Surface hardening of age-hardenable Cu–Ti dilute alloys by plasma nitriding

S. Semboshi a, b,⁎, S. Kimura b, A. Iwase b, N. Ohtsu c

a Kansai Center, Institute for Materials Research, Tohoku University, Gakuen-cho 1-1, Naka-ku, Sakai, Osaka 599-8531, Japan
b Department of Materials Science, Osaka Prefecture University, Gakuen-cho 1-1, Naka-ku, Sakai, Osaka 599-8531, Japan
c Instrumental Analysis Center, Kitami Institute of Technology, Koen-cho 165, Kitami, Hokkaido 090-8507, Japan

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A plasma-nitriding procedure was applied to enhance the surface hardness and wear toughness of practical age-hardenable Cu–4 mol% Ti alloy. Plasma nitriding at 1073 K and 1173 K leads to the formation of TiN surface layers with thicknesses of 300 nm and 350 nm, respectively, above Cu3Ti3O layers with thicknesses of approximately 700 nm and 2200 nm. In other words, the thicknesses of the surface compound layers increase with plasma nitriding temperature, which also increases the surface hardening. In particular, the hard TiN and Cu3Ti3O on the surface contribute to hardening of the surface to Vickers hardness of around 10 GPa, which is much greater than the hardness of the substrate alloy of approximately 1.6 GPa. The surface layers also modified the wear resistance significantly. Thus, an optimized plasma-nitriding procedure is a promising surface modification technique for age-hardenable Cu–Ti dilute alloys.

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1. Introduction

Age-hardenable copper–titanium (Cu–Ti) alloys have excellent mechanical strengths, stiffness, fatigue properties, and electrical conductivity [1–4], and because of these desirable features they are widely used in electrical components such as connectors and relay controls. Recently, against the background of the downsizing and streamlining of electrical devices, further enhancements in the mechanical and electrical properties of Cu–Ti alloys have become necessary, along with materials with specific functionalities. Improvement of the surface hardness and wear resistance is also needed for connector materials.

Plasma nitriding, a high-temperature surface chemical treatment, is one of the most widely used surface modification techniques for enhancing the surface properties such as the hardness, wear, and corrosion resistance of alloys based on iron and steel [5–7], titanium [8,9], aluminum [10], and magnesium-based alloys [11]. Plasma nitriding forms a nitrided zone such as a nitried layer and/or precipitates on the material surface through the reaction of nitrogen ions with nitrogen-friendly elements in the materials. The nitrided zone often improves the overall material’s hardness and wear resistance. On the other hand, plasma nitriding is generally not suitable for surface hardening of copper and copper alloys, because copper naturally incorporates very few nitrogen atoms and does not allow the formation of its nitride. Thus, the literature on plasma nitriding for copper-based alloys has been very limited. Nakata et al. reported that surface hardening was observed in Cu–Ti and Cu–manganese (Mn) binary alloys with more than 6.5 mol% Ti (5 mass%) and 11.4 mol% Mn (10 mass%), respectively [12]. This hardening occurred through the formation of a nitride layer on the copper alloy surfaces due to the large amounts of nitrogen-friendly alloying elements like Ti and Mn. This report implies the possibility that a proper plasma-nitriding procedure can provide a nitrided zone for commercial age-hardenable Cu–Ti dilute alloys (which contain only 3 to 5 mol% Ti) that could improve their surface hardening and wear resistance.

Hence, in this study, we report on the probability of surface hardening by plasma nitriding for commercially used Cu–Ti dilute alloys. Based on the phase diagram of the Cu–Ti binary system [13], age-hardenable Cu–Ti alloys are commercially manufactured by performing solution treatment in the Cu solid solution region between 1073 K and 1223 K, and then aging between 673 K and 773 K. From an engineering viewpoint, it would be convenient to combine plasma nitriding with the solid solution treatment or aging process. Therefore, plasma nitriding was carried out at 753 K, which is an aging temperature, and at 1073 K and 1123 K, which are solid solution temperatures. The surface structure after plasma nitriding was identified by grazing incident angle X-ray diffraction (GIXD) analysis and conventional transmission electron microscopy (TEM) observation. The surface hardness and wear resistance were also evaluated.

⁎ Corresponding author at: Kansai Center, Institute for Materials Research, Tohoku University, Gakuen-cho 1-1, Naka-ku, Sakai, Osaka 599-8531, Japan. Tel: +81 72 252 1163; fax: +81 72 254 9912.
E-mail address: sembossi@imr.tohoku.ac.jp (S. Semboshi).

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2. Experimental

Alloy sheet with a nominal composition of Cu–4 mol% Ti was provided by Dowa Metaltech Co., Ltd. The alloy was prepared by melting the raw materials, pure copper (99.99 mass%) and titanium (99.99 mass%), in vacuum and hot-rolling them to a thickness of 0.22 mm at approximately 1223 K, followed by quenching into water to obtain a supersaturated solid solution phase of copper. From this sheet, strips with dimensions of 15 mm × 10 mm were cut by a shearing machine. The strips were mechanically polished using a slurry with fine diamond particles to obtain a flat and clean surface. The strips were plasma-nitrided as illustrated in Fig. 1. First, they were put in a furnace heated to a target temperature of 753, 1073 K, or 1123 K in a vacuum of less than 0.1 Pa. To remove the surface oxide layer formed upon heating, the specimens were sputtered at an applied DC voltage of 500 V in an argon and hydrogen (H₂) mixture atmosphere. After the atmosphere was replaced with a nitrogen and hydrogen gas mixture at 0.2 MPa with a ratio of H₂/N₂ = 1, the specimens were plasma-nitrided at the same temperature for 6 h with an applied DC voltage of 500 V and then cooled by a nitrogen gas flow. Some of the plasma-nitrided specimens were aged at 723 K for 12 h under vacuum, which was the peak hardening condition for a supersaturated solid solution alloy [14].

The surface roughness and contours of the specimens before and after the plasma-nitriding treatment were examined by laser scanning microscopy using a Kosaka Lab. Ltd., SEF3500. The surface structure of the specimens was analyzed by GIXD diffraction using a PANalytical X’Pert diffractometer equipped with CuKα radiation (wave length: λ = 0.15418 nm) in a thin-film geometry arrangement at an incident angle of 0.5°. The cross section of the surface was observed by conventional TEM using a JEOL JEM-3010 instrument operating at 300 kV. TEM specimens were prepared using a focused ion beam (FIB) method with an FEI Quanta 3D. The elemental distribution on the specimen surfaces was analyzed by TEM-energy dispersive X-ray spectrometry (EDX) with a FEI Titan instrument operating at 300 kV. The dependence of the hardness on the depth from the surface was evaluated by a Vickers hardness tester. The Vickers hardness was measured at applied loads of 0.098, 0.245, 0.490, 0.980, 1.98, 2.94, and 4.90 N for a loading time of 10 s for each indentation. The hardness was obtained by averaging the values for more than 12 indentations after the largest and smallest values were omitted for each experimental condition. The indentation depth, \( d \) [μm], was calculated from the following equation, given the angle between the opposite faces of the indented diamond tip of 136°:

\[
d = 8.69 \sqrt{\frac{F}{H_v}}
\]

where, \( H_v \) is the Vickers hardness [GPa] and \( F \) is the applied load [N]. Furthermore, the hardness of the specimen's surface was measured by a nanoindenter using a CSIRO UNIS2000 with a Berkovich diamond indenter tip. The indentation load was 1 μN. We evaluated the wear resistance of the specimens using a reciprocation slide-type wear testing machine. In the wear testing machine, a high-carbon-chromium bearing steel sphere with a diameter of 4.76 mm and a mirror-finished surface was reciprocated linearly on the specimen surface at an interval of 5 mm with an applied load of 300 gf at a speed of 1200 mm/min for 30 min. The Vickers hardness of the high-carbon-chromium bearing steel was approximately 7.0 GPa. After the reciprocation wear testing, the surface morphology of the specimen was analyzed by laser scanning microscopy and scanning electron microscopy (SEM) with EDX.

3. Results and discussion

3.1. Surface structure

The Cu–4 mol% Ti alloy specimens plasma-nitrided at 753 K looked similar to how they looked before plasma nitriding. However, the specimens nitrided at 1073 K and 1123 K changed color from copper-like to golden yellow. This implies the formation of TiN on the surface, since its natural color is golden yellow. The calibrated average roughness values, \( R_a \), of the specimens nitrided at 1073 K and 1123 K were (0.27 ± 0.03) μm and (0.30 ± 0.02) μm, respectively, whereas the \( R_a \) before nitriding (i.e. as polished by a diamond slurry) was (0.02 ± 0.01) μm. This

![Fig. 1. Schematic diagram of plasma nitriding process. The processing conditions used in this investigation are listed in the table.](image-url)
indicates that plasma nitriding altered the roughness of Cu–Ti alloy surface, as it does for conventional steel surfaces [5–7].

Fig. 2 shows GIXD profiles for the specimens plasma-nitrided at 753, 1073, and 1123 K for 6 h. In the profile of the specimen plasma-nitrided at 753 K in Fig. 2(a), we found only peaks from a Cu solid solution with a face centered cubic (fcc) structure (lattice parameter, \(a = 0.362\) nm). In contrast, the profiles of the specimens plasma-nitrided at 1073 and 1123 K in Fig. 2(b) and (c) contain peaks from TiN (cubic, \(a = 0.424\) nm) and Cu3Ti3O (cubic, \(a = 1.124\) nm) [14], together with those from the Cu solid solution. It is therefore suggested that TiN and Cu3Ti3O compounds are formed near the surface by plasma nitriding at 1073 to 1123 K.

Fig. 3 shows a cross-sectional high-angle annular dark field (HAADF) TEM image and elemental maps of C, Ti, Cu, O, and N for a specimen plasma-nitrided at 753 K. In the specimen, a very thin layer with a thickness less than 40 nm is present under a carbon layer, which was deposited as a protective film for FIB processing (see Fig. 3(a) and (b)). The Ti, N, and O elements are condensed in this layer, although its structure is unidentified. We also note that there is a Ti-depleted layer between the thin layer and the substrate. In the substrate, fine needles containing concentrated Ti are apparent (see Fig. 3(c)), which are related to continuous precipitation of metastable Cu4Ti with a tetragonal structure [1–3,14].

Fig. 4 shows cross-sectional TEM image and elemental maps for a specimen plasma-nitrided at 1073 K. This specimen contains a surface layer with a thickness of approximately 300 nm, a second layer with a thickness of 700 nm, and the substrate. Ti, N, and O but not Cu were significantly concentrated in the surface layer, and some amounts of Cu, Ti, O, and N were dispersed in the second layer. Fig. 5 shows a cross-sectional TEM image and selected area electron diffraction (SAED) patterns taken from the surface and second layers, respectively, for the specimen plasma-nitrided at 1123 K. A surface layer, second
layer, and substrate are again apparent, as in the specimen plasma-nitrided at 1073 K shown in Fig. 4. The SAED pattern from the surface layer can be indexed to a cubic structure of TiN, and the second layer is indexed to a cubic structure of Cu$_3$Ti$_3$O. Therefore, it is concluded that TiN containing some amount of oxygen is formed as a surface layer and Cu$_3$Ti$_3$O is also formed as a second layer by plasma nitriding at 1073 and 1123 K. This identification is consistent with the GIXD analyses (see Fig. 2(b) and (c)). The thicknesses of both the surface and second layers increased with increasing plasma-nitriding temperature, from 300 nm to 350 nm for the TiN layer and from approximately 700 nm to more than 2200 nm for the Cu$_3$Ti$_3$O layer. However, we note that the thickness of the TiN layer was not as sensitive to the plasma-nitriding temperature as that of the Cu$_3$Ti$_3$O layer.

In this study, it was demonstrated that plasma nitriding at an enhanced temperature of 1073 to 1123 K leads to formation of TiN and Cu$_3$Ti$_3$O layers when there is even a low concentration of Ti (4 mol%) in the alloy. On the basis of the microstructural information presented thus far, it is proposed that the Cu$_3$Ti$_3$O layer forms first, and then the
TiN layer is formed on the substrate during the plasma-nitriding procedure. The Cu₃Ti₃O layer should form upon heating to the target temperature in a vacuum of <0.1 Pa. The results obtained in this study clearly suggest that the formation temperature of Cu₃Ti₃O layer was between 753 K and 1073 K under the vacuum. This is also supported by previous reports that an oxide layer formed easily on Cu–36 mol% Ti alloy even at 873 K in a vacuum of 0.67 Pa [15] and that a Cu₃Ti₃O phase was formed at 1218 K even at a quite low oxygen partial pressure of log \( P_{O_2} \) = −37 [16]. This oxide layer is impossible to remove completely by sputtering in a reducing atmosphere of argon and hydrogen. During the plasma-nitriding procedure, the TiN layer is formed by the reaction of activated nitrogen ions with the titanium existing in and diffused from the Cu₃Ti₃O layer. However, further work is needed to confirm whether the Cu₃Ti₃O layer is necessary for the formation of the TiN layer. It should be noted that the formation of the Cu₃Ti₃O and TiN layers was encouraged at a higher target temperature of plasma nitriding, which is confirmed by the fact that the thicknesses of the layers for the specimen plasma-nitrided at 1123 K are greater than those in the specimen plasma-nitrided at 1073 K. This suggests that the thickness of the surface layers can be controlled by optimizing the plasma-nitriding...
temperature and time. Furthermore, other plasma nitriding parameters such as the applied voltage, ration of nitrogen in the gas mixture, and so on also would be effective for controlling the surface layers. The effects of these parameters will be reported in the future.

3.2. Surface hardness

Fig. 6 shows the dependence of the surface hardness on the depth from the surface for the specimens plasma-nitrided at 753, 1073, and 1123 K. Here, we note that the depth indented by the Vickers hardness tester was always greater than the total thickness of the TiN and Cu$_3$Ti$_3$O layers (see Figs. 3 to 5). This means that the surface hardness in Fig. 6 always reflects that of the substrate, more or less. The hardness of the as-solid-solution-treated specimen was 1.3 GPa. In the specimen nitrided at 753 K, the hardness at all depths increased to approximately 2.6 GPa. This increase in hardness due to plasma nitriding at 753 K is primarily attributed to an age-induced hardening effect. In particular, aging at 753 K for 6 h was reported to yield a solid-solution-treated specimen with the peak hardening through the formation of fine needle-shaped Cu$_4$Ti precipitates, as evidenced in Fig. 3 [1–3,14]. It is also concluded that the thin surface layer, less than 40 nm thick (Fig. 3), contributed little to the surface hardness because it was so thin.

For the specimens plasma-nitrided at both 1073 and 1123 K, the hardness of the substrate was around 1.6 GPa, as measured in an area ground to remove the surface and second layers. Fig. 6 reveals that the hardness increased rapidly with decreasing penetration depth, and the hardness at depths of a few micrometers eventually reached to 3.5 GPa for plasma nitriding at 1073 K and 5.9 GPa for 1123 K. The surface hardnes of the specimens plasma-nitrided at 1073 and 1123 K were estimated to be 9.4 GPa and 10.2 GPa, respectively, from the nanoindentation measurements. We note that the depth of penetration by the nanoindenter at a load of 1 μN was estimated to be less than 3 nm. This means that the surface hardness measured by the nanoindenter primarily corresponds to that of the surface layer of TiN.
The hardness of TiN compound was reported to be 20–22.5 GPa \[17, 18\]. The hardness of Cu$_3$Ti$_3$O must be greater than that of the fcc copper solid solution, because of its large Burgers vector, although there are no quantitative data on its hardness. The surface hardness of the specimen nitrided at 1123 K was much higher than that of the specimen nitrided at 1073 K, which must be caused by the significant thickness of the TiN and Cu$_3$Ti$_3$O layers (see Figs. 4 and 5). Therefore, the increased hardness near the surface, as shown in Fig. 6, is due to the formation of hard TiN and Cu$_3$Ti$_3$O layers.

Plasma nitriding at a temperature between 1073 K and 1123 K for 6 h and subsequent cooling under a gas-flow also serves as a solid-solution-treatment for the substrate Cu–Ti alloys. Therefore, a subsequent aging process could have the potential to improve the mechanical strength of the substrates. Fig. 6 also plots the dependence of the surface hardness on the depth from the surface for the specimens plasma-nitrided at 1073 and 1123 K and then aged at 723 K for 12 h in vacuum. These curves reveal that the aging procedure increases the hardness of the plasma-nitrided specimen, which must be attributed to age-hardening of the substrate alloy. Thus, the combination of plasma nitriding and aging is a promising surface hardening treatment that can also provide excellent mechanical and physical properties of age-hardenable Cu–Ti alloys.

Fig. 7 shows the appearance of the wear track and cross-sectional height profiles of specimens subjected to plasma nitriding at 753, 1073, and 1123 K after a reciprocation sliding wear test. The specimen plasma-nitrided at 753 K was significantly worn during the wear test, and the maximum depth of the wear track was 30 μm (Fig. 7(a) and (a')). On the other hand, the surfaces of the specimens plasma-nitrided at 1073 and 1123 K were not worn (Fig. 7(b') and (c')); instead, the high-carbon-chromium bearing steel used for the wear testing was worn. This is evidenced by the fact that no wear track was detected after the wear test, as shown in the cross-sectional profile in Fig. 7(b') and (c') (the weak rippling waves with a height of 1 μm were noise due to the detection limit of the laser microscope). The wear volume determined from the laser scanning microscopy data was approximately $62 \times 10^{-3}$ mm$^3$ for the specimen plasma-nitrided at 753 K, whereas it was $3 \times 10^{3}$ mm$^{-3}$ and $2 \times 10^{-3}$ mm$^3$ for the specimens plasma-nitrided at 1073 and 1123 K, respectively, which can be regarded to be zero within the experimental accuracy.

For the specimen plasma-nitrided at 753 K, the substrate was hardened by finely dispersed precipitates to the same level as that of peak-aged materials [1–3]. Thus, the wear resistance of this specimen plasma-nitrided at 753 K should be similar to that of conventionally aged Cu–Ti alloys, even if the former is covered with a thin layer. Under this assumption, Fig. 7 indicates that the wear resistance of a peak-aged specimen should be still poor, like that in Fig. 7(a). On the other hand, we can conclude that plasma nitriding at 1073 and 1123 K provides excellent wear resistance to Cu–4 mol% Ti alloys. This is attributable to the surface layer of hard TiN, even if its thickness is only 280 nm or 350 nm. A deeper nitride zone could further improve the hardness and fatigue strength. Thus, this study demonstrates that plasma nitriding can modify the surface of practical age-hardenable Cu–Ti alloys, even if their Ti content is not so high.

4. Summary

In this study, age-hardenable Cu–4 mol% Ti dilute alloys were plasma-nitrided at 753, 1073, and 1123 K. Their surface structure, surface hardness, and wear resistance were evaluated and analyzed. Plasma nitriding at enhanced temperatures of 1073 K and 1123 K forms stable TiN as the surface layer and Cu$_3$Ti$_3$O as the second layer.
on the substrate alloy, although nitriding at 753 K led to formation of only a very thin layer. The thicknesses of the TiN and Cu$_3$Ti$_3$O layers were approximately 280 nm and 700 nm, respectively, for the specimen plasma-nitrided at 1023 K. These layers thickened to 350 nm and 2200 nm for the specimen nitrided at 1123 K. The formation of the TiN and Cu$_3$Ti$_3$O layers provided excellent surface hardness and wear toughness to the substrate alloys: the surface hardness reached to around 10 GPa, and no wear track was introduced by a wear test using high-carbon-chromium bearing steel. Thus, optimized plasma nitriding is a promising approach to modifying the surface properties of practically used Cu–Ti dilute alloys.

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