



A comparative study of microscratch and microtensile adhesion tests for nickel coatings on various substrates

Patrick Nguyen, Cédric Seguneau, Jean-Michel Desmarres, Talal Masri, Joël Alexis

► To cite this version:

Patrick Nguyen, Cédric Seguneau, Jean-Michel Desmarres, Talal Masri, Joël Alexis. A comparative study of microscratch and microtensile adhesion tests for nickel coatings on various substrates. DTIP 2-4 April 2014,, Apr 2014, Cannes, France. pp.0. hal-04080168

HAL Id: hal-04080168

<https://hal.science/hal-04080168>

Submitted on 24 Apr 2023

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.



Open Archive Toulouse Archive Ouverte (OATAO)

OATAO is an open access repository that collects the work of Toulouse researchers and makes it freely available over the web where possible.

This is an author-deposited version published in: <http://oatao.univ-toulouse.fr/>
Eprints ID: 13671

To cite this version:

Nguyen, Patrick and Segumineau, Cédric and Desmarres, Jean-Michel and Masri, Talal and Alexis, Joël *A comparative study of microscratch and microtensile adhesion tests for nickel coatings on various substrates.* (2014) In: DTIP 2-4 April 2014,, 2 April 2014 - 4 April 2014 (Cannes Côte d'Azur, France, France).

Any correspondence concerning this service should be sent to the repository administrator: staff-oatao@listes-diff.inp-toulouse.fr

A comparative study of microscratch and microtensile adhesion tests for nickel coatings on various substrates

Patrick Nguyen

Laboratoires d'expertise, CNES
Université de Toulouse, LGP, ENIT/INPT
Toulouse, France
patrick.nguyen@cnes.fr

Jean-Michel Desmarres

Laboratoires d'expertise, CNES
Toulouse, France
jean-michel.desmarres@cnes.fr

Cédric Seguineau

Fialab
Toulouse, France
cedric.seguineau@fialab.eu

Joël Alexis, Talal Masri

Université de Toulouse, LGP, ENIT/INPT
Tarbes, France
joel.alexis@enit.fr
talal.masri@enit.fr

Abstract – The present paper first focuses on discussing application ranges for the scratch test and the microtensile test. For that purpose, both have been implemented on the same nickel coating plated on several substrates, in particular a PCB, which are expected to have different adhesion behaviors. Afterward, correlations are highlighted between these two types of adhesion tests.

Keywords: *Adhesion; Coatings; Scratch test; Microtensile test*

I. INTRODUCTION

Thin films and coatings are nowadays used in many fields of advanced technology. However, interfacial debonding within a multi-layered device is a common failure mechanism. Therefore in order to improve manufacturing processes and insure components reliability, quantifying adhesion between these layers is mandatory. Several approaches are developed or used with very little consistency among them. Indeed, more than two hundred different adhesion tests have been developed over the past decades [1]. However, selecting one or several adhesion tests which fit a given thin films stack is not a trivial preliminary task and must be done carefully. Indeed, the following parameters ought to be taken into account for such a choice: the component's geometry, the nature and mechanical properties of the substrate and of the thin film stack, their thicknesses and adhesion strength range and last but not least, the test should induce mechanical stresses that best simulate the real stresses endured by the component/device while functioning. As a result, most of the time, only a few number of adhesion tests are suitable for a specific thin films stack. The aim of this study is to compare adhesion measurements data

from a well-established and standardized adhesion test with results from a relatively new and more complex technique.

II. SCRATCH AND MICROTENSILE ADHESION TESTS

Among the very large adhesion tests existing panel, the scratch test is one of the most widely used either in industry or laboratories since it is easy to implement and is a fast way to evaluate adhesion properties on a great variety of materials. In the most standard version of the scratch test, a diamond stylus is used to apply a linearly increasing normal load on the coating surface while the sample is simultaneously moved laterally at constant speed. During the scratching, several parameters such as the stylus penetration depth, the friction force or acoustic emission bursts can be monitored. The scratch residual path is then visually inspected in order to determine the critical normal loads at which different failure modes occur. However, due to the large number of intrinsic parameters (stylus geometry, loading speed, scratch speed...) and extrinsic parameters (hardness and thickness of the film, hardness of the substrate, friction coefficients, residual stresses...) of this kind of test, it is usually considered as a semi-quantitative adhesion test [2]. The wide resulting extent of results stands for the main drawback of this test. And although scratch testing procedures are usually simple, truly interpreting and understanding the stylus damaging mechanisms on the coating and substrate is a greater challenge.

Often, a single type of adhesion test is not sufficient to fully characterize adhesion properties of a film stack. Thus comparing results from several different adhesion tests is recommended most of the time. Application ranges of the uniaxial tensile adhesion test are much more restricted because

this test is merely appropriate for brittle films on softer substrates. Within various past studies it has been implemented mostly on steel substrates with diverse coatings such as NiP/talc composites, W and W(C), TiN and DLC [3-6]. More recently, a study about fragmentation behaviors of very ductile thin films (Cu) on polyimide substrates have been attempted [7]. Implementing this test is usually a bit more difficult than scratch tests but on the other hand, damaging mechanisms can be much more easily predictable and understandable. In this test, a standardized or specifically designed tensile specimen is fixed between jaws of the microtensile bench and then submitted to a constant tensile strain rate. During the loading, the substrate obviously stretches along the tensile axis while transverse parallel trough-thickness cracks are supposed to form on the coating as described by Fig. 1(a). This cracks formation arises when the amount of accumulated interfacial shear strength becomes critical and must be freed [8].

The present analysis focuses on the failure mechanisms of usual scratch tests to evaluate adhesion of metal coatings on Cu/PCB, and the use of microtensile test as an alternative. The relevance of this test is assessed by comparing the results of the two kinds of test on metallic substrates (adapted to the scratch test) and is then applied on a Ni/Cu/PCB stack.

III. SAMPLES AND EXPERIMENTS

Nickel deposits are well-known for their corrosion and wear resistance so that they are commonly used as interlayers for connectors manufacturing and wire bonding processes. In this study, 20 μm -thick nickel coatings have been electroplated on five different substrates from a nickel sulfate solution (250 g/L nickel sulfate, 60 g/L nickel chloride and 50 g/L boric acid) at 50 $^{\circ}\text{C}$ and 4 A/dm² current density. The first three substrates are three metal sheets made with the same 2024 aluminum alloy (AA 2024) but with different surface pretreatments (scraping, abrasive blasting and double zincate process). The two other substrates are a TA6V titanium alloy sheet and a standard blank FR-4 PCB with its standard 35 μm external copper layer. The scratch and tensile specimens have been designed by using a CAD software and have been extracted from the coated sheets by laser cutting with the exception of the PCB undergoing a mechanical cutting by milling. Scratch specimens are 20 x 20 x 1.2 mm³ square-shaped pieces whereas tensile specimens (flat type) have a 3.7 x 1.2 mm² reference section expanding along a 14 mm gage length as drawn on Fig. 1(b).

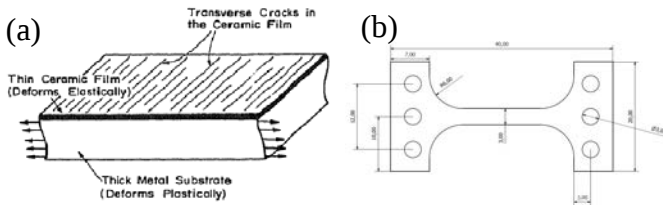


Figure 1. Schematic diagram of (a) the microtensile adhesion test principle for a brittle ceramic film coated on a ductile metal substrate [8] and (b) specimens designed for this test

Series of scratch tests were performed on the CSM[®] Micro Scratch Tester which can apply normal loads ranging from 0.03 N to 30 N by means of a Rockwell “C” diamond indenter (120 $^{\circ}$ cone with 200 μm tip radius). All the scratch lengths were fixed to 10 mm with a scratching speed of 10 mm/min.

Progressive normal loads were applied from 0.03 N to 10, 15 or 30 N (depending on the specimens adhesion strength range) and for each of the five substrates, at least five scratches have been performed to obtain statistical data. Optical microscopy followed by Secondary Electron Microscopy (SEM) and Energy Dispersive X-ray spectroscopy (EDX) were used to analyze each single scratch tracks and identify critical loads.

Concerning the microtensile test, for each five substrates at least three specimens have been tested with a 0.1 mm/min tensile strain rate. During the test, the stress-strain curve can be plotted like in conventional tensile tests. Furthermore, a CCD camera is required for the plotting of the transverse cracks density versus the specimen strain which is essential for adhesion quantification. Indeed for this test, adhesion is expressed as the critical interfacial shear stress τ and its quantification is achieved using the Agrawal and Raj model (thereafter referred as the A&R model) where δ is the coating thickness, λ the average inter-crack spacing at steady state and σ_f the tensile stress of the coating calculated by multiplying its Young’s modulus E and the strain ϵ_f when the first trough-thickness cracking arises [8].

$$\tau = \frac{\pi \delta \sigma_f}{\lambda} \quad (1)$$

IV. RESULTS AND DISCUSSION

A. Scratch tests

Following the scratch tests, different failure modes have been identified such as plastic deformation, several types of through-thickness cracking (tensile cracking, conformal compressive cracking, forward chevron cracking and longitudinal cracking) and several types of interfacial failure (chipping at the edges of the scratch groove, buckling, spallation and blistering). Insofar as critical loads related to through-thickness cracking phenomena tend to reflect the toughness of the coatings and not the interfacial toughness of the coating/substrate systems, we focused on the critical loads of buckling, spallation and blistering in order to estimate the adhesion strengths for each substrate.

The three coated AA 2024 substrates showed a rather similar chronological event: simple plastic deformation at the beginning, followed by tensile cracking then conformal compressive cracking and at last, buckling then spallation of the coating. But depending on the surface pretreatment, each kind of failure mechanism was located at different critical loads. Fig. 2(a) illustrates how multiple failure mechanisms can occur during a single scratch test. Critical loads have been determined either visually (L_{c-0}), acoustically (L_{c-a}) or via abrupt changes of the measured friction force (L_{c-f}). For all three AA 2024 substrates, a critical load L_{c-f} has been reported by a noticeable change in the slope of the curve. This L_{c-f} seems to be related to the first occurrence of compressive conformal cracks, noted L_{c-01} . At slightly higher normal load, a L_{c-a} is clearly recognizable in the form of a sudden emergence of acoustic bursts. Once again, a correlation with a particular visual event can be highlighted: gross spallation of the coating, noted L_{c-02} .

The behavior of the coated TA6V substrate is radically different. As shown on Fig. 2(b), a massive blistering of the coating quickly occurs after a first simple plastic deformation

(at $L_{c-o1} \approx 2.5$ N). This identified visual event L_{c-o1} can be confirmed too on the acoustic emissions ($L_{c-a1} \approx 2$ N). The latter is smaller than L_{c-o1} because it is assumed that underneath invisible interfacial failure can occur before any visual evidence shows up at the coating surface. On the other hand, the blistering had manifestly no influence on the measured friction force. On top of this blistering effect, longitudinal cracking is spotted promptly followed by forward chevron cracking at $L_{c-o2} \approx L_{c-a2} \approx L_{c-f} \approx 8$ N. From this point, the height of the formed blister seems to wobble, influenced by the film cracking mechanisms. In contrast to the coated AA 2024 samples, an interfacial failure appears prior to any through-thickness cracking mode. This fact demonstrates the adhesion between the Ni film and the TA6V substrate is so weak that the interfacial toughness could be smaller than the film toughness.

We have been unable to estimate the adhesion strength for the Cu/PCB substrate as no event other than plastic deformation have been found along the whole scratch groove even after applying 30 N, the highest reachable normal force. This means either the adhesion of the Ni/Cu interface is so high that it is out of the loading range of the scratch device or the Ni/Cu couple is overall too ductile to be tested by scratching. Indeed, it has been reported that when both the coating and the substrate are made with high-ductility materials, the normal and tangential stresses created by the scratching stylus tend to be totally absorbed by plastic deformation of the coating and the substrate. As a result, no interfacial debonding can be initiated in those cases [9]. Registered fluctuations of the friction force are due to the woven fiberglass reinforcement of the PCB and the short single acoustic burst is supposed to be a measurement artifact.

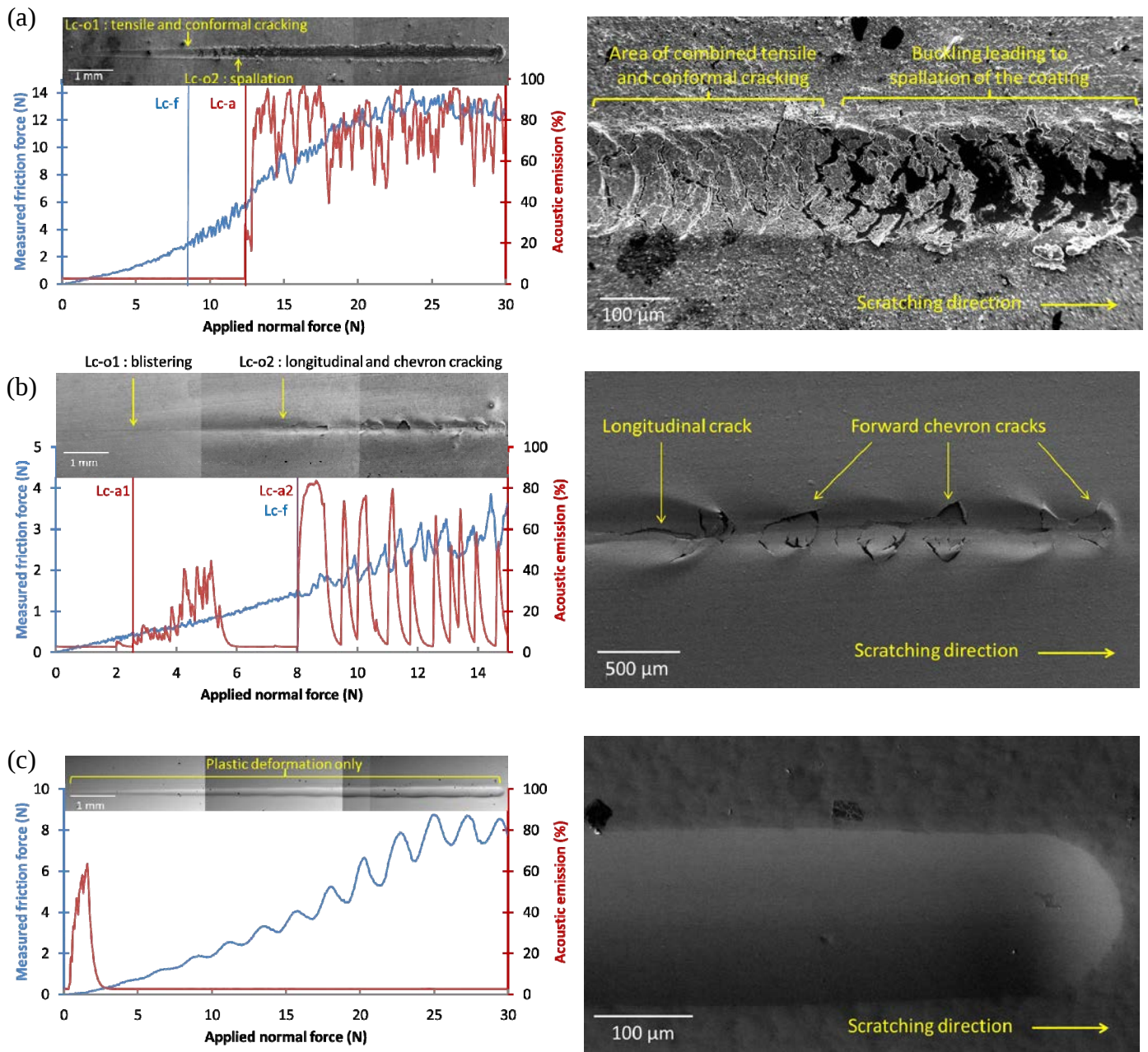


Figure 2. Critical loads identification by analysis of friction force and acoustic emission variations during a scratch test coupled with SEM micrographs of the residual scratch groove for the (a) Ni/Al double zincate stack, (b) Ni/TA6V stack and (c) Ni/Cu/PCB

Among all the type of critical loads registered, those determined by acoustic emission have been chosen as the most relevant criterion to compare adhesion of Ni on the studied substrates, especially due to the ability to detect firstly invisible interfacial failures. The processing of statistical data resulting from the whole scratch test campaign proved the ability of this test to discriminate adhesion differences between at least four out of the five chosen substrates. Table 1 sums up the mean values of acoustic critical loads corresponding to adhesive failure events on the five coating/substrate stacks.

TABLE I. SCRATCH TEST ADHESIVE FAILURE CRITICAL LOADS

Tested stack	Ni/TA6V	Ni/Al _{scraped}	Ni/Al _{blasted}	Ni/Al _{double zincate}	Ni/Cu/PCB
L_{c-a} (N)	2.41 blistering	5.99 spallation	7.60 spallation	12.44 spallation	> 30?

B. Microtensile tests

As the scratch test failed to characterize adhesion properties of the Ni/Cu/PCB, it was compulsory to find another test able to measure adhesion by applying a different mechanical stress field to samples.

According to the A&R model, the higher the adhesion is, the more the number of formed transverse cracks should increase during microtensile tests. Because this model is only applicable if the stress endured by the coating is purely uniaxial, only cracks located on homogeneously deformed areas of the specimens have been taken into account when performing the inter-crack spacing measurements. Fig. 3 shows

comparison between fractured specimens and emphasizes differences in cracks formation. In most cases, transverse cracks growing seem to initiate at the edge of the samples.

The Ni/Al_{scraped} specimens show a massive buckling of the coating especially at the vicinity and on the necking region which confirm the poor adhesion on this substrate. Besides the final mean inter-crack spacing is very wide (1053 μ m). The Ni/Al_{blasted} specimens present a better adhesion with much narrower cracks spacing (413 μ m) and the buckling is slight and limited to the edge of the necking region. As found by the scratch test, the third pretreatment Ni/Al_{double zincate} displays the higher adhesion behavior with even smaller cracks spacing (175 μ m) and nearly no buckled film parts.

It was found that the Ni/TA6V stack had the weakest adhesion: the Ni coating was completely delaminated and there was a unique through-thickness crack located at the center. Therefore, no inter-crack spacing measurement could be done on these specimens.

And finally, the Ni/Cu/PCB stack showed a rather unusual cracking behavior in comparison to the previous ones with much more dispersed crack spacing values, ranging from 475 μ m to 1100 μ m. This could indicate that the adhesion strength is not homogeneous along the length of the specimen. Insofar this stack was the only one not having undergone laser cutting (because it was not suitable for the materials composing the PCB) but have been mechanically cut by a milling machine, we could imagine that the cutting tool have locally weakened the interfacial toughness. This mechanical process could also explain the irregular spacing between cracks. Despite this fact, the maximum interfacial shear stress has been nevertheless calculated using the mean crack spacing (856 μ m).

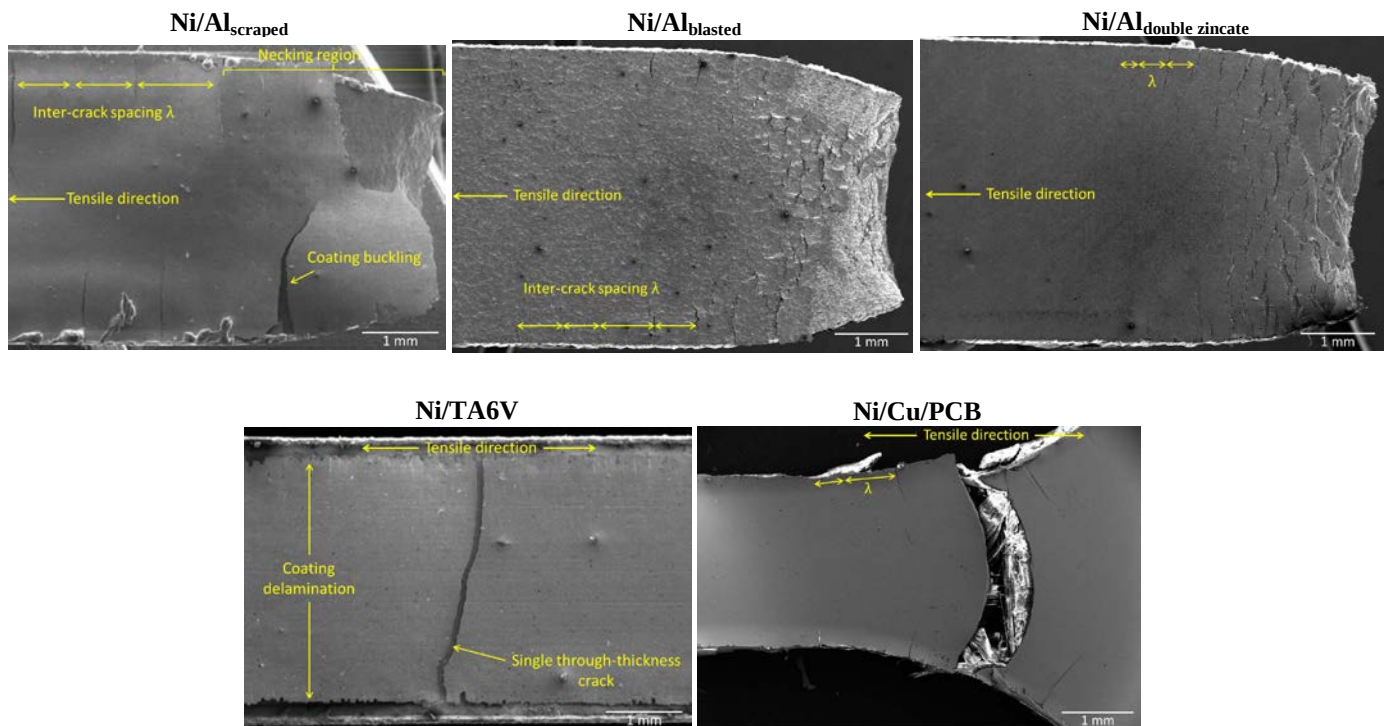


Figure 3. SEM top view micrographs from the fractured areas of the different microtensile specimens

Table II sums up the values of the first cracking strain ε_f and λ which is the final mean inter-crack spacing found after performing the microtensile test on the five studied stacks. Calculated values of the maximum shear strength τ are also provided for all stacks but the Ni/TA6V although we consider adhesion tests performed on the Ni/Al_{blasted} and the Ni/Al_{double zincate} are accurately fitting the A&R model. Indeed, the model not only suppose a pure uniaxial stress but also that the accumulation of tensile shear stresses is only freed by parallel and regularly spaced transverse cracks which would create a sinusoidal distribution of stresses along the length of the coating. Areas with minimum stresses would be located at the vicinity of cracks whereas areas of maximum stresses concentration would be located at mid-distance between two cracks.

The Ni/Al_{scraped} specimen on Fig. 3 evidently showed that during the test all the tensile shear stresses imposed by the substrate elongation are not totally converted into through-thickness cracking. Indeed the large areas of buckled coating tend to prove that a part of the energy is spent into interfacial delamination. Finally, the τ value found for the Ni/Cu/PCB is probably biased due to the weakening of the Ni/Cu bonding during the specimen mechanical cut step as mentioned previously.

TABLE II. OUTPUT VALUES AFTER MICROTENSILE TESTS

Tested stack	Ni/TA6V	Ni/Al _{scraped}	Ni/Al _{blasted}	Ni/Al _{double zincate}	Ni/Cu/PCB
ε_f (%)	4,77 %	0.40 %	1.33 %	2.21 %	2.08 %
λ (μm)	∞	1053	413	175	856
τ (MPa)	≈ 0	48	405	1586	305

V. CONCLUSION

Adhesion estimations from the scratch tests and the microtensile tests were consistent with each other concerning the TA6V and the three AA 2024 substrates. For both tests, the Ni/TA6V stack has been identified by far as the least adhesive. Then came the Ni/Al_{scraped} followed somewhat closely by the Ni/Al_{blasted} and finally, the Ni/Al_{double zincate} clearly higher.

The poor adhesion strength found for the scraped AA 2024 and the TA6V substrates are almost certainly due to the remaining of their thin native oxide layers (respectively Al₂O₃ and TiO₂) which tend to naturally weaken adhesion on these materials. Conversely, the double zincate pretreatment allows having interfaces free of native oxides and consequently provides much better adhesion abilities as confirmed by the results.

Furthermore, a noteworthy fact is that contrary to most of other adhesion tests, the microtensile test shows up to be better-fitted when adhesion of samples is higher. Indeed, with lower adhesion as for the Ni/Al_{scraped} stack, the coatings have a higher chance of dissipating shear stresses by interfacial failure mechanisms additionally to the simple transverse cracking. This makes the A&R model hardly applicable although the fraction of delaminated area can be useful to achieve a semi-quantitative adhesion assessment [6].

As for the Ni/Cu/PCB stack, it shows the difficulty in finding a proper adhesion test for a mainly ductile stack with a high adhesion metal/metal interface. Nonetheless, the microtensile test may be adapted if a proper specimen preparation is developed to minimize adhesion weakening at the edges.

ACKNOWLEDGMENT

The authors wish to acknowledge Jacques Debard (Lycée Jean Dupuy, Tarbes, France) for providing the deposited samples.

REFERENCES

- [1] A.A. Volinsky, N.R. Moody, W.W. Gerberich, "Interfacial toughness measurements for thin films on substrates", *Acta Materialia* 50 (2002) 441-466.
- [2] S.J. Bull, E.J. Berasetegui, "An overview of the potential of quantitative coating adhesion measurement by scratch testing", *Tribology International* 39 (2006) 99-114.
- [3] J. Alexis, C. Gaussens, B. Etcheverry, J-P Bonino, "Development of nickel-phosphorus coatings containing talc phyllosilicates", *Material Chemistry and Physics* 137 (2013) 723-733.
- [4] E. Harry, M. Ignat, A. Rouzaud, P. Juliet, "Cracking investigation of W and W(C) films deposited by physical vapor deposition on steel substrates", *Surface and Coatings Technology* 111 (1999) 177-183.
- [5] B.F. Chen, J. Hwang, G.P. Yu, J.H. Huang "In situ observation of the cracking behavior of TiN coating on 304 stainless steel subjected to tensile strain", *Thin Solid Films* 352 (1999) 173-178.
- [6] H.W. Choi, K-W Lee, R. Wang, K.H. Oh, "Fracture behavior of diamond-like carbon films on stainless steel under a microtensile test condition", *Diamond and related materials* 15 (2006) 38-43.
- [7] M.J. Cordill, V.M. Marx, "Fragmentation testing for ductile films on polymer substrates", *Philosophical Magazine Letter* 93:11 (2013) 618-624.
- [8] D.C. Agrawal, R. Raj, "Measurement of the ultimate shear strength of a metal-ceramic interface", *Acta Metallurgica* 37 (1989) 1625-1270.
- [9] S.J. Bull, "Failure mode maps in the thin film scratch adhesion test", *Tribology International* 30 (1997) 491-498.

Patrick Nguyen received the engineer's degree in 2012 in engineering physics from the Institut National des Sciences Appliquées (INSA, Toulouse, France). Currently he is pursuing a Ph.D degree in material sciences at the Centre National d'Etudes Spatiales (CNES, Toulouse, France) and the Laboratoire Génie de Production (LGP, Tarbes, France), working on thin films adhesion tests for failure analysis of materials and components.