Effects of the Prefabricated Cu-Ti Film on the Microstructure and Mechanical Properties of the Multiphase Coating by Thermo Plasma Nitriding on C17200 Cu Alloy

Yandan Zhu 1,*, Mufu Yan 2,*, Quanli Zhang 3, Qiwen Wang 3 and Hangyu Zhuo 3

1 School of Materials Engineering, Nanjing Institute of Technology, Nanjing 211167, China
2 National Key Laboratory for Precision Hot Processing of Metals, School of Materials Science and Engineering, Harbin Institute of Technology, Harbin 150001, China
3 College of Mechanical and Electrical Engineering, Nanjing University of Aeronautics and Astronautics, Nanjing 210016, China; zhangqil606@163.com (Q.Z.); wqw_1997@126.com (Q.W.); hellofuture310710@163.com (H.Z.)

* Correspondence: zhuyd@njit.edu.cn (Y.Z.); yanmufu@hit.edu.cn (M.Y.); Tel.: +86-451-86418617 (M.Y.)

Received: 31 August 2019; Accepted: 22 October 2019; Published: 24 October 2019

Abstract: To improve the surface wear resistance, plasma nitriding of the prefabricated Cu-Ti films on the C17200 Cu alloy is performed to investigate the effects of the composition of the Cu-Ti films on the microstructure and the mechanical properties of the modified surface. The results firstly showed that obvious microstructure evolution appeared during the thermo-plasma nitriding process, where both the surface morphology of the composed phases and the cross-sectional profiles of the multiphase coatings varied for the three types of films. Small amounts of Ti-N compounds, Be3Ti2Cu, and different types of Cu-Ti intermetallics formed in the multiphase coating after plasma nitriding, which is dependent on the composition of the prefabricated Cu-Ti film. Correspondingly, the surface hardness and the wear resistance of the C17200 Cu substrates were obviously improved, with the obtained adhesive strength of the substrate reaching a satisfactory range.

Keywords: thermo plasma nitriding; Cu-Ti film; Cu-Ti intermetallics; wear resistance

1. Introduction

The Cu-Be alloys with the Be content of 0.2 to 2.75 wt.% are widely used for their good machinability and excellent electrical conductivity, such as the conductive brushes and the tumble rings. However, the insufficient wear resistance always limits their application in these areas. The surface modification by the plasma nitriding or thermo-diffusion process is applied to improve the wear properties of the manufactured parts. Indeed, plasma nitriding of the Ti based alloys has been widely applied to improve the wear properties [1–6], and the achieved positive results lead us to expand its application in the surface treatment by the plasma nitriding of the prefabricated Ti film on the Cu alloys and Al alloys [7–10]. Unfortunately, the surface modification process by simple plasma nitriding process on the alloy substrate resulted in the weak bonding between the coating and the substrate, especially for the fabrication of thick coatings used in harsh environments. For example, a previous study showed that the thermo-diffusion of the Ti film contributed to the obviously improved surface hardness and the wear resistance [11], where the formation of nano-crystalline titanium nitride was identified [12,13], and the plasma nitriding temperature is of great significance for the obtained mechanical properties. The plasma nitriding treatment at varying temperatures indicated that the plasma nitriding at 650 °C for 4 h contributed to the formation of an optimized phase composition and mechanical properties [7,9,13],
where the Cu-Ti intermetallics of varying Cu/Ti ratios and the Ti-N compounds of different Ti content were identified. The simulation results by the first-principle study also indicated the possibility for the formation of these phases and the possible contribution to the improvement of the surface mechanical properties [14,15]. However, the low efficiency of the surface modification process prompts us to propose the novel process by combination of the fabrication of a gradient Cu-Ti film and the plasma nitriding in our recent research, which shows great potentiality to produce the multiphase coating efficiently, with the obtained wear properties at the same level [16], which can also help to solve the problem of weak bonding strength between the single-layered Ti-N coating and the subsurface layer by the formation of Cu-Ti intermetallics between the Cu substrate and the Ti-N surface layer [8]. Actually, the Cu content in the prefabricated film should also contribute to the changing mechanical properties of the coating [17,18]. However, the previous investigations paid little attention to the influence of the initial Cu-Ti film composition on the obtained mechanical properties for the multiphase coating on C17200 Cu alloys.

This paper discusses a further study on the effects of the prefabricated Cu-Ti film on the microstructure and mechanical properties of the multiphase coating by thermo plasma nitriding on C17200 Cu alloy. First, the microstructure and the surface characteristic of the prefabricated Cu-Ti film were studied. Then, the microstructure evolution during the plasma nitriding process was explored. Finally, the mechanical properties and the wear performance of the three types of coatings were evaluated.

2. Materials and Methods

2.1. Experimental Material and Method

The chemical composition of the C17200 Cu alloy is listed in Table 1. The copper alloy bar was processed into a size of 20 mm × 4.5 mm, by wire-cutting for the subsequent surface modification treatment, the structure analysis of the modified layer, and the mechanical performance test. Before the surface treatment, the substrates were solution-treated by water quench after the insulation at 790 °C for 15 min, to obtain a supersaturated solid solution, which can improve the mechanical properties of the C17200 Cu substrate as an age-hardenable alloy [13].

| Be  | Co  | Ni  | Fe  | Si  | Cu   |
|-----|-----|-----|-----|-----|------|
| 1.96| 0.10| 0.12| 0.15| 0.12| Bal. |

The prefabrication of the Cu-Ti film was carried out in a UDP450 closed-field unbalanced magnetron sputtering device. The pure Ti (99.99%) and Cu (99.99%) targets in the size of 330 mm × 134 mm × 12 mm were applied, and the copper alloy substrates were placed on the workpiece plate with a diameter of 200 mm, in the center of the vacuum chamber. A schematic illustration of the magnetron sputtering system is shown in Figure 1. The Cu-Ti film layers of different compositions were prepared on the surface of C17200 copper alloy by adjusting the power of the Cu and Ti targets, where the argon gas flow rate, the substrate bias, and the deposition time were kept constant for the magnetron sputtering process. The power parameters for the fabrication of the film with different Cu and Ti contents and the fixed processing parameters in the magnetron sputtering process are listed in Tables 2 and 3, respectively. It should be noted that the temperature of the substrate gradually rose from room temperature (20 °C) to the maximum (150 °C), as the sputtering process proceeded.
Coatings 2019, 9, x FOR PEER REVIEW 3 of 15

Table 2. The constant parameters for the magnetron sputtering process.

| Total Ar Pressure (Pa) | Substrate Biases (V) | Sputtering Time (h) | Substrate-to-Target Distance (mm) | Workpiece Speed (rpm) | Substrate Temperature (°C) |
|------------------------|-----------------------|--------------------|----------------------------------|-----------------------|---------------------------|
| 5                      | −70                   | 3                  | 120                              | 5                     | 20–150                    |

Figure 1. Schematic illustration of the magnetron sputtering system: (a) the UDP450 magnetron sputtering equipment, and (b) the internal layout.

Table 3. The target powers for the fabrication of the film with different Cu and Ti contents.

| Process | Ti Target Power (W) | Ti Target Current (A) | Cu Target Power (W) | Cu Target Current (A) |
|---------|---------------------|-----------------------|---------------------|-----------------------|
| F1      | 2500                | 7.00                  | 100                 | 0.33                  |
| F2      | 2000                | 5.69                  | 300                 | 0.84                  |
| F3      | 1000                | 3.02                  | 450                 | 1.18                  |

The plasma nitriding treatment was carried out in a homemade pulse plasma multielement furnace (LDMC-30 kW), and a hollow cathode made of stainless-steel mesh was used to assist the temperature rise, as shown in Figure 2. The copper alloy substrates with the prefabricated Cu-Ti film of different composition were subjected to the plasma nitriding treatment at 650 °C for 4 h. As the nitrogen and the hydrogen gas flow rate had influence on the phase structure of the modified layer, plasma nitriding of the Cu-Ti film was undertaken with a ratio of 0.3:0.1 L/min, to generate a high-nitrogen phase.

Figure 2. Schematic illustration of the plasma nitriding system: (a) the plasma nitriding furnace, and (b) the hollow cathode equipment.

2.2. Characterization

The phase structure for the Cu-Ti film and the multiphase coating were characterized by the Rigaku D/max-rB rotary anode X-ray diffractometer (Rigaku Corporation, Tokyo, Japan), where the
CuKα radiation was applied at the voltage of 40 kV, the current of 30 mA, the scan range from 20° to 100°, and a scan speed of 5°/min. The phase composition was identified by comparing the Bragg–Brentano X-ray diffraction (BBXRD) pattern with the standard PDF (ASTM) card. The grazing incidence X-ray diffraction (GIXRD) test with the incident angle of 1° was also undertaken to analyze the phase structure of the outmost surface layer. In addition, the phase composition of the iron oxides was identified by X-ray photoelectron spectroscopy (XPS, ESCALAB 250Xi, Thermo Fisher Scientific, Waltham, MA, USA).

The surface morphologies of the fabricated Cu-Ti film and the multiphase coating, the cross-sectional surface, and the worn tracks were examined by the SUPRA 55 SAPPHIRE scanning electron microscope (SEM, CARL ZEISS CO., LTD., Oberkochen, Germany). The elemental composition of the surface and along the cross-sectional profile was analyzed by the attached energy dispersive spectrometer (EDS, Oxford Instruments, Abingdon, UK).

The hardness and elastic modulus of the modified surface were tested by the NANO INDENTER XP type nanoindenter (MTS Systems Corporation, Eden Prairie, MN, USA). The continuous stiffness measurement (CSM) mode was used to obtain the hardness and elastic modulus at a continuous indentation depth. Four test points were conducted for each sample, and the average hardness value was taken as the final hardness.

The adhesion performance of the coating was tested by a scratch test on the MFT-4000 multifunctional material surface performance tester (Lanzhou Huahui Instrument Technology Co., LTD., Lanzhou, China). By loading the diamond stylus automatically, the stylus was drawn across the surface of the sample, where the acoustic emission signal and the frictional force-changing signal were collected as the coating layer was peeled off. The loading speed in this experiment was 100 N/min, with the maximum load of 100 N.

The wear test was performed on the Ball-On-Disk-1-AUTO type equipment (Art Teer Coating Technology LTD., China). The counterpart used was the WC ball in a diameter of 5 mm, at room temperature, and the humidity was about 50%. The test was carried out under dry friction conditions, with the loads of 4 N, the rotational speed of 200 rpm, and the test time of 1800 s. The ZYGO Nexview white-light interferometer (AMETEK, Inc., Berwyn, PA, USA) was then used to measure the surface topography and the cross-sectional profile of the worn track. The volume wear rate $\eta$ was calculated by the following formulas:

$$\Delta V = \pi d \times A,$$
$$\eta = \frac{\Delta V}{FL},$$

where $\Delta V$ is the worn volume (m³), $d$ is the diameter of the worn track (m), $A$ is the cross-sectional area of the worn track (m²), $\eta$ is the volume wear rate (m³/Nm), $F$ is the normal load (N), and $L$ is the total slide distance (m).

### 3. Results and Discussion

The composition and thickness of the three different prefabricated Cu-Ti film are listed in Table 4. It can be seen that the Ti/Cu atomic ratio of 7:1, 7:4, and 1:2 can be obtained for F1, F2, and F3, respectively.

| Materials | Coating Process | Film Composition | Film Thickness (µm) |
|-----------|----------------|-----------------|--------------------|
| C17200    | F1             | 13 Ti (at.%) 87  | 3.3                |
|           | F2             | 37 Ti (at.%) 63  | 3.0                |
|           | F3             | 67 Ti (at.%) 33  | 2.5                |

**Table 4.** The composition and thickness of the fabricated Cu-Ti film by magnetron sputtering on C17200 Cu alloys.
Figure 3 shows the XRD patterns of the F1, F2, and F3 Cu-Ti films obtained on the surface of C17200 Cu alloys. It can be seen that the main crystalline phases in the F1 film are $\beta$-Ti, Ti$_2$Cu, and a small amount of $\alpha$-Ti. For the same crystal structure between the Cu phase and $\beta$-Ti phase, the prior growth $\beta$-Ti appeared on the Cu substrate, which contributed to the peak at $2\theta = 38.2^\circ$ in the F1 film, rather than the $\alpha$-Ti phase [13,19], as shown in Figure 3a. In comparison, the main intermetallic phase of the F2 film layer is Ti$_2$Cu, and a small amount of CuTi exists. However, there is no Cu-Ti crystalline phase formed during the magnetron sputtering process for F3 film, as indicated in Figure 3c.

![XRD patterns](image)

**Figure 3.** XRD results of the fabricated Cu-Ti film on C17200 copper alloy: (a) F1, (b) F2, and (c) F3.

The surface morphology of the three types of Cu-Ti films is shown in Figure 4. It can be found that irregular polygonal grains formed in the F1 Cu-Ti film, which are uniformly and densely distributed. In comparison, the grains of the F2 film became fine, and the boundaries between the grains turned unclear, as shown in Figure 4b. Interestingly, the shape of the grains in the F3 film was ellipsoidal, and obvious porosity could be found at the grain boundaries. The changing surface morphology is attributed to the varying phase composition of the Cu-Ti film, where the varying Cu/Ti atom ratio promoted the formation of the different types of phases, including Ti grains, Cu-Ti intermetallics, Cu grains, etc. In addition, the regulation of the sputtering power not only contributes to the changing atoms ratio of the Cu/Ti atoms, but also the bombardment speed of Cu and Ti ions, which resulted in the change of the diffusion dynamics to generate a different surface morphology.

![SEM micrographs](image)

**Figure 4.** SEM micrographs of the fabricated Cu-Ti films on C17200 Cu alloy: (a) F1, (b) F2, and (c) F3.
After the fabrication of different Cu-Ti film on the surface of C17200 Cu substrates, plasma nitriding at 650 °C for 4 h was undertaken to improve the surface properties. The phase composition of the modified layer after plasma nitriding is shown in Figure 5. It can be seen that the Be₃Ti₂Cu phase formed in all of the modified layers. After the plasma nitriding of the F1 film and the F2 film for 4 h, the peak intensity of the Cu₃Ti phase in the modified layer increased due to the diffusion of Cu atoms in the substrate, while the diffraction peaks of the Ti₂Cu and CuTi phases weakened. In contrast, the diffraction peak intensity of the Cu₃Ti phase in the modified layer dropped after the nitriding of F3 film for 4 h, while the diffraction peaks of Be₃Ti₂Cu phase and Ti₂Cu phase increased. The result is consistent with the calculated results based on the thermodynamics and the first-principles study [7,15].

![XRD results of Cu-Ti films after plasma nitriding at 650 °C for 4 h.](image1)

**Figure 5.** XRD results of the Cu-Ti films after plasma nitriding at 650 °C for 4 h.

However, the diffraction peak of the Ti-N phase was not identified by the Bragg–Brentano X-ray diffraction (BBXRD) method due to the great penetration depth. In order to collect the phase information of the outmost layer, the multiphase coating was characterized by the grazing incidence XRD (GIXRD) experiments, and the results are shown in Figure 6. It can be seen that both the TiN phase and the TiN₀.₃ phase appeared in the three multiphase coatings after plasma nitriding. Combined with the BBXRD results, it can be concluded that the Ti-N phases in the surface layer are quite thin or even discontinuous. In addition, for the higher initial Ti content in F3 film, the titanium nitride of a higher Ti ratio formed.

![GIXRD results of Cu-Ti film after plasma nitriding at 650 °C for 4 h.](image2)

**Figure 6.** GIXRD results of the Cu-Ti film after plasma nitriding at 650 °C for 4 h.
The surface morphology and EDS results of F1, F2, and F3 are shown in Figure 7. From Figure 7a–c, it can be seen that a discontinuous white iron-rich phase formed on the surface after plasma nitriding for 4 h, which was caused by the sputtered Fe element in the hollow cathode made of stainless-steel mesh onto the surface of the sample. The grains below the white particles were uniform and dense. In comparison, the size of the Fe-rich grains on the surface of the F1 and F2 films after nitriding was larger, at about 1 µm in diameter. Especially for the F1 film, the iron-rich grains distributed on even the whole surface. In addition, the EDS results of the F1 and F3 film after plasma nitriding showed that the oxygen content of the modified layer increased slightly. Point EDS analysis on the white phases was undertaken in order to identify these phases, as shown in Figure 8. It can be seen that the white phase was of especially high Fe element content. Presumably, the white phases are Fe₃O₄, based on the previous study in the low-temperature plasma nitriding process [20]. There was no Cu element on the surface of F1 film after nitriding for 4 h, and the content of Cu on the surface of the F3 film was lower than that before plasma nitriding. This is attributed to the stronger affinity between Ti with N. Under the high nitrogen potential, Ti atoms and N atoms on the surface combined to form a Ti-N compound, so the Cu atoms accumulated in the subsurface layer.

![Figure 7](image-url)  
**Figure 7.** SEM micrographs and EDS results of the fabricated Cu-Ti film on C17200 Cu alloy after plasma nitriding at 650 °C for 4 h: (a) F1, (b) F2, (c) F3, (d) EDS result of region A in (a), and (e) EDS result of region B in (c).

Figure 9 shows the cross-sectional morphology and EDS results of the multiphase coating after plasma nitriding at 650 °C for 4 h. The thickness of the modified layers after plasma nitriding is about 8 µm, 7 µm, and 4 µm for F1, F2, and F3, respectively. Interestingly, discontinuous white matter appeared in the coating to a certain depth (about 500 nm from the surface) of the F3 film after plasma nitriding, which is attributed to the formation of the discontinuous Cu-rich phase, with the Cu/Ti atomic ratio of about 7:3 for the intermediate layer.
Interestingly, discontinuous white phases appeared in the coating to a certain depth (about 500 nm), influencing the hardness in the early stage is causative of hardening effect [21–24]. Similarly, the modulus of the C17200 substrate turns to be about 150 GPa after a rapid growth.

Figure 8. Elemental composition of the white phases by point EDS analysis: (a) the picked points for EDS analysis, (b) EDS result for point 1, (c) EDS result for point 2.

Figure 9. BSEM (backscattered scanning electron microscopy) micrographs of the cross-sectional surface and EDS results along the cross-sectional profile after plasma nitriding at 650 °C for 4 h: (a) and (b) for F1; (c) and (d) for F2; and (e) and (f) for F3.
The obtained hardness and modulus as a function of the indentation depth of the C17200 copper alloy substrate is shown in Figure 10. The hardness of the unmodified C17200 Cu substrate increases rapidly with the growth of the indentation depth and then gradually decreases after it reaches 5 GPa, until it keeps constant at 2.3 GPa during the unloading process. The increase in hardness in the early stage is caused by the size effect and the work-hardening effect [21–24]. Similarly, the modulus of the C17200 substrate turns to be about 150 GPa after a rapid growth.

Figure 10. Surface hardness and modulus of the C17200 copper alloy, with increasing displacement measured by nanoindentation.

After the plasma nitriding process, the measured hardness and modulus curves against the indentation depth of the fabricated coatings exhibited obvious changes. As shown in Figure 11, a lower surface hardness of the modified layer at a distance of 0 to 200 nm from the surface occurred due to the adhesion of iron on the surface from the hollow cathode material during sputtering, where a relatively loose surface layer formed. The modified layer of the F3 film obtained a maximum hardness value of 6.2 GPa at the depth of 400–600 nm, but it then decreased rapidly to be 4 GPa during the unloading process, which was the smallest among the three processes. The hardness of the modified layer of the F1 film and F2 film achieved the maximum hardness of 6 GPa at the indentation depth of 600–1100 nm, which then gradually decreased. The hardness of the F2 film and F3 film after plasma nitriding was 5.5 and 5 GPa in the unloading process, respectively. The modulus and hardness of the multiphase coatings share the same changing trend with the indentation depth, and the modulus reaches 130–150 GPa in the unloading stage. For the scattering distribution of the formed Cu-Ti intermetallics, the titanium nitrides and the iron oxides, the load-displacement curves change dependently, but the trends of the measured hardness and the modulus against the displacement keep the same.

Figure 11. Surface hardness and modulus of the multiphase coating after plasma nitriding at 650 °C for 4 h, with increasing displacement: (a) hardness and (b) modulus.
In comparison, it can be found that the hardness was significantly improved after fabricating the modified layer with a different phase structure on the surface of C17200 Cu alloy. To study the wear resistance and the wear mechanism of the C17200 Cu alloy-substrate and the modified layer, a wear-resistance test against WC ball was performed. The three-dimensional surface topography of the worn track and the friction coefficient measured for the C17200 Cu substrate are shown in Figure 12. It can be found that the worn depth of the substrate is uneven and the deepest depth of the worn track reaches 6.5 μm. During the wear process, the extruded material hardly peeled off, which accumulated at two sides of the worn track. As shown in Figure 12b, the friction coefficient reaches 0.4 at the beginning, which then stabilizes at around 0.32, during the wear process of the beryllium bronze substrate.

Figure 12. Surface topography of the worn track and the corresponding friction coefficient of C17200 copper alloy: (a) surface topography and (b) friction coefficient.

Figure 13 shows the friction coefficient curves and the wear rate of C17200 Cu alloy after plasma nitriding at 650 °C for 4 h. From Figure 13a, it can be seen that the friction coefficients of the modified layers of the three kinds of Cu-Ti films after plasma nitriding were lower than those of the C17200 Cu substrate. The friction coefficients of F1 and F2 after plasma nitriding reached 0.06 and 0.07, respectively, while the friction coefficient of F3 film remained between 0.05 and 0.07, in the first 300 s, which then increased rapidly to 0.3. Figure 13b compares the wear rates of the modified layers after plasma nitriding, which shows that the wear rate of the modified layers for F1, F2 and F3 is 1.4 × 10^{-15} \text{m}^3/\text{Nm}, 1.0 × 10^{-15} \text{m}^3/\text{Nm}, and 2.3 × 10^{-15} \text{m}^3/\text{Nm}, respectively. The improved wear rate of all three modified surfaces was achieved, which was about 94%, 96%, and 91% lower than that of the substrate, respectively. Compared with the plasma nitriding of the prefabricated pure Ti film process [7], the friction coefficient and the wear resistance were further improved.

Figure 14 is the surface morphology of the worn track and the cross-sectional profile after plasma nitriding for 4 h, at 650 °C. The depth of the worn tracks for multiphase coatings is about 0.5 μm which indicates the obviously improved wear resistance. In addition, the width of the worn track increases gradually for the F1, F2, and F3 films after plasma nitriding, which reaches about 250 μm for F3. The surface morphology shows that the wear mechanism of the modified layer is slight abrasion. EDS results of the worn tracks for area A–E are listed in Table 5. The high oxygen content indicates oxidative wear of the multiphase coating during the sliding test. The B and D points are of about 7 at.% nitrogen, while no nitrogen element is detected for the A and C points, which indicates that a very thin nitride layer was generated in the modified surface.
In addition, the high O content might result from the oxidation of Ti-N compounds, which also led to the decreasing amounts of Ti-N compounds \[5\], as well as the formation of the iron oxide (Fe$_3$O$_4$) during the plasma nitriding process and the wear-test process. The hollow cathode made of stainless-steel mesh, applied for the plasma nitriding process to assist the temperature, helps in the achievement of the uniform temperature of the substrate, and it is certain that some Fe atoms are accumulated at two sides of the worn track. As shown in Figure 12b, it can be seen that the obviously improved wear resistance indicates oxidative wear of the multiphase coating during the sliding test. The B and D points are of about 7 at.% nitrogen, while no nitrogen element is detected for the A and C points, which indicates the obviously improved wear resistance and the formation of iron oxide contributes to the improvement of the friction coefficient \[25,26\].

Figure 13. Friction coefficient and wear rate of the Cu-Ti films after plasma nitriding at 650 °C for 4 h: (a) friction coefficient and (b) wear rate.

Figure 14. SEM micrographs and the cross-sectional profile of the worn track on C17200 copper alloy after plasma nitriding at 650 °C for 4 h: (a) and (b) for F1 film; (c) and (d) for F2 film; (e) and (f) for F3 film.

In addition, the high O content might result from the oxidation of Ti-N compounds, which also led to the decreasing amounts of Ti-N compounds \[5\], as well as the formation of the iron oxide (Fe$_3$O$_4$) during the plasma nitriding process and the wear-test process. The hollow cathode made of stainless-steel mesh, applied for the plasma nitriding process to assist the temperature, helps in the achievement of the uniform temperature of the substrate, and it is certain that some Fe atoms are
sputtered by the ions. The good affinity between the O atoms and the active Fe atoms prompts the formation of Fe$_3$O$_4$ (FeO·Fe$_2$O$_3$), as illustrated by the XPS result in Figure 15. It was reported that the formation of iron oxide contributes to the improvement of the friction coefficient [25,26].

![Figure 15. X-ray photoelectron spectra for Fe2p of the fabricated multiphase coating.](image)

Nitrogen elements were not detected in the E and F regions for the modified F3 film, and the higher Cu content in the film layer indicates the existence of Cu-Ti intermetallics of higher Cu/Ti atomic ratios and the Cu grains, which are of lower hardness, so the WC ball penetrates into the substrate during the sliding test. Therefore, the improved wear resistance of the modified is attributed to the phase compositions, which should be the Ti-N compounds and Cu-Ti intermetallics.

| Table 5. Semi-quantitative EDS results for the points A–F in Figure 14 (at.%). |
|-----------------|---|---|---|---|---|---|---|
| Elements | C  | N  | O  | Ti | Fe | Cu | W  |
| A   | 16.98 | -  | 49.13 | 18.73 | 7.05 | 7.88 | 0.23 |
| B   | 8.97  | 7.3 | 45.39 | 13.72 | 19.28 | 5.34 | -   |
| C   | 11.81 | -  | 60.45 | 12.65 | 11.26 | 1.94 | 1.89 |
| D   | 14.77 | 6.75 | 45.52 | 20.96 | 5.02 | 6.98 | -   |
| E   | 15.51 | -  | 60.64 | 5.6  | 8.77 | 6.13 | 3.35 |
| F   | 21.09 | -  | 51.14 | 6.41 | 9.16 | 12.03 | 0.17 |

The diamond-scratching test on the modified surface indicates that the sudden change of the friction force occurs when the normal load reaches the critical value, as shown in Figure 16. Correspondingly, a sharp increase of acoustic signal can be observed due to the pulverization of the multiphase coating. Therefore, the critical value of the failure load can be determined based on the changes in friction force and acoustic signals. Specifically, from the scratching curve shown in Figure 16a, it can be seen that, when the load is about 10 N, the force curve of the F1 film after plasma nitriding stays at about 5 N. When the load is higher than 17 N, the friction force of the F1 and F2 films after nitriding gradually increases. As the load reaches about 40 N, the acoustic emission signal suddenly zooms, indicating the brittle fracture of the modified layer. For the scratching of the modified layer of F3 film after nitriding, the increase of the acoustic signal was detected at the position of 9 N, which shows that the surface cracking and peeling of the brittle film was induced. However, no strong acoustic signal was detected subsequently, even with the increasing friction force, which indicates that penetration into the copper alloy substrate appeared.
Figure 16. The scratching curves and surface morphology of the multiphase coating after plasma nitriding: (a) the scratching curves of F1 film, (b) SEM micrograph of the scratching groove of F1 film, (c) the scratching curves of F2 film, and (d) the scratching curves of F3 film.

4. Conclusions

In the present work, the surface modification of C17200 Cu alloy was undertaken by thermo plasma nitriding to investigate the effects of the composition of the prefabricated Cu-Ti film on the microstructure and the mechanical properties. Based on the experimental results and the corresponding discussion, the following conclusions can be achieved:

(1) Three types of Cu-Ti films with different elemental composition were fabricated. Both the surface morphology and the formed phases during magnetron sputtering changed for the varying Cu/Ti atom ratio;

(2) The composition of the multiphase coating after plasma nitriding is closely dependent on the Cu/Ti atom ratio of the prefabricated gradient Cu-Ti films, where small amounts of Ti-N compounds and the specific Cu-Ti intermetallics formed in the three types of Cu-Ti films;
(3) The friction coefficient and the wear resistance of the C17200 Cu alloys were obviously improved by the plasma nitriding of the prefabricated Cu-Ti film on C17200 Cu alloy, where the friction coefficient could reach 0.06 and the wear rate reached 90% lower than that of the substrate. In addition, a satisfactory adhesive force was obtained for the gradually changed mechanical properties of the coating.

Author Contributions: Conceptualization, Y.Z. and M.Y.; methodology, Y.Z.; software, Q.W. and H.Z.; formal analysis, Y.Z.; investigation, Y.Z.; data curation, Y.Z.; writing—original draft preparation, Y.Z. and Q.Z.; writing—review and editing, Q.Z., Q.W., and H.Z.; supervision, M.Y.; project administration, Y.Z. and M.Y.; funding acquisition, Y.Z. and M.Y.

Funding: This research was funded by the University Research Foundation of Nanjing Institute of Technology (grant number: YK201805) and the National Natural Science Foundation of China (grant number: U1537201), and “The APC was funded by the University Research Foundation of Nanjing Institute of Technology (grant number: YKJ201805).

Acknowledgments: The authors gratefully acknowledge the University Research Foundation of Nanjing Institute of Technology (Project No. YKJ201805) and the National Natural Science Foundation of China (Project No. U1537201) for the financial support of this research work.

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

References
1. Fouquet, V.; Pichon, L.; Drouet, M.; Straboni, A. Plasma assisted nitridation of Ti-6Al-4V. *Appl. Surf. Sci.* 2004, 221, 248–258. [CrossRef]
2. Oktay, S.; Kahraman, Z.; Urgen, M.; Kazmanli, K. XPS investigations of tribolayers formed on Ti and (Ti,Re)N coatings. *Appl. Surf. Sci.* 2015, 328, 255–261. [CrossRef]
3. Yıldız, B.S.; Sahin, A.Z.; Al-Garmi, A.Z.; Said, S.A.M.; Ahmed, Z.; Abdulaalem, B.J.; Sami, M. Plasma nitriding of Ti-6Al-4V alloy to improve some tribological properties. *Surf. Coat. Technol.* 1996, 80, 287–292. [CrossRef]
4. Mubarak Ali, M.; Ganesh Sundara Raman, S.; Pathak, S.D.; Gnanamoorthy, R. Influence of plasma nitriding on fretting wear behaviour of Ti–6Al–4V. *Tribol. Int.* 2010, 43, 152–160. [CrossRef]
5. Kuo, C.; Lin, Y.; Chan, A.; Chang, J. High temperature wear behavior of titanium nitride coating deposited using high power impulse magnetron sputtering. *Coatings* 2019, 9, 555. [CrossRef]
6. Adachi, S.; Ueda, N. Wear and corrosion properties of cold-sprayed AISI 316L coatings treated by combined plasma carburizing and nitriding at low temperature. *Coatings* 2018, 8, 456. [CrossRef]
7. Yan, M.F.; Zhu, Y.D.; Zhang, C.S.; Zhang, Y.X.; Wang, Y.X.; Yang, L. Microstructure and mechanical properties of copper-titanium-nitrogen multiphase layers produced by a duplex treatment on C17200 copper-beryllium alloy. *Mater. Des.* 2015, 84, 10–17. [CrossRef]
8. Liu, L.; Shen, H.H.; Liu, X.Z.; Guo, Q.; Meng, T.X.; Wang, Z.X.; Yang, H.J.; Liu, X.P. Wear resistance of TiN (Ti2N)/ti composite layer formed on C17200 alloy by plasma surface Ti-alloying and nitriding. *Appl. Surf. Sci.* 2016, 388, 103–108. [CrossRef]
9. Zhu, Y.D.; Yan, M.F.; Zhang, Y.X.; Chen, H.T.; Yang, Y. Microstructure formation and evolution mechanism of Cu-Ti coating during dual-magnetron sputtering and thermo plasma nitriding. *Vacuum* 2016, 134, 25–28. [CrossRef]
10. Taweesub, K.; Visuttipitukul, P.; Tungkasmita, S.; Paosawatyanong, B. Nitridation of Al–6%Cu alloy by Rf plasma process. *Surf. Coat. Technol.* 2010, 204, 3091–3095. [CrossRef]
11. Yang, L.; Zhang, F.Y.; Yan, M.F.; Zhang, M.L. Microstructure and mechanical properties of multiphase layer formed during thermo-diffusing of titanium into the surface of C17200 copper-beryllium alloy. *Appl. Surf. Sci.* 2014, 292, 225–230. [CrossRef]
12. Kim, Y.S.; Park, H.J.; Mun, S.C.; Jumaev, E.; Hong, S.H.; Song, G.; Kim, J.T.; Park, Y.K.; Kim, K.S.; Jeong, S.I.; et al. Investigation of structure and mechanical properties of TiZrHfNiCuCo high entropy alloy thin films synthesized by magnetron sputtering. *J. Alloy Compd.* 2019, 797, 834–841. [CrossRef]
13. Zhu, Y.D.; Yao, J.W.; Yan, M.F.; Zhang, Y.X.; Wang, Y.X.; Yang, Y.; Yang, L. High temperature plasma nitriding to modify Ti coated C17200 Cu surface: Microstructure and tribological properties. *Vacuum* 2018, 147 (Suppl. C), 163–171. [CrossRef]
14. Ghosh, G. First-principles calculations of structural energetics of Cu–Tm (Tm = Ti, Zr, Hf) intermetallics. *Acta Mater.* 2007, 55, 3347–3374. [CrossRef]
15. Zhu, Y.D.; Yan, M.F.; Zhang, Y.X.; Zhang, C.S. First-principles investigation of structural, mechanical and electronic properties for Cu–Ti intermetallics. *Comp. Mater. Sci.* 2016, 123, 70–78. [CrossRef]
16. Zhu, Y.D.; Yan, M.F.; Zhang, Y.X.; Zhang, C.S. Surface modification of C17200 copper-beryllium alloy by plasma nitriding of Cu-Ti gradient film. *J. Mater. Eng. Perform.* 2018, 27, 961–969. [CrossRef]
17. Balashabadi, P.; Larijani, M.M.; Jafari-Khamse, E.; Seyed, H. The role of Cu content on the structural properties and hardness of TiN-Cu nanocomposite film. *J. Alloy. Compd.* 2017, 728 (Suppl. C), 863–871. [CrossRef]
18. Wang, X.Q.; Zhao, Y.H.; Yu, B.H.; Xiao, J.Q.; Li, F.Q. Deposition, structure and hardness of Ti-Cu-N hard films prepared by pulse biased arc ion plating. *Vacuum* 2011, 86, 415–421. [CrossRef]
19. Joshi, V.A. *Titanium Alloys: An Atlas of Structures and Fracture Features*; CRC Press: Boca Raton, FL, USA, 2006.
20. Wang, Y.X.; Yan, M.F.; Li, B.; Guo, L.X.; Zhang, C.S.; Zhang, Y.X.; Bai, B.; Chen, L.; Long, Z.; Li, R.W. Surface properties of low alloy steel treated by plasma nitrocarburizing prior to laser quenching process. *Opt. Laser Technol.* 2015, 67, 57–64. [CrossRef]
21. Voyiadjis, G.Z.; Peters, R. Size effects in nanoindentation: An experimental and analytical study. *Acta Mech.* 2009, 211, 131–153. [CrossRef]
22. Almasri, A.H.; Voyiadjis, G.Z. Nano-indentation in FCC metals: Experimental study. *Acta Mech.* 2009, 209, 1–9. [CrossRef]
23. Elmustafa, A.A.; Stone, D.S. Nanoindentation and the indentation size effect: Kinetics of deformation and strain gradient plasticity. *J. Mech. Phys. Solids* 2003, 51, 357–381. [CrossRef]
24. Kim, J.T.; Hong, S.H.; Park, H.J.; Kim, Y.S.; Suh, J.Y.; Lee, J.K.; Park, J.M.; Maity, T.; Eckert, J.; Kim, K.B. Deformation mechanisms to ameliorate the mechanical properties of novel TRIP/TWIP Co-Cr-Mo-(Cu) ultrafine eutectic alloys. *Sci. Rep.* 2017, 7, 39959. [CrossRef] [PubMed]
25. Jauberteau, I.; Mayet, R.; Cornette, J.; Mangin, D.; Bessaoudou, A.; Carles, P.; Jauberteau, J.L.; Passerelgue, A. Silicides and nitrides formation in Ti Films coated on Si and exposed to (Ar-N2-H2) expanding plasma. *Coatings* 2017, 7, 23. [CrossRef]
26. Zhou, G.; Zhu, Y.; Wang, X.; Xia, M.; Zhang, Y.; Ding, H. Sliding tribological properties of 0.45% carbon steel lubricated with Fe3O4 magnetic nano-particle additives in baseoil. *Wear* 2013, 301, 753–757. [CrossRef]