UDK 669.058.6:544.722.54
Original scientific article/Izvirni znanstveni članek

ISSN 1580-2949
MTAEC9, 58(1)47(2024)

MEASUREMENT OF ADHESION PROPERTIES OF Ni_2Al_3 COATING WITH A MICRO SCRATCH TESTER AND AUTOMATIC SCRATCH TESTER

DOLOČITEV ADHEZIJSKIH LASTNOSTI Ni_2Al_3 PREVLEKE Z MIKROMETROM IN AVTOMATSKIM TESTERJEM RAZENJA

Ningning Li[1,2,3], Lei Xu[1*], Jin Peng[1], Xi Chen[1], Mingqi Tang[4], Jiajia Yang[1], Yan Shang[5]

[1]School of Materials Science and Engineering, North China University of Water Resources and Electric Power, Zhengzhou 450045, P. R. China
[2]Post-Doctoral Research Mobile Station of Chemistry, Henan University, Zhengzhou 450046, P. R. China
[3]Zhengzhou Dingsheng Engineering Technology Co., Ltd., Zhengzhou 450001, P. R. China
[4]Ural Institute, North China University of Water Resources and Electric Power, Zhengzhou 450045, P. R. China
[5]School of Mechanical Engineering, North China University of Water Resources and Electric Power, Zhengzhou 450045, P. R. China

Prejem rokopisa – received: 2023-06-27; sprejem za objavo – accepted for publication: 2023-12-15

doi:10.17222/mit.2023.920

A functionally graded Ni_2Al_3 coating, prepared with a two-step method of nickel electroplating and pack aluminizing, can improve the hardness of low-carbon steel and other surface performance features. However, the adhesion between the coating and the substrate is an important factor affecting these properties. The primary purpose of this study was to introduce a test for determining the adhesion of the Ni_2Al_3 coating, which included two tools, namely a micro scratch tester (MST) and a WS-2000 automatic scratch tester, used for measuring the coating adhesion and observing the scratch morphology. Results show that the adhesion is about 14 N according to the MST, which is equivalent to 56 N obtained with WS-2000. As the load increases, the scratches gradually become larger and deeper. Finally, the surface morphology shows cracks, indicating that the coating has failed.

Keywords: Ni_2Al_3 coating, automatic scratch tester, adhesion, cracks

Funkcionalno stopnjevane Ni_2Al_3 prevleke na nizko ogljičnih jeklih lahko izboljšajo njihovo površinsko trdoto. Nadalje se izboljšajo tudi druge površinske lastnosti pri dvostopenjski metodi platiranja niklja in aluminiziranja s kemičnim postopkom v parni fazi. Vendar pa je kakovost adhezije med prevleko in podlago pomemben faktor, ki vpliva na mehanske lastnosti spoja. Avtorji v tem članku opisujejo dve metodi preizkušanja kakovosti adhezije Ni_2Al_3 prevleke. Kot prvo metodo so uporabili mikrometerski tester razenja (MST; angl.: micrometer scratch tester) in kot drugo avtomatski tester razenja WS-2000. Sledile so meritve adhezije (fizikalno-kemijske vezi) med prevleko in substratom ter analiza morfologije nastalih raz. Rezultati meritev so pokazali, da je adhezija izmerjena z metodo MST približno 14 N, kar odgovarja približno 56 N pri uporabi testerja WS-2000. Z naraščajočo obremenitvijo postajajo raze večje in globlje. Nazadnje pa pri najvišjih uporabljenih obremenitvah morfologija raz pokaže začetek odpovedi (lupljenja) prevlek.

Ključne besede: Ni_2Al_3 prevleka, avtomatski tester razenja, adhezija, razpoke

1 INTRODUCTION

Functionally graded materials (FGMs) are a class of non-homogeneous composite materials that exhibit continuous and quasi-continuous changes in the structure and elements, and also performance and composition changes in the gradient. Their microstructures, physical, chemical and biological properties show continuous changes in a single phase, or a combination of phases, to achieve a particular function. FGMs are one of the crucial topics relating to the current structural and functional materials.[1] A functionally graded coating is classified according to the changes in the composition, relating to the surface technology, and its potential applications are primarily found in high-temperature, wear, corrosion and other areas.[2,3]

In recent years, a series of intermetallic compound coatings have been researched due to their high melting points, low densities and excellent corrosion resistance at high temperatures. Ni-Al intermetallic compound coatings have been applied to high-temperature alloy surfaces because they easily form a dense alumina layer at high temperatures.[4,5] Pack aluminizing is the favored method, used for preparing nickel-aluminum coatings on Ni-based alloys. However, to make nickel-aluminum coatings on other metal surfaces, a typical two-step process of nickel plating and powder aluminizing has been invented.[6–8] In addition to its advantages including high quality, simple operation, few technical difficulties and low investment in the equipment, this method also reduces the influence of the substrate chemical composition on the formation of an aluminized coating while simultaneously using a low aluminizing temperature. This low temperature can also protect the substrate properties;

---

*Corresponding author's e-mail:
xulei2022@ncwu.edu.cn (Lei Xu)

so, in recent years, increasing research on this method has been carried out.

In addition to focusing on the preparation methods, there is also research on the coating performance, such as hardness,[9] oxidation[10] and wear.[11] M. Li[10] researched the Ni-Al coating with and without a diffusion barrier, and found that the Ni-Al/Ni-Re coating exhibits better resistance to inner oxidation. T. Yu[11] studied the microstructure and high-temperature wear behavior of a laser clad TaC-reinforced Ni-Al-Cr coating, and came to the following conclusion: since Ta promotes the sintering of the protective oxide layer, by suppressing the growth of Al_2O_3, a continuous compact oxide layer develops on the worn surface of a composite coating at high temperatures, which is the main reason for improving the wear resistance of the substrate. Compared to other factors, the coating adhesion is the parameter that directly affects the other properties. For instance, the adhesion between the coating and substrate is a very important mechanical property of a hard coating, so adhesion characterization is an important research field.[12,13]

In the initial research, the hardness of the Ni_2Al_3 coating was characterized with a nanoindentation test.[14] The main research goal of this study was to investigate the adhesion of the coating, using a micro scratch tester (MST) and an automatic scratch tester. In addition to measuring the binding force, the indentation morphology of the Ni_2Al_3 coating was also observed with a microscope.

2 EXPERIMENTAL PART

2.1 Materials

The substrate used was the Q235 low-carbon steel, with a nominal chemical composition shown in **Table 1**. Detailed experimental procedures of nickel plating and pack aluminizing used on the substrate were described in our preliminary work, and the main conclusions were already analyzed and discussed.[14] For ease of explanation, the main preliminary outcomes are summarized as follows: the single Ni_2Al_3 coating phase can be fabricated with 8 *w*/% Al pack cement, and the coating thickness is approximately 30 µm, while the interdiffusion zone thickness is 20 µm, with the Al, Ni and Fe elements. The hardness of the Ni_2Al_3 coating layer characterized with nanoindentation is about 15.05 GPa, which is higher than that of the interdiffusion zone and the Q235 substrate.[14]

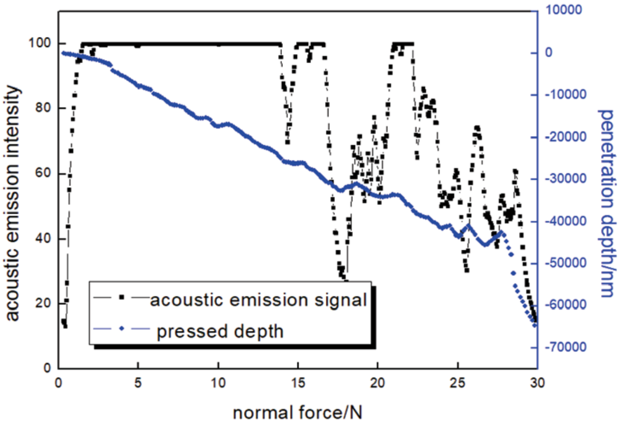

Figure 1: Acoustic emission signal and indentation depth during the loading with the MST on the Ni_2Al_3 coating

Table 1: Nominal chemical composition of Q235 low-carbon steel (*w*/%)

Composition	C	Mn	Si	S	P	Fe
Content	0.140-0.220	0.300-0.650	0.300	≤0.050	0.045	Bal.

2.2 Adhesion test

The adhesion test of the Ni_2Al_3 coating was done with the micro scratch tester and the automatic scratch tester. Namely, the micro scratch tester (MST), which came from Switzerland, was equipped with a Rockwell diamond indenter, with a radius of curvature of 100 µm, a cone angle of 120°, a loading range of 0–30 N and a loading speed of 59.4 N/min. In addition to collecting acoustic emission signals, it can also observe the scratch morphology. The WS-2000 automatic scratch tester (Zhongke Kaihua Technology Co., Ltd., China) was also used to verify the adhesion evaluation. The specific loading form included a normal loading range of 0–100 N, and a curvature radius of the diamond indenter tip of 200 µm. The cone angle was also 120°, and only acoustic emission signals were collected during the test.

3 RESULTS AND DISCUSSION

3.1 Acoustic emission signal and indentation morphology detected by the MST

Previous studies showed that the prepared Ni_2Al_3 coating thickness is approximately 30 µm.[14] **Figure 1** shows the acoustic emission signal and indentation depth as the load changes from 0 N to 30 N. It can be seen that the indentation depth gradually deepens as the loading increases. The acoustic emission intensity rapidly increases from the starting point, then there is a stable period until the loading force is about 14 N, after which it suddenly drops. Afterward, the acoustic emission intensity rises and then falls again to a lower value; later the change curve becomes very chaotic, then it reaches a stable state, and again drops to the lowest point in a disorderly manner. During the process of gradually loading normal loads along the coating surface with diamond indenters, the coating may exhibit microcracks, fractures, detachment from the substrate and plastic failure (referring to plowing). When the Ni_2Al_3 coating exhibits a binding failure, the peak of the acoustic emission signal suddenly changes. However, the interference with the acoustic signal, the presence of large particles in the coating and other factors may also generate an acoustic

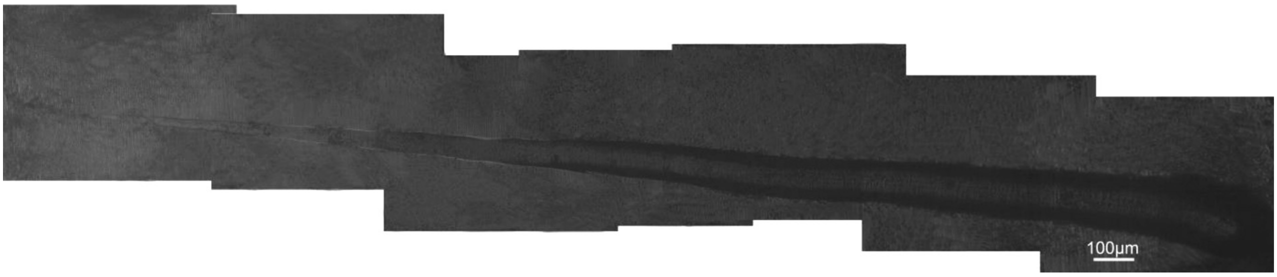

Figure 2: Overall scratch morphology of the Ni_2Al_3 coating after MST testing

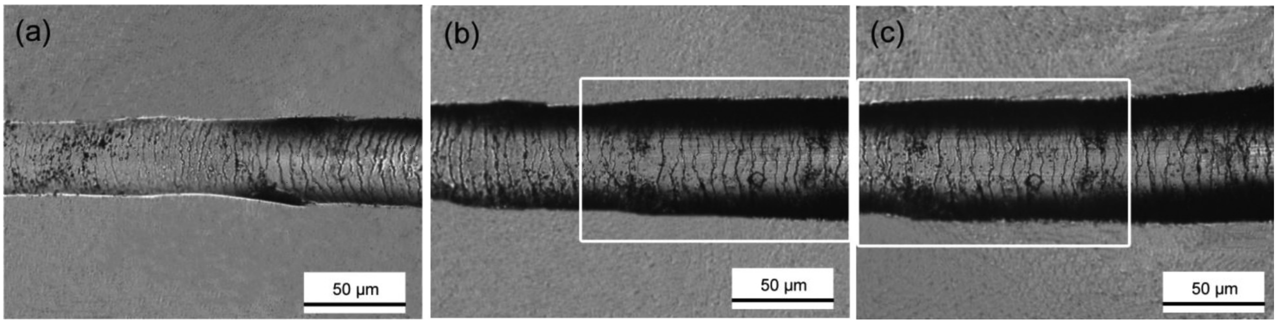

Figure 3: Scratch morphology of the Ni_2Al_3 coating in three stages of the loading process: a) low load, b) critical load L_c, c) high load

emission mutation. Therefore, it can be inferred that at the pressing depth of approximately 20–30 μm, there is a sudden change in the acoustic emission peak, followed by a more unstable one. It can be preliminarily determined that the bonding force of the Ni_2Al_3 coating is about 14 N.

Figure 2 shows the overall morphology of the scratches. It can be seen that the direction of the scratches is from left to right, and the traces develop from shallow to deep, becoming increasingly wide. The larger the black area on both sides of a scratch, the greater is the pressure, which is due to a deeper indentation. During the entire loading process, the scratch morphology was captured under the low load, critical load and high load, as shown in **Figure 3**. At the low load, the interior of the scratch is initially smooth, but as the load increases, a few cracks begin to appear within the scratch. The overall width of the scratch is small, with slight plastic deformation, as shown in **Figure 3a**. With the load increase and after an indentation inside the scratch, regular transverse cracks, originating from the surface, are caused by elastic recovery. Under the action of increasing load, the coating is gradually pressed into the substrate, and plastic deformation occurs, resulting in new transverse cracks. As the load continues to increase, the cracks gradually become denser and the direction is irregular until there is a large peeling of the coating inside the scratch, when the width of the scratch significantly widens and plastic deformation suddenly increases. At this time, the load becomes critical load L_c leading to the failure of the coating/substrate interface, as seen in **Figure 3b**. It corresponds to the load of 14 N from **Figure 1**. After the load exceeds L_c, the coating quickly fails, and the indenter directly contacts the substrate, causing a rapid increase in plastic deformation of the substrate, as shown in **Figure 3c**. There is a partial overlap with the morphology from **Figure 3b**, shown by the white box in the figure.

3.2 Acoustic emission spectrum and scratch morphology obtained with the WS-2000 scratch instrument

Figure 4 shows the acoustic emission spectrum of the sample obtained with the WS-2000 scratch tester. It can be seen that the acoustic emission signal appears weak and discontinuous when the load is between 0 N and 50 N, indicating that there is an interference signal or large particle peeling. The weak and discontinuous signal does not indicate a critical load leading to a coating failure. Between 50 N and 60 N, the peak value of the acoustic emission signal is high and continuous, indicating that the coating has peeled off and failed, and the

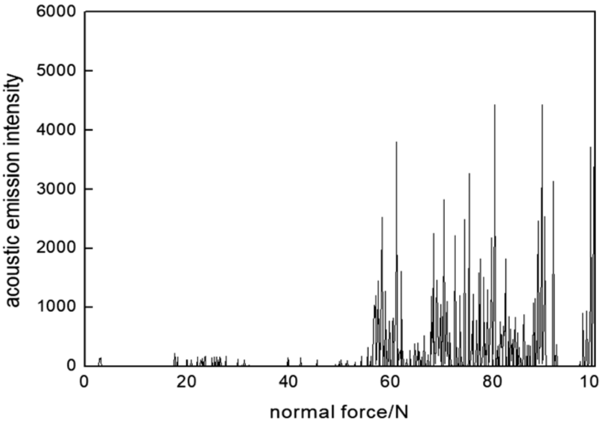

Figure 4: Acoustic emission spectra of the Ni_2Al_3 coating obtained with the WS-2000 scratch tester

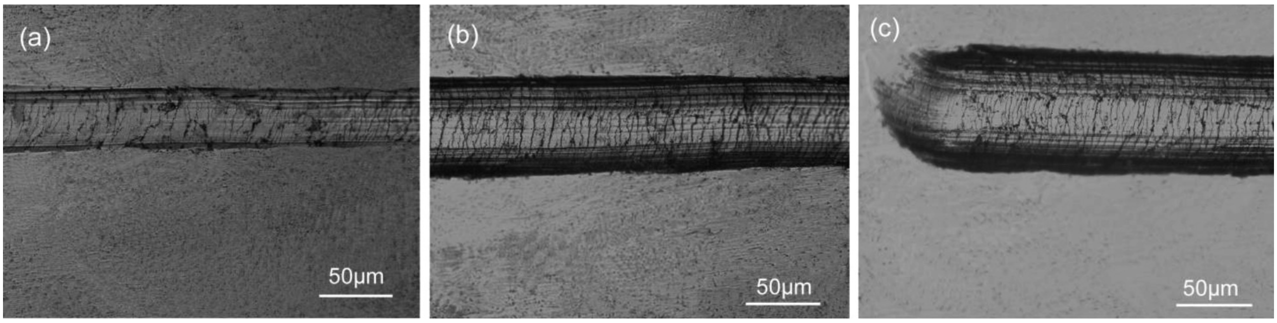

Figure 5: Morphology of the Ni_2Al_3 coating characterized by the WS-2000 scratch tester at different stages: a) start, b) middle, c) end

indenter has scratched into the substrate. From the data on the graph, it can be roughly inferred that the boundary adhesion between the coating and the substrate is about 56 N.

The scratch method is used to measure the critical load, and its value is proportional to the curvature radius square of the indenter.[15] The curvature radius used for the MST is 100 μm. The curvature radius used for the WS-2000 scratch tester is 200 μm. This means that if the critical load value measured by the MST is 14 N, it is equivalent to a critical load value of 56 N measured by the WS-2000 scratch tester. It can be seen that the two detection results match perfectly.

Figure 5 shows photos of the Ni_2Al_3 coating scratch morphology obtained with the WS-2000 scratch tester. From the figure, it can be seen that the scratches were shallow, with fewer and finer cracks at the initial stage, as shown in **Figure 5a**. **Figures 5b** and **5c** show that the shaded areas on both sides of the scratch gradually increase, indicating that the scratch depth is increasing, and the scratch surface cracks are also becoming larger and deeper, with some cracks even showing fractures.

3.3 Analysis of the Ni_2Al_3 coating adhesion

The formation of the Ni_2Al_3 coating is analyzed below. Firstly, the reaction between the aluminum powder and penetrating agent generates a series of aluminum chlorides,

$$Al + 2AlCl_3 \rightarrow 3AlCl_2 \tag{1}$$

$$2Al + AlCl_3 \rightarrow 3AlCl \tag{2}$$

Subsequently, aluminum chloride comes into contact with the nickel-plated substrate, releasing aluminum atoms. Aluminum atoms further diffuse into the nickel-plated matrix to form intermetallic compounds.

$$3[Al] + 2Ni \rightarrow Ni_2Al_3 \tag{3}$$

A schematic diagram of the Ni_2Al_3 coating formation is shown in **Figure 6** where Al represents aluminum atoms. In the first step, the coating is generated by the reaction of aluminum powder and the catalyst. In the second step, aluminum atoms diffuse into the nickel-plated surface. Finally, the coating is formed on the surface, and it is mainly composed of the Ni_2Al_3 phase. In addition to the internal diffusion of aluminum atoms, iron atoms diffuse outward to form a diffusion zone between the coating and substrate, which contains Fe, Ni and Al.[10,14] This indicates that the coating and substrate have achieved metallurgical bonding, which is the highest form of bonding strength.

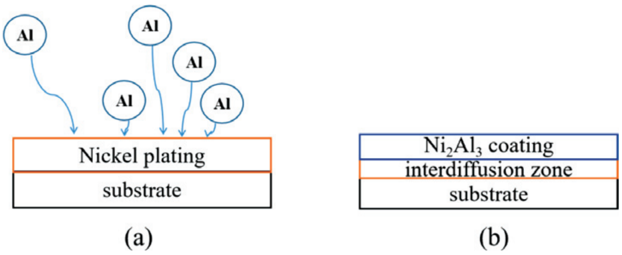

Figure 6: Schematic diagram of the Ni_2Al_3 coating formation

4 CONCLUSIONS

From the study, the following conclusions can be drawn:

(1) The critical bonding force L_c of the Ni_2Al_3 coating is 14 N according to the MST, and the scratch morphology shows that as the loading increases, the scratch gradually becomes larger and wider, while cracks and fractures are also observed simultaneously.

(2) The critical load value measured with the WS-2000 scratch tester is 56 N. According to the morphology observed, the scratch depth increases and the surface cracks also become larger and deeper.

(3) The Ni_2Al_3 coating is formed due to the internal diffusion reaction, during which aluminum atoms penetrate the nickel-plated layer, forming a metallurgical bond between the infiltrated layer and substrate, which results in a high bonding strength.

Acknowledgment

This research was funded by the Key R & D and Promotion Project of the Henan Province (Science and Technology Research) (No. 232102220052), the Key Scientific Research Projects of Higher Education Institutions in the Henan Province (No. 24A460017) and the High-Level Introduction of Talent Research Start-Up

Fund of the North China University of Water Resources and Electric Power (No. 4001/40680).

5 REFERENCES

[1] Y. Tang, Z. S. Ma, Q. Ding, T. Wang, Dynamic interaction between bi-directional functionally graded materials and magneto-electro-elastic fields: A nano-structure analysis, Compos. Struct., 264 (**2021**) 8, 113746, doi:10.1016/j.compstruct.2021.113746

[2] M. J. Yu, A. X. Feng, L. J. Yang, M. E. Thomas, Microstructure and corrosion behaviour of 316L-IN625 functionally graded materials via laser metal deposition, Corros. Sci., 193 (**2021**), 109876, doi:10.1016/j.cors ci.2021.109876

[3] S. Chandrasekaran, S. Hari, M. Amirthalingam, Functionally graded materials for marine risers by additive manufacturing for high-temperature applications: Experimental investigations, Structures, 35 (**2022**), 931–938, doi:10.1 016/j.istruc.2021.12.004

[4] X. Z. Fan, L. Zhu, W. Z. Huang, Investigation of NiAl intermetallic compound as bond coat for thermal barrier coatings on Mg alloy, J. Alloy. Compd., 729 (**2017**), 617–626, doi:10.1016/j.jallcom.2017.09.190

[5] X. Chen, C. Li, S. J. Xu, Y. Hu, G. C. Ji, H. T. Wang, Microstructure and Microhardness of Ni/Al-TiB2 composite coatings prepared by cold spraying combined with post annealing treatment, Coatings, 9 (**2019**) 9, 565, doi:10.3390 /coatings9090565

[6] X. X. Zhao, X. M. Li, M. F. Li, C. G. Zhou, Comparison of the corrosion resistance of Ni$_2$Al$_3$ coating with and without Ni-Re interlayer in dry and wet CO$_2$ gas, Corros. Sci., 159 (**2019**), 108121, doi:10.1016/j.corsci. 2019. 108121

[7] Y. D. Wang, Y. P. Zhang, G. Liang, Q. L.Ding, Low temperature formation of aluminide coatings on the electrodeposited nanocrystalline Ni and its oxidation resistance with La$_2$O$_3$/CeO$_2$ nanoparticle dispersion, Vacuum, 173 (**2020**), 109148, doi:10.1016/j.vacuum.2019.109148

[8] Y. T. Zhao, Z. H. Tian, B. B. Li, H. P. Ren, Effect of rare earth(CeCl3) on oxidation resistance of Ni$_2$Al$_3$/Ni composite coatings on heat-resistant steel, Rare. Metal. Mat. Eng., 48 (**2019**) 11, 3452–3432, doi:CNKI: SUN: COS E.0.2019-11-002

[9] K. Mausam, M. Goyal, Development of nanocrystalline Ni-Al coatings and its thermal stability, Mater. Today: Proced., 37 (**2021**) 2, 3189–3193, doi:10.1016/j.matpr.2020.09.059

[10] M. Li, C. Kong, J. Zhang, C. Zhou, D. J. Young, Oxidation behavior of Ni-Al coating with and without a Ni-Re diffusion barrier in dry CO$_2$ gas at 650 °C, Corros. Sci., 149 (**2019**) 1, 236–243, doi:10.1016/j. corsci. 2019. 01.021

[11] T. Yu, H. Tang, Microstructure and high-temperature wear behavior of laser clad TaC-reinforced Ni-Al-Cr coating, Appl. Surf. Sci., 592 (**2022**), 153263, doi:10.1016/j.apsusc.2022.153263

[12] B. J. Harder, M. J. Presby, J. A. Salem, S. M. Arnold, S. K. Mital, Environmental barrier coating oxidation and adhesion strength, J. Eng. Gas. Turb. Power, 143 (**2021**), 031004, doi:10.1115/1.4049414

[13] G. Singh, A. Saini, B. S. Pabla, Preparation and characterization of Sr-doped HAp biomedical coatings on polydopamine-treated Ti6Al4V substrates, Surf. Rev. Lett., 30 (**2023**) 1, doi:10.1142/S0218625 X21410092

[14] N. N. Li, L. Xu, L. Huang, Y. T. Tong, Z. Q. Jiang, K. L. Li, Preparation and hardness of a functionally graded Ni-Al coating, Mater. Tehnol., 57 (**2023**) 1, 27–33, doi:10.17222/mit.2022.650

[15] Y. F. Gao, H. T. Xu, W. C. Oliver, G. M. Pharr, Effective elastic modulus of film-on-substrate systems under normal and tangential contact, J. Mech. Phys. Solid., 56 (**2008**) 2, 402–416, doi:10.1016/j.jmps.2007.05. 015