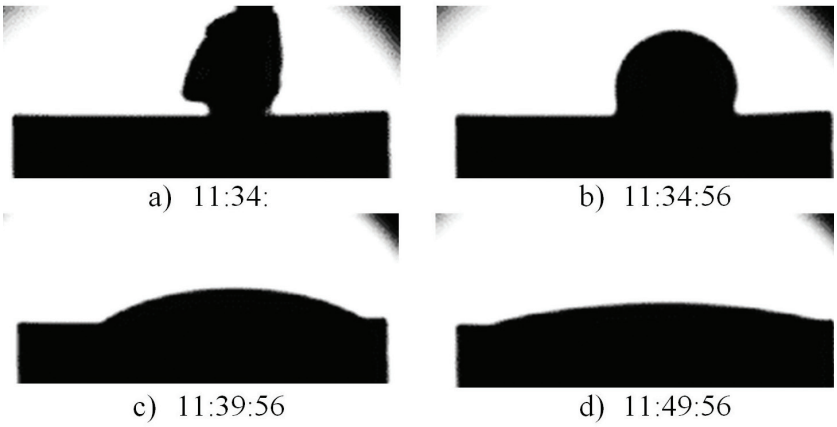


Fig. 2. Process of AgZr1 alloy drop formation: a) sample of weighted metals, b) a drop just after reaching the melting point, c) the drop after 5 minutes of heating, d) the drop after 15 minutes of heating.
Rys. 2. Proces formowania się kropli stopu AgZr1: a) naważka metali, b) kropla po osiągnięciu temperatury topnienia, c) kropla po 5 minutach wygrzewania, d) kropla po 15 minutach wygrzewania.

tes. Surface roughness (R_a), measured by an ALHA-STEP profilograph, was as follows: 6.5 nm for vitreous carbon, 4.5 nm for diamond and 30 nm for graphite (measuring length, L_c = 400 μm).

The wettability tests were carried out in ultra-high vacuum (5 × 10^{-3} Pa), at a temperature of 1243 K. After reaching this temperature, the samples were heated for 15 minutes and then cooled to RT. Both heating and cooling were performed at a rate of ~ 11 K/min. During the experiment, the drops were imaged by high-resolution digital camera at a rate of one frame per second. In order to calculate a contact angle θ, the collected images were analyzed using ASTRAView software, developed by CNR-Instituto per l'Energetica e le Interfasi – U.T. di Genowa (Italy) [17 - 18]. After the wettability tests, the solidified couples Ag/C, AgTi1/C and AgZr1/C were subjected to structural characterization by scanning electron microscopy (SEM) and energy dispersive X-ray (EDX) analysis on the Zeiss Auriga SEM microscope. The cross-sections perpendicular to the surface of the substrate were investigated.

3. Results and discussion

The above experiments show clearly that the additive of 1 wt.% Ti or Zr improves wettability and increases adhesion in the Ag/C system, regardless of the kind of the substrate applied. The spreading kinetics of various forms of carbon by liquid silver and its alloys as well as the values of contact angles are presented in Figs. 3 and 4.

Just after melting the Ag sample on the vitreous carbon substrate, the contact angle θ was equal to 100°, and next after about 8 minutes it slightly increased to 106°, remaining practically constant during further heating of the Ag/C_v couple (Fig. 3a). A similar effect was observed in the Ag/C_d system with θ = 106° (Fig. 3b), contrary to the Ag/C_g system in which θ was as high as 145° (Fig. 3c). These results represent experimental evidence of the effects of the allotropic form of carbon and substrate roughness on the value of contact angle in the Ag/C system.

In all the studied cases, the additive of 1 wt.% Ti or Zr to Ag caused a marked decrease in the contact angle. In the AgTi/C_v system, the value of θ_0, formed immediately after the material melting, was 114° and then it was reduced to 87° in 146 s, followed by a systematic decrease up to the final value of θ_f = 26° during further heating.

In the AgZr1/C_v system, the value of θ_0 was 171° and within 43 s the contact angle was reduced abruptly to 72° and finally reached θ_f = 13°.

It should be noted that due to the applied procedure of the *in situ* alloy preparation directly during the wettability tests, the initial values of contact angles (θ_0) represent the apparent values because at that time the drop of the alloy is still being formed and its shape often not ideal, especially from the point of view of the required symmetry.

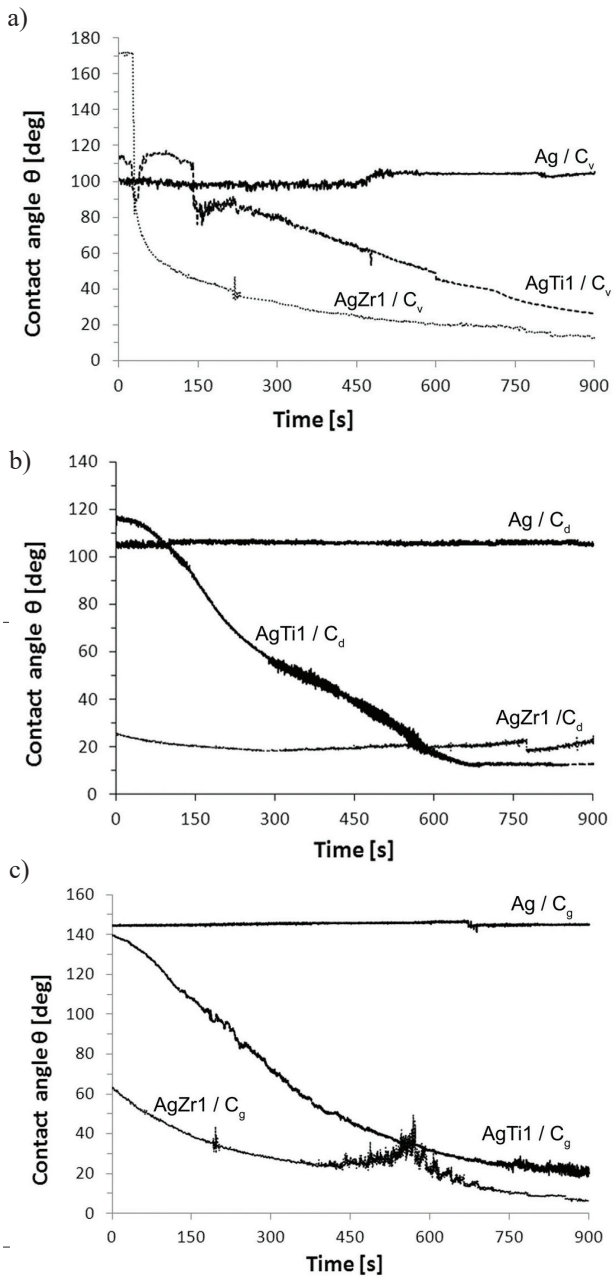


Fig. 3. Wettability kinetics in the Ag/C system (temperature: 1243 K, vacuum: 10^{-3} Pa) with different substrates: a) vitreous carbon – C_v, b) diamond – C_d, c) graphite – C_g.
Rys. 3. Kinetyka zwilżania w układzie Ag/C (temperatura: 1243 K, próżnia: 10^{-3} Pa), podłoże: a) węgiel szklisty - C_v, b) diament - C_d, c) grafit - C_g.

On the basis of the analysis of the curves representing the spreading kinetics it can be concluded that in the case of the non-reactive Ag/C system for all three studied substrates, the silver drop reached its equilibrium shape practically immediately after melting. Due to the additive of titanium or zirconium, the shape of the drop was varying during the whole period of the heating process. These observations are in line with the literature data,

which show that in non-reactive systems, the time of the drop spreading may be shorter than 1 s, in contrast to the reactive systems, where the spreading time can range from several seconds up to several hours [19 - 21], which is related to the formation of transition regions at the drop/substrate interface. Such layers can be formed due to a mutual solubility of components or they can result from the formation of the new phases as the products of a chemical reaction. After the crystallization of the liquid is terminated, the appearence of a solid/solid joint, can be observed, its nature depending on the kind of a system and the related type of liquid-solid interactions.

After wettability tests, metallographic specimens were subjected to EDX linear scan profiles of AgTi1/C and AgZr1/C interfaces (Figs. 5 - 8). In all these cases, the analysis of chemical composition revealed the formation of continuous reaction product layers. In the case of diamond

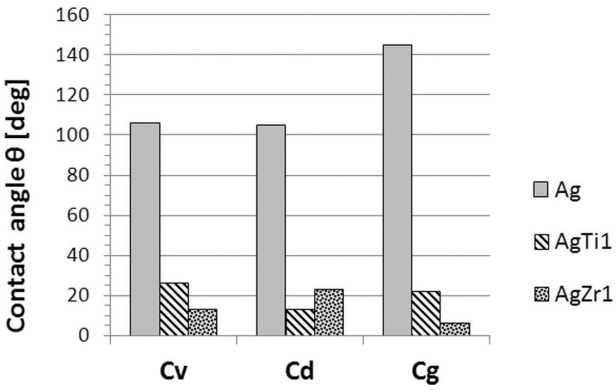
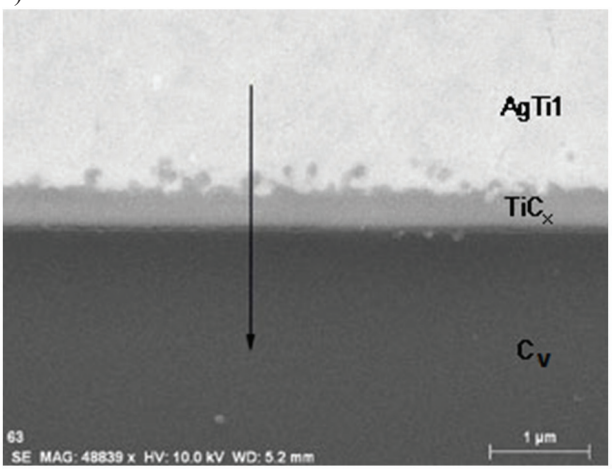


Fig. 4. Contact angels of pure Ag and its alloys AgTi1 and AgZr1 on investigated substrates (C_v – vitreous carbon, C_d – diamond, C_g – graphite).
Rys. 4. Kąty zwilżania na badanych podłożach (C_v – węgiel szklisty, C_d – diament, C_g – grafit).

a)



b)

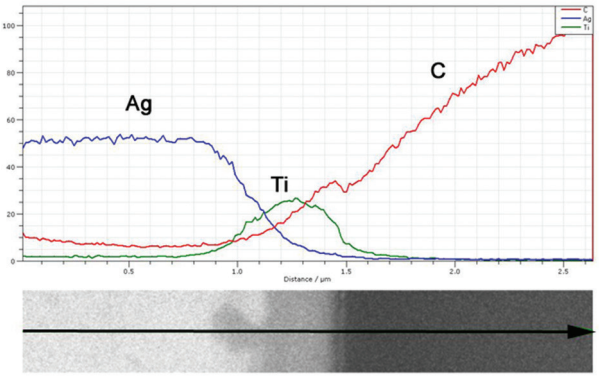
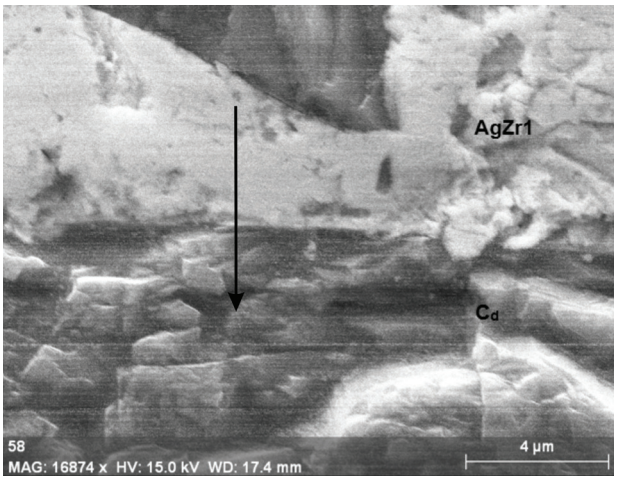


Fig. 5. SEM image of the AgTi1/C_v interface (a) and compositional line analysis (b).
Rys. 5. Granica międzyfazowa AgTi1/C_v (a) i rozkład liniowy zawartości pierwiastków (b).

a)



b)

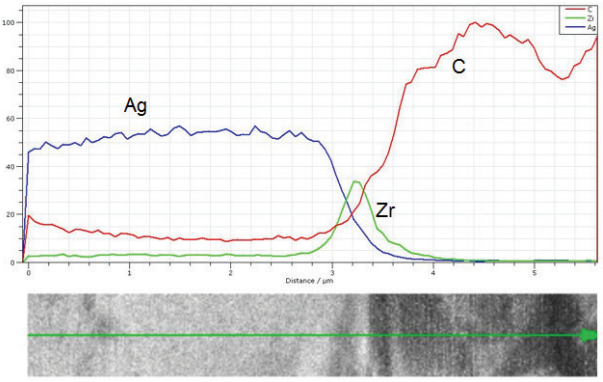


Fig. 6. SEM image of the AgZr1/C_d interface (a) and compositional line analysis (b).
Rys. 6. Struktura granicy międzyfazowej AgZr1/C_d (a) i rozkład liniowy zawartości pierwiastków (b).

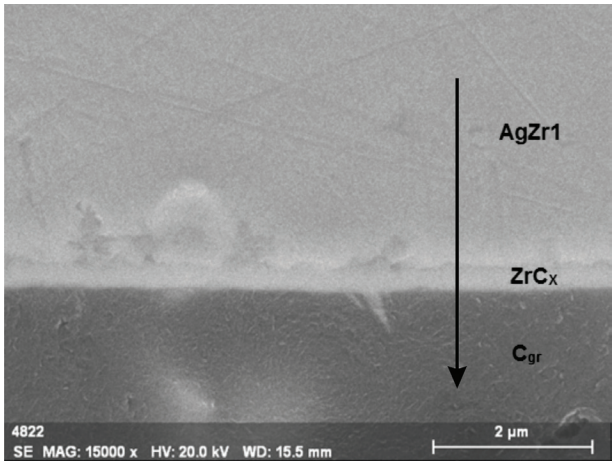
substrates, the attempts to perform correct micro-sections failed. Nevertheless, it was observed that both titanium and zirconium additives have good interfacial bonding accompanied with an increased concentration of Ti or Zr and carbon within the interface region (Fig. 6), which suggests the existence of TiC_x or ZrC_x carbide.

In the case of interaction between AgZr1 alloy with graphite substrate, the wetting, SEM and EDS analyses of the interfaces allowed us to identify not only the formation of intermediate regions of about 300 nm thickness (Figs. 7 - 8), but also the appearance of infiltration of the liquid alloy into the substrate open pores. Fig. 8 presents a high Zr concentration within the interface region and the impregnated zones.

SEM observations of the interfaces in AgTi1/C and AgZr1/C couples revealed the presence of transition regions of a thickness of about 300 nm (Fig. 5 - 8). According to the results of the linear scan profiles performed by EDX technique, AgTi1/C and AgZr1/C systems are characterized by the increased concentrations of carbon and reactive elements (Ti or Zr), which suggests the formation of carbides (Fig. 5 - 7). Following literature data [22 - 23] it may be concluded that the forming transition regions can be composed of non-stoichiometric carbides (MeC_x type). In Refs. [22 - 23], Frage et al. investigated wettability in the Ag/TiC and Ag/TiC_x systems in vacuum (10^{-3} Pa) at a temperature of 1323 K and demonstrated that liquid silver does not wet stoichiometric TiC forming the contact angle θ of 120° after 15 minutes. However, adding Ti additive to Ag significantly reduced the value of θ up to 30 - 35º for 4 at.% Ti and 60° for 2.25 at.% Ti. Similarly, θ value decreases with a decrease in C content in TiC_x, namely from 120° for x = 1 to about 30º for x = 0.55.

Tab. 1 summarizes the values of the work of adhesion (W_A) calculated from the Young-Dupre equation (1). The values of the surface tension of pure Ag and its alloys AgTi1 and AgZr1 the same as those for pure silver (916 mJ/m^2 [24 - 27]) were used in the calculations. It was justified by the results of Novakovic et al. [28] who calculated the surface tension of pure Ag and Ag-Ti and Ag-Zr alloys by the QCA (Quasi Chemical Approximation) method. The negligible difference between these values at a temperature of 1473 K that is 230 K above the testing temperature of this study was also evidenced (Fig. 9).

a)



b)

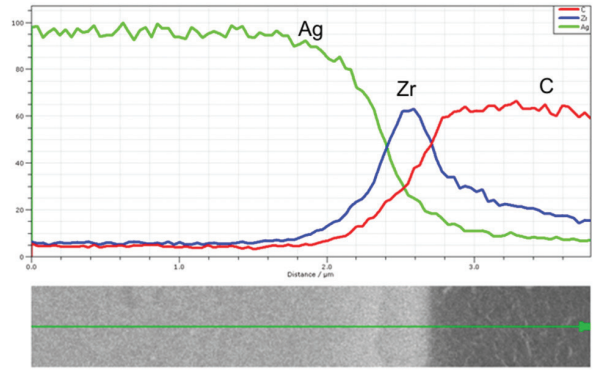
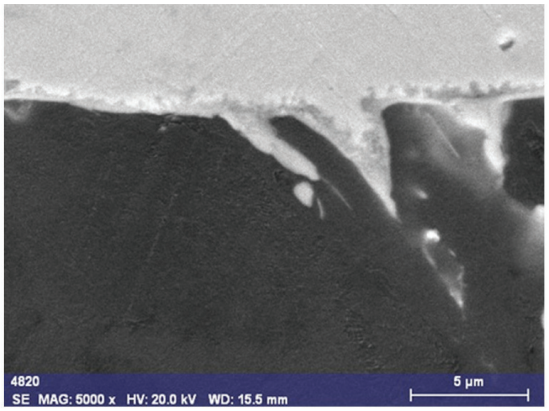
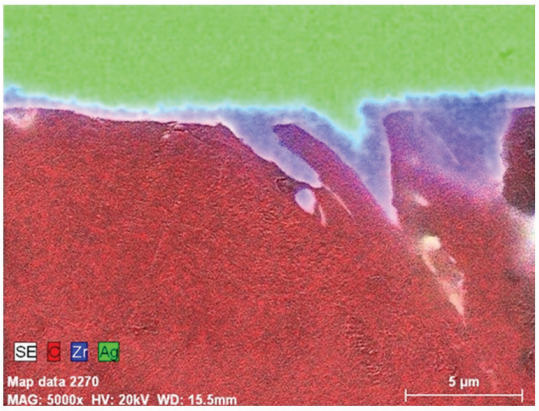


Fig. 7. SEM image of the AgZr1/C_g interface (a) and compositional line analysis (b).
Rys. 7. Granica międzyfazowa AgZr1/C_g (a) i rozkład liniowy zawartości pierwiastków (b).



a)



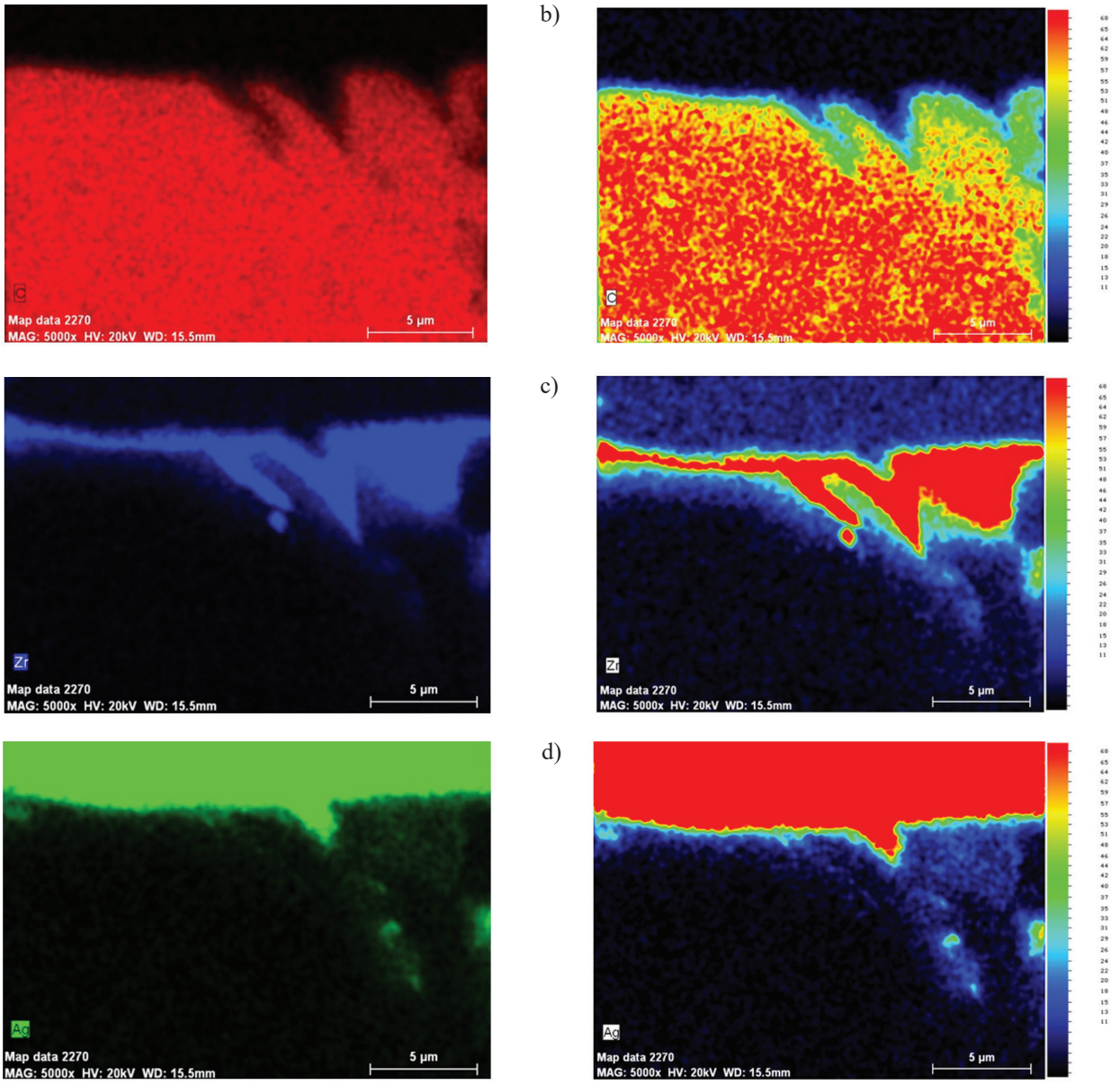


Fig. 8. SEM image of AgZr1/C_g interface and surface distribution of C, Zr, Ag (a); surface distribution of elements (left hand side) and the corresponding intensity x-ray map (right hand side) of: C (b), Zr (c), Ag (d).
Rys. 8. Granica międzyfazowa AgZr1/C_g i powierzchniowy zbiorczy rozkład pierwiastków C, Zr, Ag (a); powierzchniowy rozkład poszczególnych pierwiastków (strona lewa) i odpowiadająca im mapa intensywności sygnału rentgenowskiego (strona prawa): C (b), Zr (c), Ag (d).

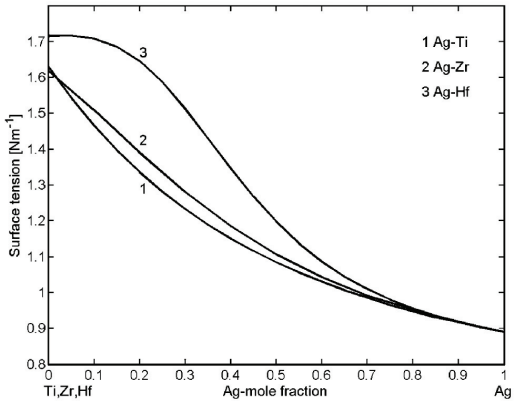


Fig. 9. Surface tension isotherms of liquid AgTi, AgZr and AgHf alloys calculated by the QCA method at $T = 1473$ K [28].
Rys. 9. Napięcia powierzchniowe ciekłych stopów AgTi, AgZr, AgHf, obliczone metodą QCA, dla temperatury 1473 K [28].

Tab. 1. The effects of alloying additions and the type of carbon material on the values of contact angle and work of adhesion in Ag/C system.
Tab. 1. Wpływ dodatków stopowych oraz rodzaju materiału węglowego na wielkość kątów zwilżania i pracę adhezji w układzie Ag/C.

Substrate	Metal	Surface energy σ_{LV} [mJ/m²]	Contact angle Θ [°]	Work of adhesion W_A [mJ/m²]
Vitreous carbon	Ag	916	106	664
	AgTi1	916	26	1739
	AgZr1	916	13	1809
Diamond	Ag	916	105	679
	AgTi1	916	12	1812
	AgZr1	916	24	1753
Graphite	Ag	916	145	166
	AgTi1	916	21	1771
	AgZr1	916	6	1827

However, a decrease in the contact angle due to the addition of active elements in this study allowed to increase almost three times the work of adhesion in the Ag-alloy/C system, in comparison with that for pure silver.

4. Conclusions

Liquid pure silver does not wet examined carbon substrates and shows week adhesion of the type of carbon material used. In contrast, the type of carbon material affects the value of the contact angle which at the temperature near the melting point of pure silver (1243 K) is for glassy carbon - about 106°, for the diamond - 105°, for graphite - 145°.

Introduction of a small amount (1 wt.%) of carbide forming Ti or Zr additions into silver results in a significant improvement of wettability. Depending on the type of carbon material, a reduction in the contact angle to 12 - 26° and up to 6 - 24° was found in the case of the AgTi1 and AgZr1 alloys respectively. Reactively formed interfacial layers (TiC_x and ZrC_x) are responsible for a significant improvement of wettability in the examined systems. This effect is accompanied with almost threefold increase in the work of adhesion, in comparison with that for pure silver.

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