ANALYSIS AND INTERPRETATION OF THE MICROMECHANICAL PROPERTIES MEASUREMENTS OF ELECTRODEPOSITED NICKEL COATINGS ON DIFFERENT SUBSTRATES

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Abstract: Fine-grained nickel coatings were electrodeposited by direct current (dc) regime onto different substrates: polycrystalline cold-rolled copper, polycrystalline brass and single crystal (100)-oriented silicon. These composite structures belong to different type of laminated composite systems. The influence of the substrate material and coating plating parameters on microstructural and mechanical properties, such as hardness and adhesion, was characterized by

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the Vickers microindentation test for different loads. Above critical indentation depth (usually around 10% of the coating thickness), the measured hardness is the so-called "composite hardness", because the substrate participates in the plastic deformations during indentation. Three composite hardness models (Korsunsky, Chicot-Lesage and Chen-Gao), constructed on different principles, were chosen for fitting the experimental results in order to determine the coating hardness and the critical reduced depth as the adhesion parameter. The coating hardness is mainly influenced by the current density, because increase in current density leads to decrease in grain size and increase in coating hardness. The critical reduced depth as the parameter of adhesion depends on the substrate material.

Keywords: Vickers microhardness; composite hardness; nickel electrodeposition; film adhesion, critical reduced depth

INTRODUCTION

Knowledge about the technology of manufacturing the desired material and its mechanical properties is extremely important when talking about the integrity of the material and the integrity of the devices that contain it. It enables the prediction or interpretation of fractures and the identification of the failure modes of materials and devices. The use of thin films and coatings has become very valuable in various engineering applications, such as improving wear and corrosion resistance, reducing electrical resistance or friction or in the fabrication of microelectromechanical devices, etc. (Mittal, 1976; Lewis, Reynolds & Gagg, 2004).

All technologies for obtaining thin coatings imply the existence of a substrate on which a coating will be formed and such structures can be considered as composite systems. The mechanical properties of these structures are specific and differ from the mechanical properties of bulk materials. For the characterization of these systems, composite hardness measurements and adhesion assessment are among the most important.

Since the thickness of the coatings is very small, the measured composite hardness is affected by a number of factors such as the microstructure of the coating and the substrate, the absolute hardness of the coating and the substrate and their relative hardness ratio, the thickness of the coating and its adhesion to the substrate, the indentation depth, etc. (Cammarata, 1994; Chicot & Lesage, 1995; Lamovec, Jovic, Randjelovic, Aleksic & Radojevic, 2008).

Electrodeposition (*ED*) is a reliable and widely used technology for obtaining the coatings on conductive substrates. It is low-temperature technique with high deposition rates, applicable to materials that differ greatly in their composition, crystallographic orientation or grain size. The microstructure and the mechanical properties of electrodeposited coatings are affected by the processing parameters (Ebrahimi, Bourne, Kelly & Matthews, 1999; Datta & Landolt, 2000).

The technology of obtaining nickel coatings by electrodeposition is known and very well developed. Electrodeposited nickel (ED Ni) coatings may have very good mechanical properties and be strengthened and hardened which is achieved by controlling the grain size and microstructure (Fritz, Mokwa & Schnakenberg, 2001).

Composite hardness and adhesion models

By applying the method of indentation to composite systems, the so-called composite hardness can be calculated, which contains the response of the film and the substrate to the plastic deformation. There is a need to obtain the hardness of the coating separately. There are several hardness models that are constructed on different principles.

Descriptive model of Korsunsky et al. is applicable to either plasticity- or fracture-dominated behavior with all scales measured relatively to the coating thickness. They introduced the term "the total work-of-indentation" during hardness testing, which consists of two parts: the plastic deformation in the substrate and the deformation and/or fracture energy in the coating. According to this model, the composite hardness, H_C, is expressed by Eq.1:

$$H_C = H_S + \left[\frac{1}{1+k'\left(d^2/t\right)}\right]\cdot\left(H_F - H_S\right),\quad k' = \frac{k}{49\cdot t} \tag{1}$$

where k is a dimensionless parameter of the material which expresses the response mode of the composite system to indentation, d is the indentation diagonal, t is the thickness of the coating, H_S is the substrate hardness and H_F is the coating hardness. This model does not allow the calculation of the composite hardness and film hardness for each individual load, but for the entire range of selected loads (Korsunsky, Gurk, Bull & Page, 1998).

The predictive model of Chicot-Lesage allows relatively simply calculation of the coating hardness from standard composite hardness measurements for every particular indentation load, knowing only the coating thickness and the substrate hardness. The model is constructed on the analogy between the variation of the Young modulus of reinforced composites as a function of the volume fraction of particles and the variation of the composite hardness between the substrate hardness and the coating hardness (Lesage & Chicot, 2005; Lesage, Pertuz, Puchi-Cabrera & Chicot, 2006).

Analogous to Meyer´s law, for each composite coating-substrate system, there is a similar relation between the measured indentation diagonal d and the applied load P:

$$P = a^{*}\cdot d^{n^{*}} \tag{2}$$

The hardness depends on the load, and the variable part of the hardness number with the load is expressed by the factor n^*. The authors adopt a function that connects the coating thickness t, indentation diagonal d and the factor n^*:

$$f\left(\frac{t}{d}\right) = \left(\frac{t}{d}\right)^{m} = f \quad where \quad m = \frac{1}{n^{*}} \tag{3}$$

The composite hardness H_C can be expressed as follows:

$$H_C = (1-f)\Big/\left(1/H_S + f\cdot\left(\frac{1}{H_F}-\frac{1}{H_S}\right)\right) + f\cdot\left(H_S + f\cdot\left(H_F - H_S\right)\right) \tag{4}$$

The absolute hardness of the film H_F is calculated as the positive root of next equation:

$$A \cdot H_F^2 + B \cdot H_F + C = 0$$

with

$$A = f^2 \cdot (f - 1)$$
$$B = (-2 \cdot f^3 + 2 \cdot f^2 - 1) \cdot H_S + (1 - f) \cdot H_C \quad (5)$$
$$C = f \cdot H_C \cdot H_S + f^2 \cdot (f - 1) \cdot H_S^2$$

The Meyer´s composite index m is calculated by a linear regression performed on all experimental points obtained for analyzed coating-substrate system:

$$\hbar\ d = m \cdot \hbar\ P + b \quad (6)$$

With a known value of m, the hardness of the film H_F can be calculated.

A method by Chen and Gao was developed for evaluation of the adhesion properties of the thin films and coatings. The method is based on a composite hardness model because adhesion was found to affect microhardness. The model introduces the depth weight factor function to estimate the contribution of local hardness to composite hardness. The equation used for the approximate calculation of composite hardness and adhesion parameter for the thin films and coatings is as follows:

$$H_C = H_S + \left[\frac{(m+1) \cdot t}{m \cdot b \cdot D}\right] \cdot (H_F - H_S) \quad (7)$$

H_S and H_F are hardness of the substrate and the film, t is coating thickness, D is the indentation depth, m is the power index and b the critical reduced depth beyond which the material will have no effect on the measured hardness.

A low value of the critical reduced depth b (ratio between the radius of the plastic zone the indentation and the indentation depth) corresponds to poor adhesion while large value of the critical reduced depth b corresponds to good adhesion as shown in Fig.1.

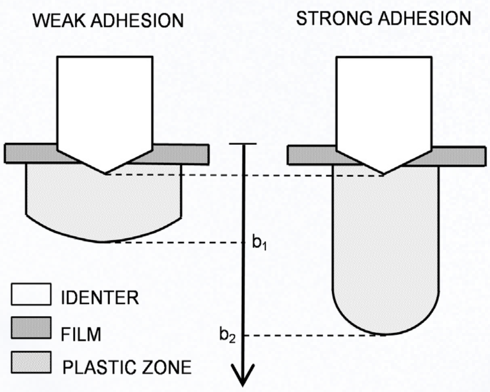

Fig. 1 *Schematic representation of deformation associated with indentation in a coated substrate for a weak adhesion (left) and strong adhesion (right).*

Using the indentation diagonal d instead of the indentation depth D, according to the expression $d = 7 \cdot D$, and introducing the relation $\Delta H = H_S - H_C$, the equation becomes:

$$\Delta H = \left[\frac{7 \cdot (m+1) \cdot (H_S - H_F)}{m \cdot b} \right] \cdot (t/d) \tag{8}$$

It was found that the power index m is 1.2 for a system of hard film on soft substrate and 1.8 for a soft film on a hard substrate. The critical reduced depth b as the parameter for the assessment of adhesion can be calculated according to the Eq.8, together with experimental values of H_C, H_F and d, (Hou, Gao & Li, 1999; Chen & Gao, 2000).

Experimental procedure

The materials selected for the formation of the composite systems were electrodeposited by fine-grained nickel coatings on three different substrates: polycrystalline copper and brass foils and single crystal Si wafers with (100) orientation. Sputtered 100Å Cr and 1000Å Au layers were deposited on the Si semiconductor substrate as an adhesion and nucleation layer. Electrodeposition was performed by using the direct current galvanostatic regime from a sulfamate electrolyte consisting of 300 g/l Ni $(NH_2SO_3)_2 \cdot 4H_2O$, 30 g/l $NiCl_2 \cdot 6H_2O$, 30 g/l H_3BO_3 and 1 g/l saccharine, with pH-value and the temperature of the process maintained at 4.00 and 50°C, respectively. The current density values were maintained at 10 mA/cm^2 and 50 mA/cm^2 and the rates of the deposition for all the substrates were experimentally determined. The deposition time was determined according to the plating surface (2cm^2) and projected thickness of the deposit (10μm).

The mechanical properties of the substrates and the composite systems are characterized by a Vickers microhardness tester ″Leitz, Kleinharteprufer DURIMET I″ using up to 15 loads ranging from 4.9 N down to 0.049 N. Three indentations were made and the average value of the diagonal was determined by measuring six indentation diagonals for each load. With the average value of the diagonal, the mean value of the hardness was calculated. The experimental data were fitted with GnuPlot (http://www.gnuplot.info/).

RESULTS AND DISCUSSION

Absolute hardness of the substrates

Vickers microhardness measurements were performed on the uncoated substrates in order to calculate the absolute hardness of the substrates, and on the various coated substrates. With the average value of the indentation diagonal d and known applied load P, it is possible to calculate the composite hardness H_C using the Eq. (9):

$$H_C = 0.01854 \cdot P \cdot d^{-2} \tag{9}$$

where the constant 0.01854 is the geometrical factor for the Vickers pyramid. Eq. (9) representing the classical Meyer law.

It was found that the proportional specimen resistance (*PSR*) model is suitable for calculation of the value of load-independent microhardness of the substrates (Li & Bradt, 1991).

$$P = a_1 \cdot d + \left(P_c / d_0^2\right) \cdot d^2 \tag{10}$$

P_c is the critical applied load above which the microhardness becomes load independent and d_0 is the corresponding diagonal length of the indent. The slope of the straight line of dependence P/d against d gives the value for the calculation of the load independent microhardness. According to this model, the calculated values of load independent microhardness for the substrates, H_S, are 0.37 GPa for the copper foil, 1.41GPa for the brass foil and 6.49 GPa for the Si (100) wafers.

Composite hardness and film hardness were determined for the two different types of composite system according to different coating-substrate hardness ratio: hard electrodeposited Ni film on soft substrates of Cu, and brass and soft film of electrodeposited Ni on hard substrate of (100)-oriented Si.

Hard electrodeposited Ni coating on soft substrates of Cu and brass

The change of the composite hardness, H_C, with relative indentation depth, h/t, (indentation depth h through coating thickness t), is shown in Fig. 2. Nickel coatings on copper and brass substrates are 10-µm thick and were obtained with two current densities (10 and 50 mA/cm²).

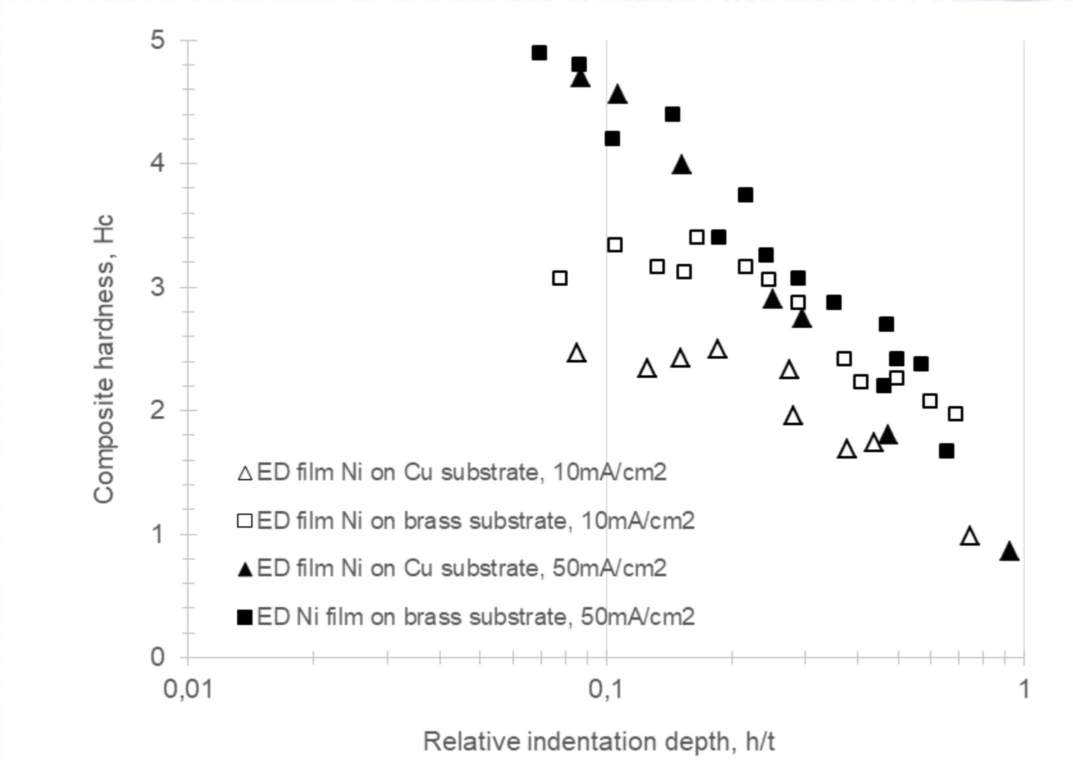

Fig.2. *Variation of the composite hardness H_C, with relative indentation depth, h/t, for electrodeposited Ni coatings on Cu and brass substrates. All coatings are 10µm thick. The dashed lines represent the hardness values of the copper (0.37 GPa) and brass (1.41 GPa) substrates.*

For the values of $h/t \leq 0.1$, the hardness response was found to originate only from the coating. The coatings obtained with a higher current density (50 mA/cm²) appeared harder than those deposited with 10 mA/cm². For hard coating on soft substrate composite systems, with increasing the relative indentation depth h/t ($0.1 \leq h/t \leq 1$), the composite hardness H_C decreases until the hardness of the substrate (H_S) is reached as shown by the dashed lines in Fig.2.

The experimental data for these systems were fitted by Eq. (1) which represents the composite hardness model of Korsunsky et al. Previous research has confirmed that the application of the Korsunsky model is adequate for this type of composite system (Lamovec, Jovic, Aleksic & Radojevic, 2009). H_S was taken as 0.37 GPa for the copper and 1.41 GPa for the brass substrate, according to the experimentally obtained values. Curve-fit data produced from the model validation process for four electrodeposited Ni coatings are given in Table 1.

Table 1. *Values of the fitting results according to the Korsunsky model for the 10-μm thick Ni coatings on Cu and brass substrates*

Quantity	K model	Asymptotic standard error
Electrodeposited Ni coating (10 μm, 10 mA/cm2) on Cu substrate		
H_F / GPa	2.68	±0.11
k´	0.0087	±0.0017
Electrodeposited Ni coating (10 μm, 50 mA/cm2) on Cu substrate		
HF / GPa	5.4	±0.12
k´	0.029	±0.002
Electrodeposited Ni coating (10 μm, 10 mA/cm2) on brass substrate		
HF / GPa	3.05	±0.185
k´	0.1976	±0.018
Electrodeposited Ni coating (10 μm, 50 mA/cm2) on brass substrate		
HF / GPa	5.74	±0.718
k´	0.259	±0.022

Higher values of the composite hardness for the Ni coating on brass substrate coating system come from the contribution of the hardness of brass as a substrate. The agreement of the hardness values of Ni coatings on different substrates according to the model of Korsunsky is very satisfactory.

Soft electrodeposited Ni coating on hard (100)-oriented Si substrate

The change of the composite hardness H_C, with relative indentation depth h/t, for the Ni coatings of 10-μm thickness on Si (100) substrate deposited with two different current densities 10 and 50 mA/cm^2 is shown in Fig.3.

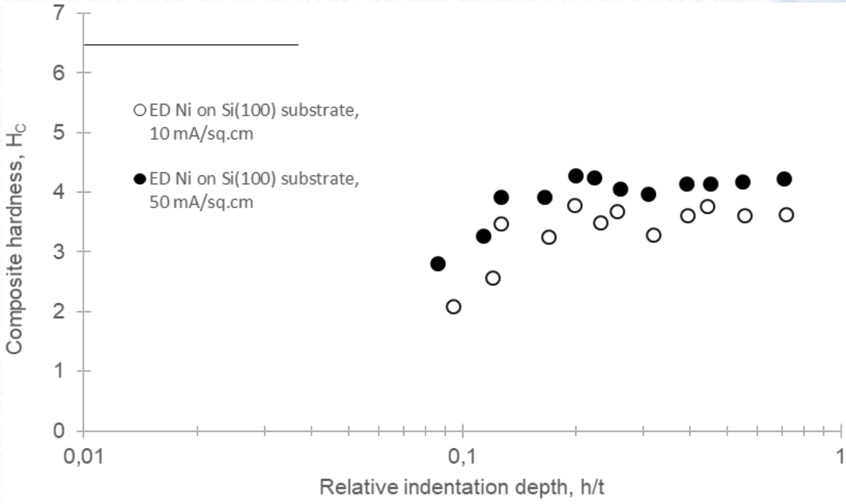

Fig.3. *Variation of the composite hardness H_C, with relative indentation depth h/t, for electrodeposited Ni coatings on Si (100) substrate. Ni coatings are 10 μm thick. The solid line indicates the hardness of the Si (100) substrate (H_S = 6.49GPa).*

It was found that for shallow penetration depths ($h/t \leq 0.1$), the response is of the coating only. It is considered that the indentation response in the region $0.1 \leq h/t \leq 1$, corresponds to the whole composite coating-substrate system. In contrast to the hardness response of the "hard coating on soft substrate" system (Fig.2), the system of the "soft coating on hard substrate" is characterized by an increase in composite hardness with relative indentation depth (Fig.3). Because deposition with a higher current density leads to a reduction in the grain size in the coatings (Lamovec, Jovic, Randjelovic, Aleksic & Radojevic, 2008), coatings obtained with the higher current density (50 mA/cm^2) have a higher composite hardness H_C than those deposited with the 10 mA/cm^2.

The experimental data for this system was fitted with the model of Chicot-Lesage (Eq.4). *Hs* was taken as 6.49 GPa, which is the experimentally determined hardness value for the Si (100) oriented substrate. The coatings are 10-μm thick. The results are shown in Fig.4.

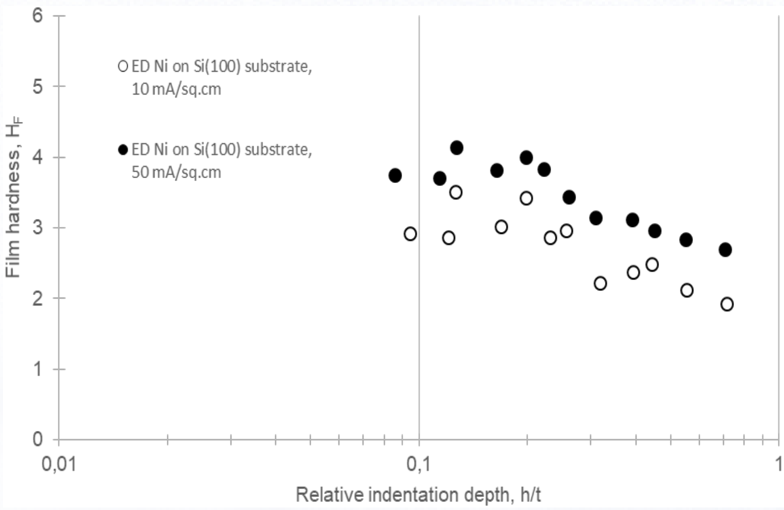

Fig.4. *Variation of the coating hardness H_F, with relative indentation depth h/t, for the system consisted of electrodeposited Ni coatings on Si (100) substrate according to the Chicot-Lesage composite hardness model.*

The values obtained for the coating hardness H_F, are not constant but depend on the applied load P, thickness of the coating t and the current density. These variations can be associated with various physical phenomena such as indentation size effect, the elastic contribution of the substrate for low loads, cracking the coating around the indent, etc. (Lesage et al., 2005).

Evaluation of coating adhesion

According to the model of Chen and Gao, adhesion affects the measured composite hardness (Chen & Gao; 2000; Magagnin, Maboudian, Carraro, 2003; Lamovec et al., 2019). This model was used to evaluate the adhesion of ED Ni coatings on copper, brass and Si (100) substrates, calculating the critical reduced depth b. The results for the coating hardness H_F, obtained using the models of Korsunsky and Chicot-Lesage, were used in the calculation. In Table 2, the results of the critical reduced depth b, are given.

Table 2 *Critical reduced depth values b, for the systems of electrodeposited Ni coatings on the Cu, brass and Si (100) substrates*

Sample		Critical reduced depth, b
ED Ni on Si (100) substrate	10 mA/cm^2	8.43
	50 mA/cm^2	8.95
ED Ni on Cu substrate	10 mA/cm^2	13.71
	50 mA/cm^2	15.44
ED Ni on brass substrate	10 mA/cm^2	14.08
	50 mA/cm^2	16.13

When increasing the indentation depth, the hardness difference decreases more rapidly due to poor adhesion and this is directly reflected in the value of critical reduced depth. Increasing values of the critical reduced depth correspond to increasing adhesion. The results show the dependence of the adhesion quality on the type of composite system, i.e. substrate type and microstructure of substrate and coating. The ED Ni coatings on Si (100) substrate show weaker adhesion compared to the ED Ni coatings on Cu or brass substrates, regardless of the existence of an adhesion sublayer. Increasing the current density leads to achieving a finer coating microstructure and improving the adhesion of the coatings to the substrates for all composite systems.

CONCLUSION

For the analysis of mechanical properties of different laminate composite systems, nickel coatings are electrodeposited on copper, brass and silicon substrates. These substrates differ in their chemical composition, microstructure and mechanical properties. The change in the microstructure and consequently the properties of the nickel coatings was achieved by changing the current density during electrodeposition (10 mA/cm^2 and 50 mA/cm^2). The thickness of the coatings was kept constant at 10-μm.

The tendency of the composite hardness to change depends on the type of the composite system. This means differences in the mechanical properties of Ni coatings and substrates (polycrystalline and ductile metals and monocrystalline brittle semiconductor): the hardness of the substrate, the hardness of the coating, their relative differences and thickness of the film.

Two important mechanical properties, hardness and adhesion, were analyzed by the Vickers indentation method. Adhesion of the coatings on the substrates influences the hardness values of the composite system.

Ni coatings on Cu and brass substrates represent composite systems of "hard coating on soft substrate" type. In order to obtain the absolute hardness of the Ni coatings H_F, according to earlier research, the composite model of Korsunsky was applied. The values of the composite hardness H_C, for the system ED Ni on brass are higher than for the system ED Ni on Cu substrate due to higher hardness value of the brass substrate (1.41 GPa for the brass and 0.37 GPa for the Cu substrate). The values of the coating hardness H_F, depend on the current density and are in good agreement for both substrates (2.68GPa and 3.05 GPa for 10 mA/cm^2 and 5.4GPa and 5.74 GPa for 50 mA/cm^2).

Nickel coatings on Si (100) substrate can be considered as "soft coating on hard substrate" composite system type. For hardness analysis, composite model of Chicot-Lesage was chosen and applied to experimental measurements of composite hardness in order to obtain the hardness of Ni coatings. The values obtained for the coating hardness H_F, depend on the applied load, i.e. indentation depth. With increasing the indentation depth and approaching the substrate, H_F had descending character.

Model of Chen and Gao, based on the composite hardness measurements, introduces the critical reduced depth *b*, as the adhesion assessment parameter. A large value of the critical reduced depth corresponds to good adhesion. The similar values of *b* are obtained for the Ni coatings on Cu and brass substrates, slightly larger for the brass substrate. Significantly lower values for *b* are obtained for the Ni coatings on Si substrates, which indicates a weaker adhesion of these coatings compared to the previously analyzed systems.

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