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Improved the Wear Resistance of Ti/Cu Multilayer Film by Nitriding

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Abstract: In this study, Ti/Cu multilayer film was deposited by magnetron sputtering and then nitrided at 800 and 900 °C in N_2. The microstructure and wear performance were studied. The deposited Ti/Cu multilayer film mainly consisted of Ti and Cu phases. After nitriding, the film mainly consisted of Cu_4Ti_3, CuTi, and TiN phases, indicating the interface reaction and nitriding reaction occurring. The surface microstructure of the Ti/Cu multilayer film became denser after nitridation. The wear resistance of the Ti/Cu multilayer film improved after nitriding. After nitriding at 900 °C for 2 h, the maximum wear track depth of the multilayer film was ~0.73 μm, which is just 65% of the deposited Ti/Cu multilayer film. The wear mechanism of the Ti/Cu multilayer film before and after nitriding was abrasive and adhesive wear.

Keywords: magnetron sputtering; Ti/Cu multilayer film; nitriding; wear resistance

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Citation: Fang, H.; Zhao, H.; He, J. Improved the Wear Resistance of Ti/Cu Multilayer Film by Nitriding. *Coatings* **2022**, *12*, 987. https://doi.org/10.3390/coatings12070987

Academic Editor: Sławomir Kowalski

Received: 4 May 2022
Accepted: 9 July 2022
Published: 13 July 2022

1. Introduction

In recent years, the Cu based metallic multilayer films have aroused the researchers' attention as the promising materials meeting the requirement for the harsh environment, owing to their desirable properties, such as high toughness, stable chemical inertness, and good adhesion [1–3]. However, for the severe tribo-applications, the service life of these metallic multilayer films is limited because of the relative low hardness and wear resistance [4,5]. Compared with the metallic multilayer films, the metallic-ceramic multilayer films exhibit higher hardness and better wear resistance, which are viable for the tribo-applications for the surface of the moving parts (such as bearings, pistons, and gears) [6–8]. These films are often deposited using one-step method (physical/chemical vapor deposition) by the researchers. However, because of the metal Cu with the weak chemical affinity to ceramics, the layer–layer interfaces prepared using a one-step method have difficulty bond well, then their whole performance would be affected [9].

In many industrial applications, the nitriding is an effective method to enhance the surface hardness of the metals by forming metallic nitrides [10]. Recently, some researchers have nitrided the deposited metallic films to improve their performance. For instance, Zhang et al. [11] first deposited Cr film on Al substrate and then nitrided it to prepare a Cr-N/Al-Cr multilayer; their results showed that the surface hardness increased from 1.57 GPa (Al) to 9.21 GPa with a denser microstructure and a lower friction coefficient by the formation of nitrides and interfacial reactive diffusion. Wang et al. [12] also prepared the Mo_2N films with a superconducting effect by depositing, and high-temperature Mo films were nitrided. These studies suggest that the deposition + nitriding (two-step method) could be a promising technology to prepare the Cu-metallic multilayer films with the improved properties by nitriding the metallic. In addition, the elemental diffusion at the interfaces of Cu and metallic under heating action could promote their bonding strength. Among the Cu-metallic multilayer films, Cu-Ti based films have been widely studied [13–15]. According to Ref. [9], Cu-TiN multilayer films have better mechanical performance compared to Cu-Ti films. However, few studies on Cu-TiN multilayer films have been reported and no studies on the nitriding of the Cu-Ti multilayer films to form Cu-TiN multilayer films have been reported.

In this context, we prepared Cu-Ti multilayer film and then nitrided it at 800 and 900 °C. Their microstructure was analyzed, and the wear resistance was assessed.

2. Materials and Methods

Al_2O_3 ceramic pieces (Size: 100 mm × 100 mm × 1 mm) were used as the film substrate. Ti target (Purity: 99.99%, Size: Φ140 mm × 10 mm) and Cu target (Purity: 99.99%, Size: 1360 mm × 125 mm × 10 mm) were used as the sputtering materials. The schematic diagram of the preparation and nitridation process of the Ti/Cu multilayer film is displayed in Figure 1. Firstly, the Al_2O_3 substrate was ultrasonic cleaned to remove the surface contaminants. Then, they were put into the sputtering chamber to deposit the film. Before deposition, the base pressure was 5.0×10^{-3} Pa. Ar was used as the sputtering gas, and the pressure was adjusted to 0.19 Pa. The Ti target power was 10 kW with a deposition rate of 0.7 nm/s, and the Cu target power was 36 kW with a deposition rate of 0.83 nm/s. Each Ti or Cu layer thickness was 100 nm, and it repeated 5 times with the deposition sequence of Ti/Cu/Ti/Cu/Ti/Cu/Ti/Cu/Ti/Cu. Finally, the deposited Ti/Cu multilayer film was placed in a quartz tube furnace by injecting with purity-99.99% N_2. The temperate was set at 800 and 900 °C (Heating rate: 10 °C/min) for 2 h.

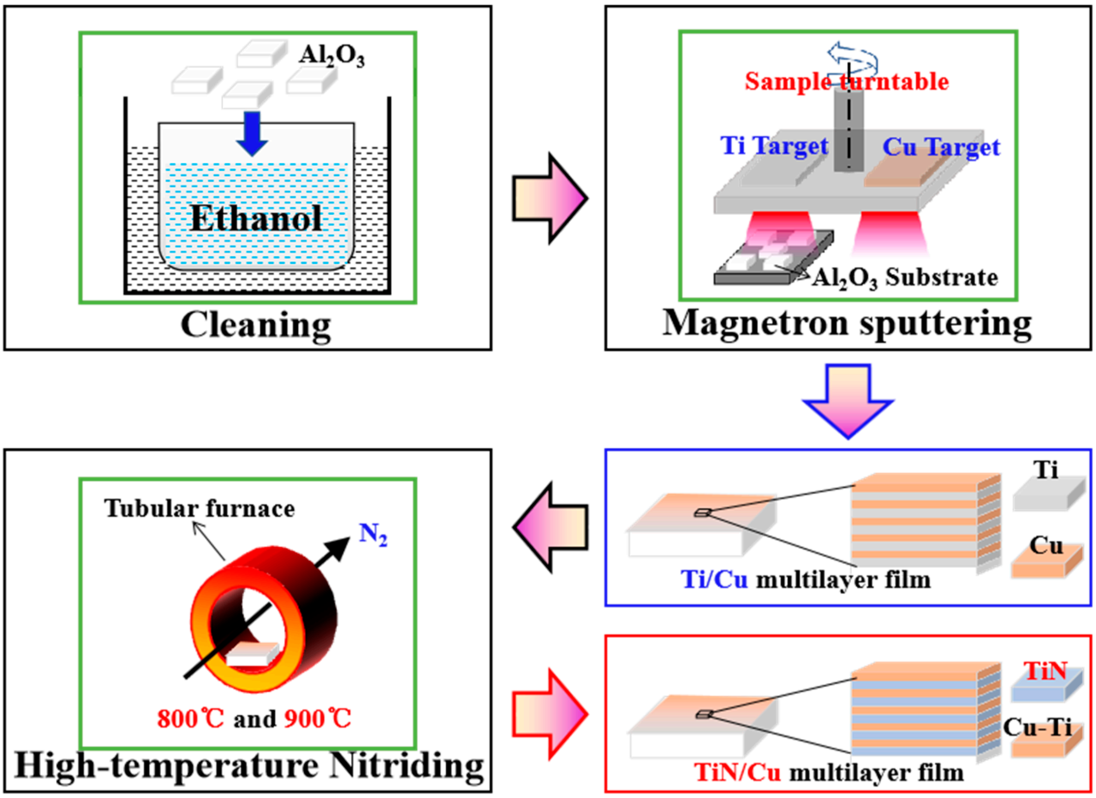

Figure 1. Schematic diagram of the preparation and nitridation process of the Ti/Cu multilayer film.

For the Ti/Cu multilayer film, their phase was determined by D/max2500 X-ray diffractometer (XRD, Rigaku, Tokyo, Japan) with a Cu Kα source, the scanning angle was 20°–80°, the measurement speed was 4°/min, and the working power was 30 kW. Their surface and wear track morphologies were observed by LaB6 scanning electron microscopy (SEM, Acceleration voltage: 30 kV, JSM-6510A, JEOL, Tokyo, Japan). The hardness (Scratch load: 10 g) and cohesion strength (Scratch load force range: 0–100 N (Loading rate: 40 N/min)) were assessed using a scratch meter (WS-2005, Zhongkekaihua Technology Development Co., Ltd., Lanzhou, China). Their friction coefficient and wear track profile were assessed using an SFT-2M tribometer (Friction counterpart: GCr15, Loading: 10 N, Time: 2 min, Speed: 400 r/min, Radius: 3 mm (Zhongkekaihua Technology Development Co., Ltd., Lanzhou, China)).

3. Results

Figure 2 displays the XRD patterns (Scanning angle: 20–80°) of the Ti/Cu multilayer film before and after nitriding. The deposited Ti/Cu multilayer film mainly consists of Ti phase (PDF card: 44-1294) and Cu phase (PDF card: 04-0838). A small amount of TiO_2 phase was also detected. After nitriding at 800 °C for 2 h, besides TiO_2 phases, Cu_4Ti_3, CuTi, and TiN phases were also detected in the multilayer film. The TiN phase (PDF card: 38-1420) was formed from the nitridation reaction of Ti in a high-temperature N_2 atmosphere. In addition, the presence of Cu_4Ti_3 and CuTi phases indicates that the Ti/Cu interface reaction occurred during the nitriding process, which is because of the high temperature promoting the Ti/Cu element diffusion. This could increase the cohesive strength of the multilayer film. Similarly, after nitriding at 900 °C for 2 h, the phases of TiO_2, Cu_4Ti_3, CuTi, and TiN were also detected in the multilayer film. The peak intensities of the reacted phases (Cu_4Ti_3, CuTi, and TiN) increase, indicating the degree of interface reaction and nitriding reaction increasing. The higher temperature could promote the diffusion and activation of the Ti/Cu/N elements and then form more reacted phases. No copper nitride phases were formed because Cu and nitrogen are difficult to react and present at this experiment conditions (Cu_3N would decompose at ~450 °C).

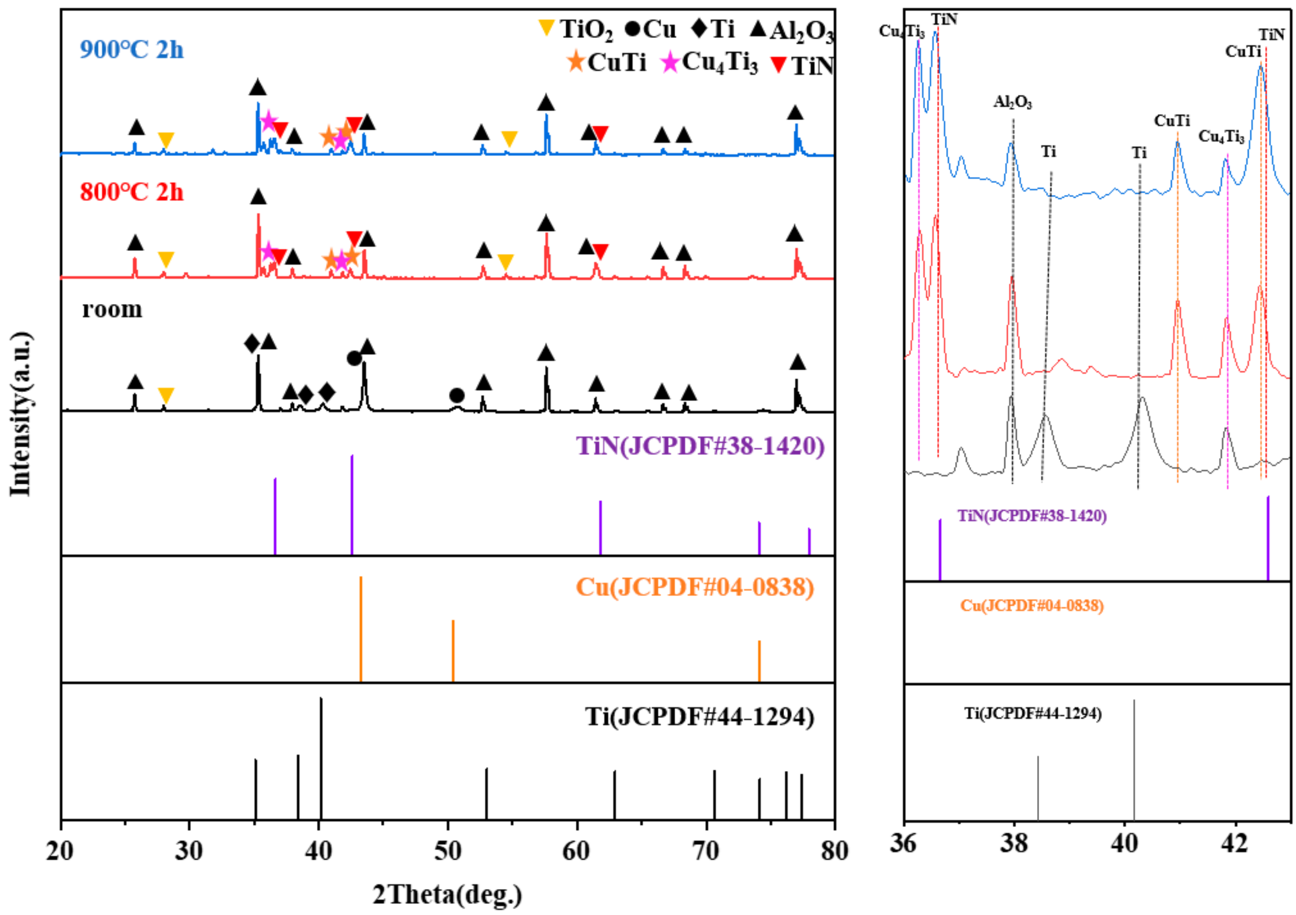

Figure 2. The XRD patterns of the Ti/Cu multilayer film before and after nitriding.

Figure 3 displays the surface SEM images of the Ti/Cu multilayer film before and after nitriding. The surface grains of the Ti/Cu multilayer film are large and many pores present between these grains. After nitriding at 800 and 900 °C for 2 h, the surface-grain sizes and inter-grain porosity of the multilayer film decrease. Compared with 800 °C, the grain sizes are smaller and the porosity is lower after nitriding at 900 °C. These suggest that the surface microstructure of the multilayer film becomes denser after nitridation owing to the elemental diffusion and reaction.

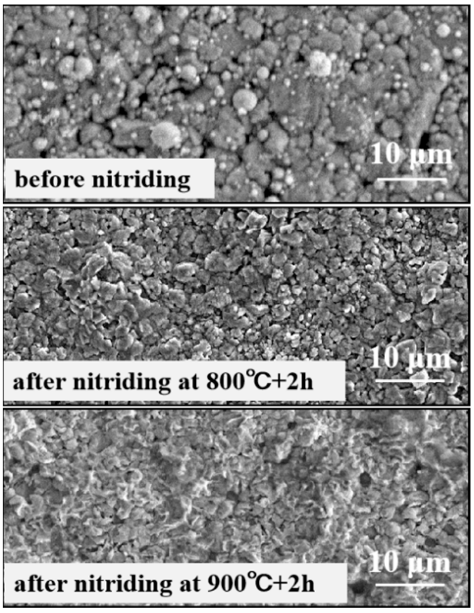

Figure 3. The surface SEM images of the Ti/Cu multilayer film before and after nitriding.

Figure 4 displays the scratch properties of the Ti/Cu multilayer film before and after nitriding. Here, the scratch method was used to assess the film hardness (H = (24.98 $\times$ m)/x^2, where H is scratch hardness number, m is the scratch load, g; x is the scratch track width, μm) and interface cohesion strength. The scratch track width and its corresponding scratch hardness number of the deposited Ti/Cu multilayer film are ~130 μm and ~0.015 (Figure 4a,c), and those of the nitrided multilayer film at 900 °C are ~115 μm and ~0.019 (Figure 4b,c), respectively, indicating that the hardness of the deposited Ti/Cu multilayer film increases after nitriding at 900 °C for 2 h. In addition, the critical loading force of the deposited Ti/Cu multilayer film is ~34 N. After nitriding at 900 °C for 2 h, the critical loading force exceeds 100 N, indicating that the cohesion strength of the multilayer film increases. After nitriding at 900 °C for 2 h, the increased hardness is owing to the formation of TiN phase and intermetallic compounds, and the improved cohesion strength is because of the element diffusion and interfacial reaction.

Figure 5 displays the tribological properties of the Ti/Cu multilayer film before and after nitriding. The wear track width of the deposited Ti/Cu multilayer film is ~453 μm (Figure 5a), and that of the nitrided multilayer film at 900 °C is ~400 μm (Figure 5b). As displayed from the wear track profiles (Figure 5c), the maximum wear track depth of the deposited multilayer film is ~1.12 μm. After nitriding at 900 °C for 2 h, the maximum wear track depth of the multilayer film is ~0.73 μm; this applies to the thickness of the multilayer film—which is just 65% of the deposited multilayer film. As displayed from the friction coefficient curves (Figure 5d), they fluctuate between 0.4 and 0.5. These above results indicate that the wear resistance of the Ti/Cu multilayer film improves after nitriding.

Based on the phase and surface morphology of the Ti/Cu multilayer film before and after nitriding, the improved wear resistance could be attributed to the following factors: (1) the increased surface hardness; (2) the improved cohesive strength of the interface; (3) the denser microstructure. For the deposited Ti/Cu multilayer film, the wear characteristics of the furrow and transfer debris are observed (Figure 5a). After nitriding, the wear characteristics of transfer debris, spalling, and stripping pits are observed, coupling without the furrow. Thus, the wear mechanism of the Ti/Cu multilayer film before and after nitriding is abrasive and adhesive wear.

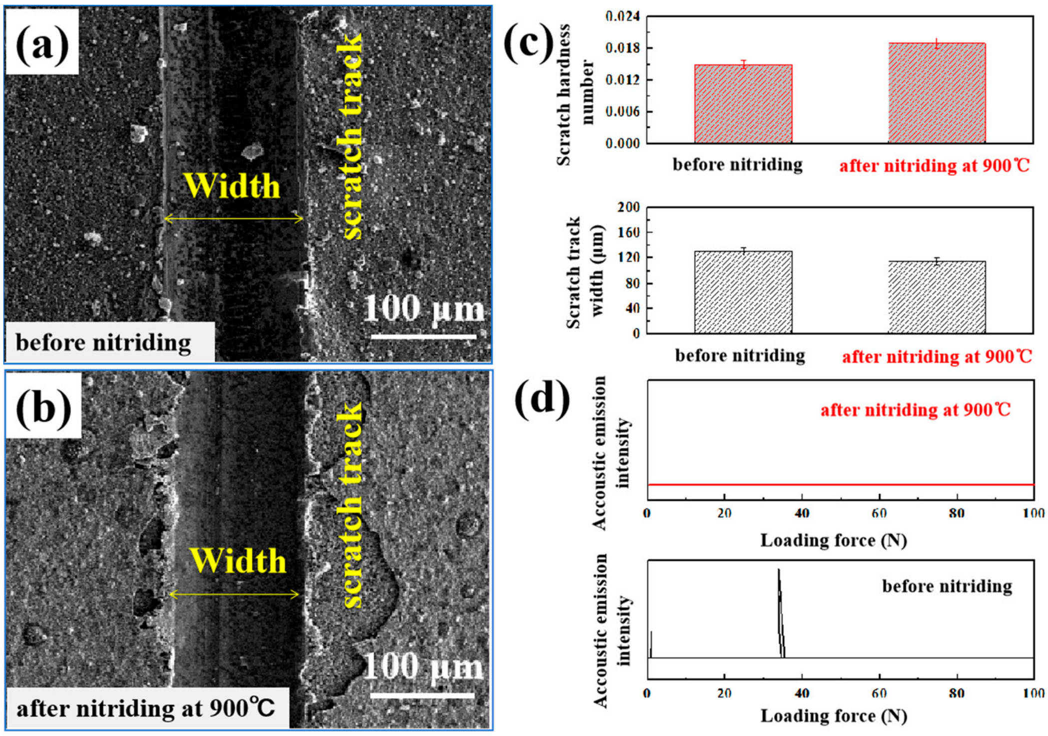

Figure 4. The scratch properties of the Ti/Cu multilayer film before and after nitriding: (**a**,**b**) scratch track morphologies, (**c**) scratch hardness number and track width, (**d**) critical loading force.

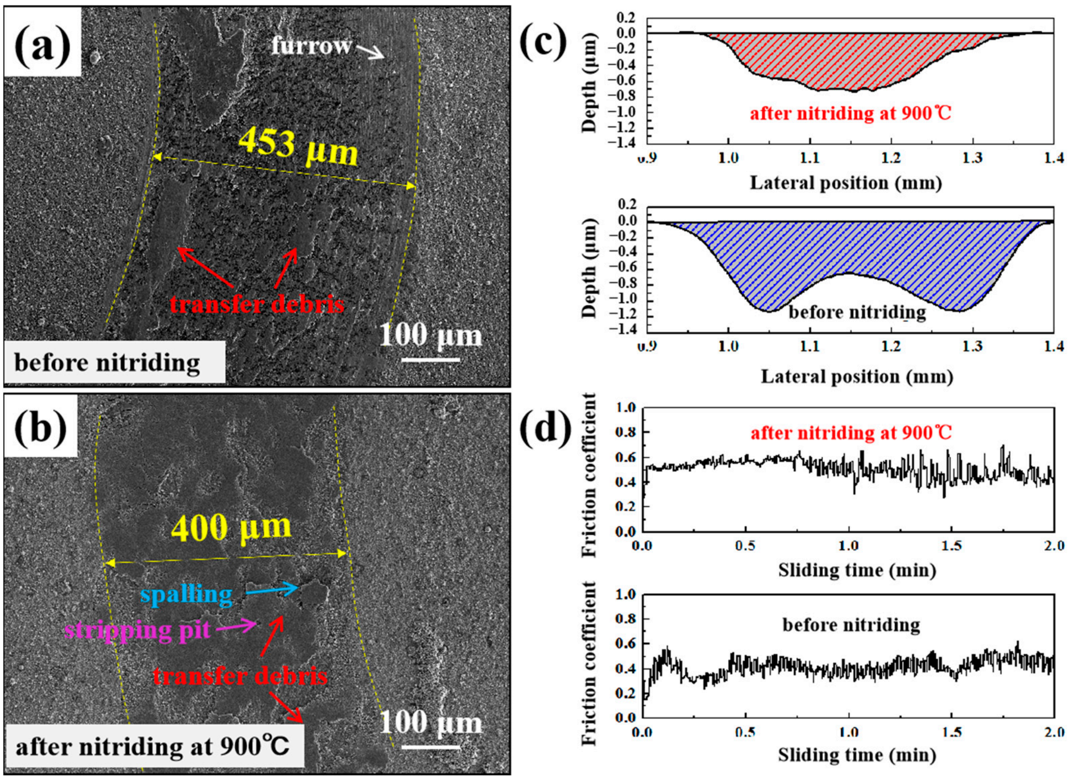

Figure 5. The tribological properties of the Ti/Cu multilayer film before and after nitriding: (**a**,**b**) wear track morphologies, (**c**) wear track profile, (**d**) friction coefficient.

4. Conclusions

In this work, we prepared Cu-Ti multilayer film and then nitrided it at 800 and 900 °C. The microstructure and wear performance were analyzed. The deposited Ti/Cu multilayer film mainly consisted of Ti phase, Cu phase, and a small amount of TiO_2 phase. After nitriding, Cu_4Ti_3, CuTi, and TiN phases were also detected. The higher temperature could promote the diffusion and activation of the Ti/Cu/N elements and then form more reacted phases. The surface microstructure of the multilayer film also became denser after nitridation owing to the elemental diffusion and reaction. The wear track width and depth of the deposited Ti/Cu multilayer film were ~453 and ~1.12 μm, and those of the nitrided multilayer film at 900 °C were ~400 and ~0.73 μm. The wear resistance of the Ti/Cu multilayer film improved after nitriding, and its wear mechanism was abrasive and adhesive wear.

Author Contributions: Conceptualization, H.F. and H.Z.; methodology, H.Z.; software, H.F.; validation, H.F., H.Z. and J.H.; formal analysis, H.F.; investigation, H.F.; resources, H.Z.; data curation, H.F.; writing—original draft preparation, H.F.; writing—review and editing, H.Z.; visualization, J.H.; supervision, J.H.; project administration, H.Z.; funding acquisition, H.Z. All authors have read and agreed to the published version of the manuscript.

Funding: This work was supported by the National Natural Science Foundation of China (52102064) and China Postdoctoral Science Foundation (2019M660965).

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: The data used to support the findings of this study are available from the corresponding author upon request.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Wu, K.; Zhang, J.Y.; Zhang, P.; Wang, Y.Q.; Liu, G.; Zhang, G.J.; Sun, J. Fracture behavior and adhesion energy of nanostructured Cu/Mo multilayer films. *Mater. Sci. Eng. A* **2014**, *613*, 130–135. [CrossRef]
2. Zhang, J.Y.; Zhang, X.; Liu, G.; Zhang, G.J.; Sun, J. Scaling of the ductility with yield strength in nanostructured Cu/Cr multilayer films. *Scr. Mater.* **2010**, *63*, 101–104. [CrossRef]
3. Zhou, Q.; Ren, Y.; Du, Y.; Hua, D.P.; Han, W.C.; Xia, Q.S. Adhesion energy and related plastic deformation mechanism of Cu/Ru nanostructured multilayer film. *J. Alloys Compd.* **2018**, *772*, 823–827. [CrossRef]
4. Hu, M.; Gao, X.M.; Weng, L.J.; Sun, J.Y.; Liu, W.M. The microstructure and improved mechanical properties of Ag/Cu nanoscaled multilayer films deposited by magnetron sputtering. *Appl. Surf. Sci.* **2014**, *313*, 563–568. [CrossRef]
5. Qiu, Y.H.; Bai, Q.; Fu, E.G.; Wang, P.P.; Du, J.L.; Chen, X.F.; Xue, J.M.; Wang, Y.G.; Wang, X.J. A novel approach to extracting hardness of copper/niobium (Cu/Nb) multilayer films by removing the substrate effect. *Mater. Sci. Eng. A* **2018**, *724*, 60–68. [CrossRef]
6. Chowdhury, S.; Gupta, R.; Prakash, S.; Behera, L.; Gupta, M. Role of interlayer thickness on interdiffusion in Ti/TiN multilayers. *Appl. Surf. Sci.* **2021**, *564*, 150430. [CrossRef]
7. Kim, Y.J.; Byun, T.J.; Lee, H.Y.; Han, J.G. Effect of bilayer period on CrN/Cu nanoscale multilayer thin films. *Surf. Coat. Technol.* **2008**, *202*, 5508–5511. [CrossRef]
8. Dang, C.Q.; Li, J.L.; Wang, Y.; Yang, Y.T.; Wang, Y.X.; Chen, J.M. Influence of multi-interfacial structure on mechanical and tribological properties of TiSiN/Ag multilayer coatings. *J. Mater. Sci.* **2017**, *52*, 2511–2523. [CrossRef]
9. Pathak, S.; Li, N.; Maeder, X.; Hoagland, R.G.; Baldwin, J.K.; Michler, J.; Misra, A.; Wang, J.; Mara, N.A. On the origins of hardness of Cu-TiN nanolayered composites. *Scr. Mater.* **2015**, *109*, 48–51. [CrossRef]
10. Takesue, S.; Kikuchi, S.; Misaka, Y.; Morita, T.; Komotori, J. Rapid nitriding mechanism of titanium alloy by gas blow induction heating. *Surf. Coat. Technol.* **2020**, *399*, 126160. [CrossRef]
11. Zhang, F.Y.; Ding, Y.; Yan, S.; He, J.N.; Yin, F.X. Microstructure evolution and mechanical performance of Cr-N/Al-Cr multilayer coatings produced by plasma nitriding Cr-coated Al alloy. *Vacuum* **2020**, *180*, 109540. [CrossRef]
12. Wang, C.; Wang, Y.H.; Wu, X.; Li, X.K.; Luo, J.W. The preparation and superconducting properties of Mo_2N nano films by high temperature nitriding method. *Mater. Lett.* **2021**, *287*, 129292. [CrossRef]
13. Cao, Y.; Wei, N.X.; Han, X.X.; Guo, C.H.; Du, J.G.; He, W.B.; Ma, J.; Jiang, F.C. Mechanical response of titanium tri-aluminide intermetallic alloy. *Mater. Sci. Eng. A* **2017**, *706*, 242–248. [CrossRef]

14. Zhou, H.R.; Chang, L.; Fu, K.K.; Huang, H.; Niu, R.M.; Liao, X.Z.; Sheppard, l.; George, L.; Martinu, L. Improvement of flow strength and scratch resistance of Ti/Cu nanocrystalline metal multilayer thin films by tailoring layer thickness and modulation ratio. *Surf. Coat. Technol.* **2020**, *404*, 126461. [CrossRef]
15. Yang, C.T.; Zhang, S.R.; Luo, J.H.; Li, Y.; Li, Y.R. Research of optical and structural properties in Cu/Ti multilayer films. *Vacuum* **2005**, *80*, 317–323. [CrossRef]