Spontaneous inversion of the submicron ceramic layer deposited on steel and the copper droplet positioned on their top (case of ceramic poorly wetted by liquid Cu)

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Received: 3 August 2021

Accepted: 23 December 2021

Published online:

7 January 2022

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ABSTRACT

In this paper, 50 ... 680 nm thick AlN-Al₂O₃ coatings are deposited by magnetron sputtering on the surface of a steel substrate and a piece of copper is melted on top of the ceramic. Upon heating the ceramic layer is cracked, and the phase inversion of the two top phases from steel/ceramic/copper configuration to the steel/copper/ceramic configuration takes place within 30 s of liquid time of copper. This phase inversion process is accompanied by a Gibbs energy change of about -1.78 J/m^2 , due to good wettability of solid deoxidized steel by liquid copper in contrary to poor wettability of the ceramic by the copper. When copper is melted on AlN-Al₂O₃ coating with its thicknesses smaller than a critical value of about $170 \pm 60 \text{ nm}$, liquid copper droplets hanging down into the cracks within the ceramic reach the solid steel surface at the bottom of the cracks, thus the flow of Cu down along the cracks is enabled. However, when copper is melted on AlN-Al₂O₃ with its thickness larger than the critical value of $170 \pm 60 \text{ nm}$, Cu first forms a non-wetting droplet on top of the ceramics, and only after a certain incubation time it starts flowing down the cracks. This incubation time was found to depend linearly on the thickness of the ceramic, as cracks are filled from the bottom upwards by liquid copper via the evaporation–condensation mechanism. By the end of the process, the steel/copper/ceramic configuration is further stabilized by gravity.

Handling Editor: N. Ravishankar.

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GRAPHICAL ABSTRACT

Introduction

The importance of smart engineering of the internal interfaces of joining materials (i.e. soldering and brazing materials) at the nanoscale has been recognized in the recent decades [1]. Consequently, research was started to examine the applicability of nanotechnology for the scientific progression of joining technologies in which the initial structures of the components to be joined are preserved thanks to lower temperatures of joining, being due to melting point depression of nano-structured joints [2–4].

One possible application of nanotechnology is the deposition of nano-multilayers (NML's) on the surface of the parts/tools to be joined. These coatings consist of a few nm thick layers, in which the metal layers serve as the braze material being separated from each other by inert barriers of higher melting point, such as different ceramics (oxides, nitrides) or

refractory metals (e.g. W). These multilayers can be considered as special hybrid joining materials, consisting of periodically alternating bilayers. Cu is one of the most widely used brazing materials with a rather high melting point of 1085 °C. Consequently, the reported studies primarily focus on Cu-based NML's such as: Cu/AlN [5, 6], Cu/W [7–9], or Ag–Cu based [10, 11] nano-multilayers.

Interesting phenomena have been reported as a side product of development of brazing technologies, in which metal-1 melted on the surface of oxide-coated solid metal-2 spread along the oxide/metal-2 interface. For example, Cohen et al. [12] found that a liquid gold-nickel (82Au–18Ni) alloy undermined the surface oxide layer of a chromium-containing stainless steel. This phenomenon consisted of two successive sub-processes: the breakthrough of the liquid alloy through the oxide layer, followed by spread of the same along the oxide/steel interface. A similar phenomenon was reported by Gale et al. [13] for Ni–

Si–B braze, which was found to undermine the oxide layer on the Ni–Al substrate. The process initiated only after a certain incubation time, which was found to be the time required for the chemical reaction between the molten braze and the surface oxide layer. Xu et al. [14, 15] observed the undermining phenomenon for Zn–Al braze melt along the interface of the oxide layer / Al/Al₂O_{3p} composite. To initialize the undermining process in this case, first it was necessary to break the oxide layer of the liquid braze by pinpricking it. They found that the spreading of the melt was linear with time, which is mainly characteristic of reactive wetting. However no indication of chemical reaction was observed in their case, thus the observed phenomenon was explained by another mechanism, the presence of a thin precursor film ahead of the macroscopically observable spreading front that provided lubrication to the propagation of the liquid metal.

It can be stated that although the results of the above observations are similar, the underlying mechanism is different depending on the characteristics of the investigated system and the experimental conditions. In our previous study [16], the micro- and nanostructure of the magnetron sputtered Cu/AlN–Al₂O₃ NMLs were investigated and their thermal behavior was characterized in details. The current study focuses on the wetting behavior of the Cu/AlN–Al₂O₃/CrMo4 steel system, explaining and modeling the observed phenomena.

Experimental conditions and materials

Deposition of AlN–Al₂O₃ ceramic layer

An AlN–Al₂O₃ ceramic layer was deposited on the surface of 42CrMo4 steel (1.7225) substrates by magnetron sputtering method, using high purity Al (99.999%) target. The initial pressure of the chamber was $< 5 \times 10^{-5}$ mbar. The size and the composition

of the steel samples are listed in Table 1. Prior to deposition the surface of the steel samples was prepared by the following steps: (i) grinding by SiC paper of grades 500 and 800, (ii) polishing by diamond paste with particle size of 0.5 μm , (iii) rinsing by distilled water and ethanol, (iv) 5 min ultrasonic cleaning in petroleum ether.

The deposition parameters of the ceramic layer are shown in Table 2. The coating was prepared by reactive sputtering method, introducing N₂ and O₂ gases into the chamber, and using radio frequency (RF) power source. The temperature of the sample stage during the deposition was between 30 and 40 °C. Four different ceramic thicknesses were obtained: 50, 170, 340 and 680 nm.

The elemental composition (EDS) of the surface of the coated CrMo4 steel samples are summarized in Table 3. Al, O and N refer to the composition of the ceramic layer, while the other elements are from the steel substrate. However, let us note that EDS is not particularly suitable for accurate quantitative analysis of O and N contents. The complex phase-structure of the AlN–Al₂O₃ coating obtained under identical conditions was discussed in details in our previous study [16].

Evaporation and wettability tests

The evaporation rate of liquid Cu was determined on the surface of two different Al₂O₃ plates: one with smaller particle size (sample 1), and one with larger particle size (sample 2). The dimensions of the Al₂O₃ plates are: $10.25 \times 10.25 \times 1.4$ mm and $10 \times 8 \times 1$ mm, respectively, for samples 1–2. Prior to the experiments the 5 ± 0.5 mg Cu pieces and the Al₂O₃ plates were ultrasonically cleaned in ethanol for 5 min. The evaporation tests were performed in a horizontal vacuum tube furnace (Sunplant Ltd, Hungary) equipped with a CCD camera, at a

Table 1 Size and EDS composition of the 42CrMo4 steel substrates used in our experiments

Size (mm)	Composition (wt%)				
	Si	Mo	Cr	Mn	Fe
$7 \times 5 \times 3.5$ ($l \times w \times h$)	0.2	0.2	0.9	0.7	98

Table 2 Deposition parameters of AlN–Al₂O₃ ceramic layer

Process parameters	Values
Power source	RF
Working pressure (bar)	7.6×10^{-6}
Ar flow (s-cm ³ /min)	90
N ₂ and O ₂ flow (s-cm ³ /min)	20
Power (W)	150
Deposition rate (nm/s)	$\cong 0.02$

Table 3 EDS composition of the 340 nm thick AlN-Al₂O₃ ceramic layer, deposited on the surface of 42CrMo4 steel

Element	N	O	Al	Si	Mo	Cr	Mn	Fe
Composition								
w%	2	10.2	9.4	0.1	0.2	0.7	0.5	76.9
at%	5.7	25.2	13.7	0.2	0.1	0.5	0.4	54.3

temperature of 1090 ± 5 °C, with a holding time of 15 min. The applied pressure during the test was in the range of 5.5×10^{-8} to 1.0×10^{-7} bar.

The wettability investigation was performed placing 5 ± 0.5 mg Cu on the surface of the 42CrMo4 steel samples, previously coated with AlN-Al₂O₃ ceramic layers. In addition, control experiments were also carried out on the surface of uncoated steel substrates under identical conditions. The wetting experiments were carried out in the same tube furnace at the same temperature of 1090 ± 5 °C during 2 min in the pressure range of 8.0×10^{-8} to 2.0×10^{-7} bar.

Characterisation techniques

The melting and evaporation process of Cu were recorded by a CCD camera of the tube furnace with a speed of 1 frame/s. The contact angle, surface area and volume of the liquid copper droplet were measured by the ImageJ software from the silhouette of the Cu droplet. The volume (V_{cap} , m³) and the liquid/gas surface area ($A_{l/g}$, m²) were calculated using the following equations, supposing that the geometry of the Cu droplet is a regular spherical cap:

$$V_{cap} = \frac{h\pi}{6} (3r^2 + h^2) \quad (1a)$$

$$A_{l/g} = \pi(r^2 + h^2) \quad (1b)$$

where r (m) is the base radius of the Cu droplet and h (m) is the maximum height of the Cu melt. The reported contact angle values are an average value of 5 measurements, while the reported surface area and volume values are an average of 3–3 measurements.

The surface morphology and microstructure of the wetted samples were investigated using Helios G4 PFIB CXe plasma focused ion beam scanning electron microscope (PFIB-SEM) equipped with EDAX Octane Elect EDS System with APEXTM Analysis Software.

Primary experimental results

Evaporation rate of liquid Cu droplets

The volume change of liquid Cu droplet, measured on the Al₂O₃ samples as function of time is shown in Fig. 1. For sample 1 the volume decreases from about 0.53 ± 0.01 mm³ to about 0.46 ± 0.01 mm³ during the time duration of 900 s, while the free surface area of the droplet decreases from 2.60 to 2.40 mm². Thus, the average rate of evaporation per unit free surface area is calculated as $(0.53 \pm 0.01 - 0.46 \pm 0.01) / (900 * (2.50 \pm 0.1)) = -(3.1 \pm 1.0) \cdot 10^{-5}$ mm/s = -31 ± 10 nm/s. For sample 2 the volume decreases from about 0.64 ± 0.01 mm³ to about 0.59 ± 0.01 mm³ during the time duration of 900 s, while the free surface area of the droplet decreases from 3.04 to 2.84 mm². Thus, the average rate of evaporation per unit free surface area is calculated as $(0.64 \pm 0.01 - 0.59 \pm 0.01) / (900 * (2.94 \pm 0.1)) = -(1.9 \pm 0.8) \cdot 10^{-5}$ mm/s = -19 ± 8 nm/s. These two values overlap. The merged interval of evaporation rates of liquid Cu per unit free surface area is found as -25 ± 15 nm/s.

Time dependence of contact angles and visible volumes of the Cu droplets

Four photos characterizing the experiment with uncoated steel are shown in Fig. 2. Immediately prior to melting (Fig. 2b) the edges of the initial Cu (Fig. 2a) became rounded, then at the moment of melting (Fig. 2c) liquid Cu spread very fast along the surface of the steel substrate, reaching a contact angle of $35 \pm 2^\circ$ (Table 4). With time the Cu droplet spread further along the surface, reaching a contact angle of $16 \pm 2^\circ$ after 30 s (Fig. 2d, Table 4). By the same time, the volume of the Cu droplet is decreased to 83% of its initial value (Table 5), probably due to grain boundary penetration of steel by liquid Cu (see Fig. 3 and [17, 18]). No sign of reaction was found at the Cu/steel interface.

The time-dependent contact angle values are given in Table 4. The time-dependent values of the visible volume of liquid Cu relative to its initial volume are listed in Table 5 (compensation is applied due to evaporation of Cu from Fig. 1). The initial volume of the liquid is found from the mass of the Cu sample divided by the density of liquid Cu (8.00 g/cm³ [19, 20]). One can see that for samples with 50 and

Figure 1 Time dependence (starting from the moment of melting) of visible volume (a) and free surface area (b) of liquid copper droplet melted on two Al_2O_3 substrate.

170 nm the starting volume is already below 100% at the moment of melting due to immediate penetration upon melting.

As follows from Table 4, at the moment of melting for samples with 340 nm and 680 nm thick ceramic coatings the contact angles of $116 \pm 3^\circ$ and $111 \pm 3^\circ$, respectively are found, being similar to the contact angle values measured for macroscopic AlN and Al_2O_3 substrates [21–23]. This is because the adhesion energy between the metallic liquid and ionic/covalent solid substrate is ensured only by weak van-der-Waals forces, in contrary to strong adhesion energy

between liquid Cu and solid steel ensured by strong metallic bonds across the interface. As also follows from Table 4, for samples with 170 and 50 nm ceramic thickness values the first measured contact angle is within the interval measured for the bulk ceramic and for the bulk steel substrates. This is connected partly with the partial penetration of the liquid droplet into the pores of the ceramic coating (Table 5) and partly due to the “wetting transparency” of thin films as revealed in [24–26], or rather due to wetting translucency of the same [27].

Figure 2 Melting process of Cu placed on the surface of 42CrMo4 steel: **a** initial state, **b** right before melting, **c** at the moment of melting, **d** 30 s after melting.

Table 4 Contact angles of Cu melted on the surface of uncoated and coated 42 CrMo4 steels by AlN-Al₂O₃ ceramic layer

Time (s)	Contact angle of Cu (°)				
	No coating	50 nm coated	170 nm coated	340 nm coated	680 nm coated
0	35 ± 2	41 ± 2	69 ± 8	116 ± 3	111 ± 3
1	32 ± 3	31 ± 3	36 ± 2	115 ± 4	109 ± 3
8	31 ± 2	16 ± 3	18 ± 1	115 ± 4	108 ± 4
9	31 ± 2	16 ± 4	14 ± 3	19 ± 2	109 ± 4
12	31 ± 2	11 ± 1	9 ± 3	12 ± 2	108 ± 3
15	19 ± 2	8 ± 1	9 ± 2	11 ± 3	107 ± 3
23	18 ± 2	6 ± 1	6 ± 2	9 ± 4	107 ± 3
24	18 ± 2	6 ± 1	6 ± 2	9 ± 4	29 ± 2
30	16 ± 2	6 ± 1	6 ± 3	10 ± 2	10 ± 2

In the case of the 170 nm thick AlN-Al₂O₃ layer (Fig. 4), Cu formed a droplet with a contact angle of $69 \pm 8^\circ$ at the moment of melting (Fig. 4c). After 1 s, however, liquid Cu suddenly spread along the surface resulting a contact angle of $36 \pm 2^\circ$. Simultaneously, the visible volume of Cu decreased to 59%, confirming the partial penetration of Cu into the pores of the ceramic. After 12 s, the contact angle

decreased further to $9 \pm 3^\circ$. Moreover, as follows from Fig. 4e–f, solid particles are visible on the top of the droplet, indicating that the ceramic layer is floated to the surface of the droplet and agglomerated there. As follows from Table 4, the contact angles for all coated substrates come approximately to the same value of $8 \pm 3^\circ$ within 30 s of liquid time of copper. It

Table 5 Visible volume ratios of Cu melted on the surface of uncoated and coated 42CrMo4 steel by AlN-Al₂O₃ ceramic layer

Time (s)	$\frac{V_{vis}}{V_0} \times 100(\%)*$				
	No coating	50 nm coated	170 nm coated	340 nm coated	680 nm coated
0	100	79 ± 5	72 ± 5	100	100
1	96 ± 7	79 ± 2	59 ± 4	98 ± 2	98 ± 7
8	97 ± 8	56 ± 9	33 ± 4	100 ± 4	101 ± 5
9	97 ± 5	55 ± 8	21 ± 5	59 ± 4	102 ± 6
12	97 ± 7	50 ± 5	19 ± 4	42 ± 8	102 ± 7
15	97 ± 6	21 ± 5	13 ± 4	29 ± 7	100 ± 6
23	93 ± 6	—	—	—	98 ± 6
24	91 ± 7	—	—	—	59 ± 3
30	82 ± 7	—	—	—	42 ± 7

* V_{vis} visible volume of Cu measured at the given time, V_0 initial volume of Cu

Figure 3 Cross-sectional PFIB-SEM image of the Cu droplet on the surface of the uncoated 42CrMo4 steel showing grain boundary penetration.

is worth to note that this value is lower compared to $16 \pm 2^\circ$ obtained without ceramic coating.

The time dependences of the contact angle and visible volume of Cu droplets are shown in Fig. 5. Based on Fig. 5a, the incubation time of the non-wetting/wetting transition can be defined as the time needed to lower the contact angle below 90° (see also [28]).

As follows from Fig. 6, the incubation time has a zero value at and below a critical ceramic thickness of about $7.5/0.045 = 170 \pm 60$ nm, while above this critical thickness the incubation time is a linear function of the ceramic thickness. It means that for samples with 340 and 680 nm ceramic thicknesses some process of constant linear velocity leads to the non-wetting/wetting transition, while the same process is not needed for the sample with 50 and 170 nm ceramic thicknesses.

As also follows from Fig. 5, for the samples of 50 and 170 nm thick ceramic coatings another incubation time is present even after the contact angle is below 90° . Additional 4 s are needed before the visible volume (and also the contact angle) start decreasing further. It is also worth to note that this second incubation time is hidden by the first process for samples with 340 and 680 nm ceramic thicknesses. In other words, the second process (with incubation time of 4 s) terminates before the non-wetting/wetting transition takes place for samples with 340 and 680 nm ceramic thicknesses.

Inner structural changes of the samples after melting Cu on their top

Top images of the surface of the samples after the wetting experiments are shown in Fig. 7. It can be seen that liquid Cu spreads along the surface of the steel coated by the ceramic layer (Figs. 7b–e) to a greater extent than on the uncoated steel (Fig. 7a), being in agreement with the smaller contact angle found in Table 4 for samples coated by ceramic. On the surface of the uncoated steel, the grain structure of the solidified Cu can be seen. However, in the cases of the coated steel plates, the wrinkled, cracked ceramic layers can be observed, suggesting that Cu undermined the ceramic layer or the ceramic layer floated up to the Cu surface. This observation is similar to the literature reports [12–15] on liquid metals undermining the surface oxide layers on solid metals. This finding is further confirmed by the cross sectional elemental map taken after the experiment (Fig. 8) with the Cu layer situated between the steel substrate and its original ceramic coating. Thus,

Figure 4 Melting process of Cu placed on the surface of 42CrMo4 steel, previously coated with 170 nm thick AlN-Al₂O₃ layer: initial state (a), right before melting (b), at the moment of melting (c), 1 s after melting (d), 8 s after melting (e), 15 s after melting (f).

during 30 s of Cu liquid time the initial steel/ceramic/copper configuration was inverted into the steel/copper/ceramic configuration.

Additional experiments were carried out on the surface of C45 (1.1191) mild steel, coated with 340 nm thick AlN-Al₂O₃ layer. Similar wetting behavior was observed as Cu undermined the ceramic layer, which suggests that the observed phenomenon is not associated with the higher Cr and Mo content of the steel.

As an additional consequence of the phase inversion, the ceramic layer was cracked into a large number of plates (Fig. 9a), that were not observed in the performed control experiments in the absence of Cu under the same experimental conditions. Higher magnification revealed the presence of parallel cracks within the structure of these plates (Fig. 9b, c), exposing the lighter Cu phase below some of the cracks. It is postulated that Cu flowed under the ceramic layer through these cracks. The parallel appearance of these cracks can be explained by the polished steel surface having parallel polishing tracks; the cracks in the ceramic are probably initiated by the polishing tracks on the steel substrate.

Discussion

The structural changes documented in the previous sub-chapter can be summarized as follows. The initial state is a room temperature steel substrate covered by a 50 ... 680 nm thick AlN-Al₂O₃ coating obtained by magnetron sputtering with a piece of solid copper of mass 5 ± 0.5 mg positioned on top of it. After melting the copper, the two top phases were found inverted within less than 30 s of holding time, i.e., the initial steel/ceramic/copper system was transformed into the steel/copper/ceramic system. The thicker is the original AlN-Al₂O₃ coating the longer it takes to inverse the two top phases; this incubation time increases from about 8 s to about 23 s for AlN-Al₂O₃ thickness values of 340 and 680 nm, correspondingly, while there was no incubation time for 50 and 170 nm thicknesses.

From point of view of macroscopic physics all is clear here, as the two top phases on the steel substrate are positioned in the final state in order of their decreasing densities from bottom to top: the denser copper phase in the bottom and the less dense AlN-

Figure 5 Contact angle of Cu as function of time (a) and the visible volume ratio of liquid Cu droplet as function of time (b), measured on the surface of 42CrMo4 steel previously coated with

Al₂O₃ phase on the top of it. However, gravity usually has a negligible role compared to interfacial

AlN-Al₂O₃ layers with different thicknesses (time is measured from the moment of melting of Cu).

forces in positioning nano-phases, and so a more reasonable mechanism is needed to explain what

Figure 6 The measured incubation time of non-wetting/wetting transition (see Fig. 5a) as function of the thickness of deposited ceramic coating.

happened during less than 30 s while the originally top copper phase was in a liquid state.

A schematic description of the processes during our experiments

The first important process took place during heating of the steel/ceramic/Cu system, before the copper phase was melted. This is the formation of a network of vertical cracks in the ceramics (Fig. 10, state 2). The crack formation is due to the large mismatch in heat expansion coefficients of the steel substrate and the ceramic coating deposited on its surface. Indeed, the linear heat expansion coefficient of steel is around $12 \times 10^{-6} \text{ K}^{-1}$ [29], in contrary to the heat expansion coefficient of AlN ($5.3 \times 10^{-6} \text{ K}^{-1}$) [30] and Al_2O_3 ($8.1 \times 10^{-6} \text{ K}^{-1}$) [31]. Thus, steel is expanded more rapidly upon heating compared to the ceramic coating on its surface, resulting in the cracking of the ceramic. As the ceramic coating is quite rigid, this size-increase difference leads to the formation of a large amount of vertical cracks in the ceramic layer. These vertical cracks connect the bottom steel phase with the top copper phase. However, before melting copper, the vertical cracks are “empty”, i.e., contain only low-pressure gas from the surrounding vacuum.

By the time when melting of copper takes place, the surface of steel at the bottom of the cracks is deoxidized due to the combined effect of high temperature, high vacuum and carbon content of steel [28]. When copper melts, it can form a poorly wetting droplet on top of the ceramic with a contact angle above 90° (Table 4, Fig. 10 Route 2, state 3). This poorly wetting copper droplet is not able to penetrate into the cracks of the ceramic coating. However, liquid copper

hanging down into the crack might reach the deoxidized steel bottom of the crack, being wetted very well by liquid copper (Fig. 10, Route 1, state 3). This can take place for large enough width of the cracks and for small enough thickness of the ceramic coating (for details see below). For this combination of parameters this mechanism is sufficient to explain how liquid copper appears below the ceramics within very short time after melting the copper. However, if this is not the case (for too small widths of the cracks and/or for too thick ceramic coatings) some further explanation is needed how liquid copper appears below the ceramic.

As a consequence of the combination of high temperature and high vacuum, liquid copper evaporates along all its free surfaces (Fig. 11), including its interface with the formed cracks within the ceramic. Due to good wettability of the deoxidized steel substrate by liquid copper, the inversion of the phases is accompanied by a negative interfacial energy change, being the driving force of the process. This might take place via the mechanism of evaporation–condensation (Fig. 10, Route 2, state 4). Once liquid copper appears at the bottom of the cracks, two parallel processes take place. First, liquid copper will penetrate into the small cracks at the steel/ceramic interface. Second, the thickness of the liquid copper will gradually increase within the cracks and finally will reach the bottom part of the macroscopic liquid copper droplet (Fig. 10 Route 2, state 5). In this way the liquid copper connected with strong adhesion to the bottom steel is merged with the macroscopic liquid copper droplet on the top of the ceramic. Based on the driving force (see below), this will ensure the flow of liquid copper from top of the ceramic to the steel/ceramic interface through the cracks of the ceramic. As a result, the visible volume of liquid copper gradually decreases on top of the ceramic as well as does the visible contact angle. In the final state the two top phases are inverted (Fig. 10, Route 1 state 4 and Route 2 state 6).

The overall thermodynamic driving force of phase inversion

The phase arrangements in the initial and final states (as observed in our experiments) are schematically shown in Fig. 12.

Figure 7 Top images of the surface of 42CrMo4 steel plates after the wetting experiments by 5 ± 0.5 mg liquid Cu, previously coated by AlN-Al₂O₃ ceramic layers of the following thicknesses: 0 nm (a), 50 nm (b), 170 nm (c), 340 nm (d), 680 nm (e).

Let us write the equation for the Gibbs energy change (ΔG , J) per unit horizontal surface / interface area (A , m²) accompanying this process:

$$\frac{\Delta G}{A} = (\sigma_{cer/g} + \sigma_{Cu/cer} + \sigma_{steel/Cu}) - (\sigma_{Cu/g} + \sigma_{Cu/cer} + \sigma_{steel/cer}) \quad (2a)$$

where $\sigma_{cer/g}$ (J/m²) is the surface energy of the ceramic, $\sigma_{Cu/cer}$ (J/m²) is the interfacial energy of the Cu/ceramic interface, $\sigma_{steel/Cu}$ (J/m²) is the interfacial

energy of the steel/Cu interface, $\sigma_{Cu/g}$ (J/m²) is the surface tension of liquid Cu, $\sigma_{steel/cer}$ (J/m²) is the interfacial energy at the steel/ceramic interface. Let us apply the definition of adhesion energy after Dupré (W , J/m²) to different interfaces with steel:

$$W_{steel/Cu} = \sigma_{steel/g} + \sigma_{Cu/g} - \sigma_{steel/Cu} \quad (2b)$$

$$W_{steel/cer} = \sigma_{steel/g} + \sigma_{cer/g} - \sigma_{steel/cer} \quad (2c)$$

where $\sigma_{steel/g}$ (J/m²) is the surface energy of the steel. Now, let us express $\sigma_{steel/Cu}$ and $\sigma_{steel/cer}$ from

Figure 8 Elemental map of the cross-section of 42CrMo4 steel coated with 680 nm AlN-Al₂O₃ with the Cu layer situated between the steel substrate and its original ceramic coating (the sample was tilted with 52° during the measurement, explaining why both the surface and the cross-section of the Al-containing ceramic layer is visible).

Eqs. (2b), (2c) and let us substitute the resulting equations into Eq. (2a). After some simplifications and re-arrangements the following equation is obtained:

$$\frac{\Delta G}{A} = W_{steel/cer} - W_{steel/Cu} \quad (2d)$$

The stronger is the bond across the interface, the larger is the value of the adhesion energy characterizing it. The only bond across the interface between metallic steel and ionic ceramic is the weak van-der-Waals bond, so $W_{steel/cer}$ has a low value with order of magnitude of 0.1 J/m² [33]. On the other hand, strong metallic bond connects the two phases across the interface between metallic deoxidized steel and metallic liquid copper, and so $W_{steel/Cu}$ has a large value with order of magnitude of 1 J/m² [34]. Substituting a small value minus a large value into Eq. (2d) we find that $\Delta G/A$ will have a negative value with order of magnitude of -1 J/m². The adhesion energies can also be expressed from the measured contact angles, using the Young-Dupré equation:

$$W = \sigma_{lg} \cdot (1 + \cos \theta) \quad (2e)$$

where $\sigma_{lg} = 1.29$ J/m² [34, 35] is the surface tension of liquid copper at the temperature of the experiment. Using the measured contact angle of Cu on the surface of ceramic (115°), and steel (16°), the difference

Figure 9 PFIB-SEM top images of the surface of AlN-Al₂O₃ ceramic layer, deposited on the surface of 42CrMo4 steel, after the wetting experiment: 170 nm thick ceramic layer (a, b) in different magnifications and 680 nm thick ceramic layer (c).

between the two adhesion energies is $W_{Cu/cer} - W_{Cu/steel} = -1.78$ J/m². This is the driving force for the phase inversion schematically shown in Fig. 12.

Figure 10 The schematic of processes that probably took place in our experiments. Route 1 is valid for relatively large crack width and/or for relatively small ceramic thicknesses, while Route 2 is valid for relatively small crack width and/or for relatively large ceramic thicknesses.

Figure 11 Calculated phase diagram of the copper–oxygen system [16] based on data by Barin [32] with p1 being the interval of oxygen partial pressures during our wetting experiments and point w corresponding to the working point in our experiments.

The condition of penetration of liquid copper into the cracks

Gravity pulls the liquid copper sitting on top of the ceramic coating down into its cracks. On the other hand, penetration of liquid copper into the cracks of the ceramics is opposed by the interfacial capillary force [36–39]. In this sub-chapter, these two opposing forces are analyzed to show whether liquid copper will penetrate or not through the cracks in the ceramic. The pressure acting on the bottom surface of liquid copper down into the cracks due to gravity (p_g , Pa) is written as:

$$p_g = \rho \cdot g \cdot h \quad (3a)$$

where $\rho = 8000 \text{ kg/m}^3$ is the density of liquid copper around its melting point [19, 20], $g = 9.81 \text{ m/s}^2$ is the acceleration due to gravity, h (m) is the maximum height of the liquid copper drop above the level of the ceramic measured as $h = 0.90 \text{ mm}$ for the sample with the ceramic thickness of 340 nm. Substituting these values into Eq. (3a): $p_g \leq 71 \text{ Pa}$.

The interfacial capillary pressure (p_{cap} , Pa) acting vertically on the liquid (in fact on the liquid/ceramic/vapor triple line) at the opening of the cracks is written as [36–38]:

$$p_{cap} = \frac{2}{d} \cdot \sigma_{l/g} \cdot \cos \Theta_{Cu/cer} \quad (3b)$$

where $\Theta_{Cu/cer} = 115^\circ$, the contact angle of liquid copper on the surface of ceramic (Table 4), d (m) is the width of the crack. Equation (3b) corresponds to the vertical parallel walls of the cracks within the ceramic separated from each other at a distance of d . Table 6 shows the width of the cracks formed in the 50...680 nm thick ceramic layers. The width of these cracks is in the range between 40...2100 nm, i.e., $d = (0.4...21) \times 10^{-7} \text{ m}$. Substituting the parameters found here into Eq. (3b): $p_{cap} = -(0.5...27) \text{ MPa}$. The negative sign of the interfacial capillary pressure indicates that this pressure pushes liquid copper out of the cracks.

Adding the pressure due to gravity ($p_g \leq 71 \text{ Pa}$) and the interfacial capillary pressure of $p_{cap} = -(0.5...27) \text{ MPa}$ the result is obviously a negative pressure, meaning liquid copper will not be able to penetrate the vertical cracks of the ceramic coating. Thus, the most obvious mechanism how liquid copper can flow downwards to solid steel through the cracks in the ceramic is excluded. However, this result also means that liquid copper on top of the ceramics will be hanging down into the cracks as shown in Fig. 13.

The condition for liquid copper to reach the steel bottom of the cracks

The maximum distance (Δh , m) to which liquid copper hangs down into the crack is calculated from the geometry of Fig. 13 as:

Figure 12 Schematic phase arrangements in the initial and final states.

Table 6 Average width of the cracks formed in the AlN-Al₂O₃ ceramic layers deposited on steel substrate and Δh calculated by Eq. (4)

AlN-Al ₂ O ₃ ceramic layer thickness (nm)	Average width of cracks (nm)	Δh (nm), Eq. (4)
50	90 ... 1010	10 ... 112
170	40 ... 1930	4.4 ... 214
340	40 ... 1990	4.4 ... 221
680	50 ... 2100	5.6 ... 233

Figure 13 Liquid copper hanging down into the crack formed within the ceramic. At large enough distance between the two ceramic walls and at small enough ceramic thickness the hanging down copper droplet will touch the steel surface at the bottom of the crack.

$$\Delta h = \frac{d}{2} \cdot \left[\frac{1}{\sin(\Theta_{Cu/cer} - 90)} - \sqrt{\frac{1}{\sin^2(\Theta_{Cu/cer} - 90)} - 1} \right] \quad (4)$$

Substituting the value of $\Theta_{Cu/cer} = 115^\circ$ into Eq. (4) the expression $\Delta h = 0.111 \cdot d$ is obtained. This equation is used to calculate the Δh values in the last column of Table 6. As follows from Table 6, the actual ceramic layer thicknesses of 50 and 170 nm appear in the calculated Δh intervals, explaining why the penetration of liquid copper into the cracks of these samples started immediately after melting copper (Fig. 5) and why for these cases the incubation time for non-wetting/wetting transition was found to be zero (Fig. 6).

However, as follows from the same Table 6, the ceramic thicknesses for the two other samples (340 and 680 nm) are larger than the Δh values. That is why some incubation time was needed for the non-wetting/wetting transition for these samples (see Fig. 5, 6).

As follows from the approximated equation given in Fig. 6, at the critical ceramic thickness of about

170 ± 60 nm the expected incubation time is about zero. This critical ceramic thickness interval overlaps the estimated interval of Table 6: $\Delta h = 4.4 \dots 233$ nm, confirming the approximated validity of our model.

The mechanism of crack filling by liquid copper for thick ceramic coatings

As follows from Fig. 5 and 6, some incubation time is needed for liquid copper to start filling the cracks in samples with 340 ... 680 nm ceramic thickness. Thus, this process should take place with some different mechanism from the samples with 50 and 170 nm ceramic thickness. To understand this different mechanism, let us take the reciprocal of the slope of the line in Fig. 6 as $1/(0.0450 \text{ s/nm}) = 22 \text{ nm/s}$. This is the empirically found filling rate of the cracks by liquid Cu for samples coated by 340 ... 680 nm ceramic. A remarkably similar average value is obtained in absolute values for the evaporation rate of liquid copper under identical conditions (same temperature, same vacuum level): $25 \pm 15 \text{ nm/s}$ (see Sect. 3.1). The coincidence of the absolute values of the evaporation rate and the crack filling rate by liquid copper under identical conditions provides a strong indication that the cracks in the thicker ceramic layers are filled by liquid copper via the evaporation–condensation mechanism.

Separation of the ceramic layer from the steel substrate

When the cracks in the ceramic are filled up by liquid copper (in this or that way), the fractured ceramic platelets become surrounded by the liquid Cu. At this point, two opposing forces act on the ceramic platelets: the adhesion force (F_a) keeping the ceramic attached to the surface of steel, and the buoyancy force, lifting the ceramic from the steel surface. These two forces can be expressed as:

$$F_b = \rho_l \cdot V_p \cdot g \quad (5a)$$

$$F_a = W_{steel/cer} \cdot P_p \quad (5b)$$

where $\rho_l = 8.00 \text{ g/cm}^3$ is the density of liquid Cu [19, 20], $V_p \text{ (m}^3\text{)}$ is the volume of the platelets, $P_p \text{ (m}^2\text{)}$ is the perimeter of the ceramic platelets in contact with the steel substrate, and $W_{steel/cer} \cong 0.1 \text{ J/m}^2$ is the adhesion energy between the steel substrate and the ceramic [33]. The dimensions of the fractured ceramic platelets are summarized in Table 7. Substituting all values into Eqs. (5a), (5b): $F_b = (7.9 \dots 12,274) \times 10^{-14} \text{ N}$ and $F_a = (2.4 \dots 23.4) \times 10^{-6} \text{ N}$. This means that the buoyancy force cannot overcome the adhesion force. Thus, to separate the ceramic coating from the steel substrate liquid Cu needs to penetrate into the pores between the ceramic platelets and steel substrate.

The time needed to separate the ceramic coating from the steel substrate

As it was calculated in Sect. 4.2, the ceramic/steel interface is energetically less favorable compared to the copper/steel interface. Due to this driving force, liquid Cu will penetrate horizontally into the pores of the steel/ceramic interface, resulting to the detachment of the ceramic layer from the surface of steel. As it was explained in Sect. 3.2, this process takes about 4 s for the samples with 50 nm and 170 nm ceramic thicknesses. However, the same process takes place parallel to the filling the cracks in the ceramic by liquid Cu via the evaporation–condensation mechanism for samples with 340 ... 680 nm. That is why for these two samples with thick ceramic layers the two incubation times (one for filling the cracks and the second one for separating the ceramic from the steel) cannot be distinguished.

Table 7 Dimensions of the fractured ceramic platelets

Parameters of the ceramic platelets	Values
$l_p \text{ (}\mu\text{m)}$	10 ... 92
$w_p \text{ (}\mu\text{m)}$	2 ... 25
$P_p \text{ (}\mu\text{m)}$	24 ... 234
$V_p \text{ (}\mu\text{m}^3\text{)}$	1 ... 1564
$d_s \text{ (}\mu\text{m)}$	0.15 ... 1.97
$d_n \text{ (}\mu\text{m)}$	0.36 ... 4.65

The floating time of the ceramic platelets to the top of liquid Cu

After the cracks in the ceramic are filled by liquid Cu and the ceramic platelets are separated from the steel substrate, floating of the ceramic platelets to the surface of liquid Cu starts driven by a larger density of liquid Cu compared to the ceramic. Let us estimate the floating velocity of the ceramic platelets by the modified Stokes law. Under steady conditions the three main forces acting on a ceramic platelet floating in a liquid are in equilibrium as:

$$F_g = F_b + F_d \quad (6a)$$

where $F_g \text{ (N)}$ is the gravity force, $F_b \text{ (N)}$ is the buoyancy force and $F_d \text{ (N)}$ is the drag force. The gravity force can be expressed as:

$$F_g = \rho_p \cdot V_p \cdot g \quad (6b)$$

where ρ_p is the density of the ceramic platelets. The drag force can be written by the modified Stokes equation extended to non-spherical objects [40, 41]:

$$F_d = \pi \cdot \eta \cdot v_{st} \cdot (d_n + 2 \cdot d_s) \quad (6c)$$

where $\eta = 4.0 \text{ mPas}$ is the dynamic viscosity of liquid Cu [19, 42], $v_{st} \text{ (m/s)}$ is the relative velocity between the particle and the melt, $d_s \text{ (m)}$ is the diameter of a sphere having the same specific surface area as the settling non-spherical particle, $d_n \text{ (m)}$ is the diameter of a sphere whose projected area is the same as the area of the object projected normal to its direction of motion. The latter quantities are modelled as:

$$d_s = \frac{3 \cdot l_p \cdot w_p \cdot d}{l_p \cdot w_p + l_p \cdot d + w_p \cdot d} \quad (6d)$$

$$d_n = 2 \sqrt{\frac{w_p \cdot d}{\pi}} \quad (6e)$$

The values calculated by Eqs. (6d), (6e) are given in Table 7 as $d_s = 0,15 \dots 1,97 \mu\text{m}$ and $d_n = 0,36 \dots 4,65 \mu\text{m}$. Substituting Eqs. (5a), (6b), (6c) into Eq. (6a), the steady state velocity of a floating ceramic platelet is expressed as:

$$v_{st} = \frac{(\rho_p - \rho_l) \cdot V_p \cdot g}{\pi \cdot \eta \cdot (d_n + 2 \cdot d_s)} \quad (6f)$$

The density of the AlN-Al₂O₃ ceramic layer can be calculated approximately as the mean value of the AlN and Al₂O₃ phases: $\rho_{AlN} = 3250 \text{ kg/m}^3$ and $\rho_{Al_2O_3} = 3950 \text{ kg/m}^3$ [43, 44], thus $\rho_{AlN-Al_2O_3} \approx$

3,600 kg/m³. Substituting the values given above and in Table 7 into Eq. (6f): $v_{st} = -(5.1 \dots 625) \mu\text{m/s}$. The negative sign refers to floating of the ceramic platelets, against the direction of the gravity vector. The maximum height of the solidified Cu spread on the surface of the steel was measured between 41...80 μm , hence it takes the ceramic platelets to reach the top surface of Cu about 0.07 ... 15.69 s. It means that the fractured ceramic platelets reach the top surface of liquid Cu droplet within some seconds, that takes place before the solidification of Cu ($< 2 \text{ min}$).

Agglomeration of the ceramic platelets on the top of liquid Cu

Two neighboring platelets are shown in Fig. 14 situated on the top surface of liquid Cu in two different situations: relatively far from each other and relatively close to each other. As was shown above, liquid copper poorly wets the surface of the ceramic with about 115° of contact angles. That is why the curved liquid meniscus is formed between the two platelets (see left hand side position in Fig. 14). However, if the two platelets appear closer to each other, the extra surface area of the curved liquid is decreased (see right hand side position in Fig. 14). That is why the process of agglomeration of the ceramic platelets on top of liquid Cu is a spontaneous process accompanied with a negative Gibbs energy change. For more details about the interfacial meniscus force pulling the two platelets closer to each other on the free liquid surface see [36, 37].

Improved wetting of steel substrate by liquid copper covered by ceramic platelets

As follows from Table 4, the final contact angle of liquid Cu on steel substrate is decreased from $16 \pm 2^\circ$ to $8 \pm 3^\circ$ when the top surface of liquid copper is coated by ceramic platelets. To explain this, let us express the contact angle from Eq. (2e):

$$\cos \theta = \frac{W}{\sigma_{lg}} - 1 \quad (7)$$

Let us estimate the adhesion energy between liquid Cu and solid steel by substituting into Eq. (2e) the surface tension of liquid Cu (1.29 J/m^2 [34, 35]) and the measured contact angle of 16° : $W = 2.53 \text{ J/m}^2$. The same value of adhesion energy is expected between liquid Cu and solid steel regardless how the top surface of liquid Cu looks like. However, the fact that the top liquid Cu is at least partly covered by agglomerated ceramic particles will decrease its surface tension. The surface energy of Al_2O_3 extrapolated to the temperature of our experiments is about 0.95 J/m^2 , while the same for AlN is about 2.5 J/m^2 (see [45] and references thereof). As a result, Al_2O_3 will be surface active and the resulting surface energy of our ceramic will be around $1.1 \pm 0.1 \text{ J/m}^2$. Supposing the full top surface area of liquid Cu is covered by such ceramic platelets, the contact angle can be estimated by substituting $W = 2.53 \text{ J/m}^2$ and $\sigma_{lg} = 1.1 \text{ J/m}^2$ into Eq. (7): $\cos \theta = 1.3$. Although this value is a mathematical non-sense, physically it means $\theta = 0^\circ$. In fact, the top liquid Cu surface is coated only partly by the ceramic platelets, and so the contact angle of Cu (coated partly by platelets) on steel is expected in the range of $0 \dots 16^\circ$. As follows

Figure 14 Schematic of the process of agglomeration of ceramic platelets on top surface of liquid Cu.

from Table 4, the experimental values of $8 \pm 3^\circ$ appear in this interval.

Conclusions

1. It was shown that when a steel substrate is coated at room temperature by AlN-Al₂O₃ sub-micron thick ceramic layer and later this system is heated to 1090 °C, the ceramic layer is cracked with the formation of a series of vertical cracks due to mismatch of heat expansion coefficients of steel and the ceramic. Particularly, the ceramic is found to crack into a large number of plates of 100 ... 500 microns of horizontal diameter with 0.04 ... 2.1 µm thick cracks within them. It is also shown that in vacuum (8×10^{-8} to 2×10^{-7} bar) and at 1090 °C the surface of steel is spontaneously deoxidized at the bottom of the cracks, so potentially it is well wettable by liquid copper (if liquid copper comes into contact with this steel surface).
2. It is shown that the phase inversion of the two top phases from steel/ceramic/copper configuration to the steel/copper/ceramic configuration is accompanied by a Gibbs energy change per unit horizontal surface/interface area of about -1.78 J/m^2 . This is due to good wettability of solid deoxidized steel by liquid copper in contrary to poor wettability of the ceramic by the same liquid copper.
3. When copper is melted on top of the AlN-Al₂O₃ ceramic layer for ceramic thicknesses smaller than a critical value of $170 \pm 60 \text{ nm}$, the visible contact angle of liquid copper is $\Theta < 90^\circ$. The reason for this is that the droplets hanging down into the cracks of the ceramic can reach the solid steel surface at the bottom of at least some of the cracks, thus forming a wetting shape.
4. When copper is melted on top of the AlN-Al₂O₃ ceramic layer for ceramic thicknesses larger than a critical value of $170 \pm 60 \text{ nm}$, it first forms a non-wetting droplet on the top of the ceramics and only after a certain incubation time liquid copper starts flowing down the cracks driven by the driving force explained above. It was shown that this incubation time depends linearly on the deposited ceramic thickness and the rate of crack filling by liquid copper is about 22 nm/s. This rate is shown to be about the same as the rate of evaporation of liquid copper under the same conditions per unit free surface area, found in independent experiments as $-25 \pm 15 \text{ nm/s}$. This proves that liquid copper fills the cracks within the ceramic via the evaporation—condensation mechanism for ceramic thickness larger than $170 \pm 60 \text{ nm}$.
5. The presence of a second incubation time was also observed for the cases of AlN-Al₂O₃ ceramic layers with a thickness smaller than $170 \pm 60 \text{ nm}$. It was found, that the adhesion force attaching the ceramic layer to the surface of the steel is larger than the buoyancy force within the liquid copper surrounding the fractured ceramic platelets. Thus, liquid Cu first needs to penetrate into the pores of the ceramic/steel interface, to detach the ceramic platelets from the surface of steel, which resulted in the appearance of the second incubation time. However, in the case for the samples with 340 ... 680 nm ceramic thickness, this process takes place parallel to the filling of the cracks in the ceramic via the evaporation—condensation mechanism. That is why for these samples the two incubation times cannot be distinguished
6. Regardless of the mechanism of flow of liquid copper down along the cracks, liquid copper will penetrate into the gap between the solid steel and ceramic and finally the whole volume of liquid copper will appear underneath the ceramic, i.e. the original coating of steel is lifted up by liquid copper. In this way the phase inversion of the two top phases on steel substrate takes place within 30 s of liquid time of copper for the ceramic coatings of 680 nm thickness and below. Within this relatively short time the non-wetting liquid copper droplet originally positioned on top of ceramic coating appears underneath and lifts the ceramic coating up. Although this is mostly due to interfacial forces, by the end of the process the steel/copper/ceramic system is additionally stabilized by gravity.

Acknowledgements

This study was carried out as part of the GINOP-2.3.2-15-2016-00027 “Sustainable operation of the workshop of excellence for the research and

development of crystalline and amorphous nanostructured materials” project implemented in the framework of the Szechenyi 2020 program. The realization of this project was supported by the European Union.

Funding

Open access funding provided by University of Miskolc.

Declarations

Conflict of interest The authors declare that they have no conflict of interest.

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