Effect of treatment time on characterization and properties of nanocrystalline surface layer in copper induced by surface mechanical attrition treatment

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Abstract. Nanocrystalline surface layers were synthesized on pure copper by means of surface mechanical attrition treatment (SMAT) at various treatment times. The microstructural features of the surface layers produced by SMAT were systematically characterized by optical microscopy (OM), transmission electron microscopy (TEM) and X-ray diffraction (XRD) analysis. Hardness and surface roughness measurements were also carried out. It is found that the thickness of the deformed layer increased from 50 to 500 μm with increasing treatment time from 10 to 300 min, while the average grain size of the top surface layer decreased from 20 to 7 nm. Hardness of the all SMATed samples decreased with depth. Furthermore, the hardness of the top surface layer of the SMATed samples was at least two times higher than that of the un-treated counterpart. Surface roughness results showed different trend with treatment time. Amounts of PV and R_a values first sharply increased and then decreased.

Keywords. Nanocrystalline; copper; surface mechanical attrition treatment; hardness; surface roughness.

1. Introduction

It is well known that the majority of failure modes of engineering materials such as wear and corrosion are highly sensitive to the microstructure and properties of the materials surface. Accordingly, in most cases, material failures initiate at the surface. So, surface modification is expected to be a good and effective way to optimize the surface characteristics of the materials. Nanostructured materials (with grain size <100 nm) have been the subject of the widespread investigations over the past two decades because of their superior properties such as high strength, hardness and diffusivity in comparison with those coarse grain types (Lu *et al* 1991; Wei *et al* 2008). Nanocrystalline materials can be synthesized by various techniques such as inert gas condensation (IGC) (Gleiter 1989), mechanical alloying (MA) (Suryanarayana 2001), electrodeposition (Lu *et al* 2005; Shen *et al* 2005), crystallization from amorphous materials (Sun and Lu 1997) and severe plastic deformation. Among these techniques, severe plastic deformation has been widely used in order to form nanocrystalline materials (Wu *et al* 2002; Meyers *et al* 2006). Although any means of introducing large plastic strains in metals may lead to grain refinement, two principal methods for subjecting a material to severe plas-

tic deformation have gained more acceptance, i.e. equal-channel angular pressing (ECAP) (Iwahashi *et al* 1996) and surface mechanical attrition treatment (SMAT). Experimental results indicate that the more common grain size of materials after ECAP process is about 200 nm, but grains as small as 50 nm can be reached in Al alloys. An alternative procedure to introduce high plastic strains is SMAT. This is a recently developed method that can induce grain refinement into the nanometer regime on the surface of the bulk materials. The basic principle of the treatment is generation of high plastic deformation on the top surface layer of the specimen by means of repeated multidirectional and random collision of flying stainless steel balls (Lu and Lu 1999; Wang *et al* 2003; Lu and Lu 2004; Revesz and Takacs 2007; Blonde *et al* 2010). SMAT has some benefits relative to other surface nanocrystallization methods. For example, it does not result in a difference in chemical composition between the nanocrystalline surface layer and matrix. Moreover, it is a simple, flexible and low-cost method. Indeed, SMAT manufactures contamination-free and porous-free samples (Zhang *et al* 2003; Lu *et al* 2006; Wen *et al* 2008). In recent years, the mechanism of surface nanocrystallization by SMAT process has been systematically investigated in pure metals, i.e. iron (Tao *et al* 2002; Wang *et al* 2003), cobalt (Wu *et al* 2005, 2007), titanium (Guo *et al* 2004; Wen *et al* 2007, 2008), copper (Wang *et al* 2003, 2010; Li *et al* 2008), zirconium (Zhang *et al* 2008; Zhang

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and Han 2009), Ni (Wei *et al* 2009) and alloys, i.e. Al alloys (Wu *et al* 2002; Dai *et al* 2004, 2005), AISI 316 stainless steel (Lu *et al* 2006; Roland *et al* 2006), AISI 304 stainless steel (Zhang *et al* 2003), AZ91D magnesium alloy (Sun *et al* 2008a, b; Wei *et al* 2008), NiTi alloy (Hu *et al* 2009), and Ni₃Al alloy (Ren *et al* 2006). These investigations have demonstrated that the grain refinement mechanism depends strongly on the lattice structure and stacking fault energy (SFE) of the treated material, and on the other hand, processing parameters, including the treatment time, diameter of the balls and vibration frequency used in the treatment. We emphasize that there is a lack of literature about the effect of the treatment time on the properties of the refined layer, particularly in the long term. In the present study, pure copper was used as the initial material. In order to investigate the effect of the treatment time on the properties of the surface layer, SMAT was performed at various periods of time. Nanocrystalline structures were characterized by different techniques, and the coarse grain copper was used for comparison.

2. Experimental

A commercial purity copper (99.9 wt%) disc (30 mm in diameter and 5 mm in thickness) was used as the initial sample in this experiment. Prior to SMAT, the copper samples were annealed at 923 K for 2 h to obtain homogeneous coarse-grained structure. Nanocrystallization of the samples was carried out by using SMAT treatment. Schematic of the SMAT set-up used in this study is shown in figure 1. The surface of the bulk samples was subjected to periodic bombardments of stainless steel balls (8 mm in diameter) in a vacuum chamber at various times (10, 30, 60, 120, 180 and 300 min) at a vibrating frequency of 50 Hz. An optical microscopy (Olympus BX51M) was used to observe the microstructural development along a section perpendicular to the treated surface of the samples. Before microstructural observation, the samples were electrolytically etched in 10 wt% phosphoric acid. Microstructural feature in the surface layer of the SMATed sample (treated for 300 min) was characterized by using a Philips EM-420 transmission electron microscope (TEM) (Philips Electronics, Amsterdam, The Netherlands), operating at a voltage of 120 kV. Thin foil samples for TEM observations were prepared first by mechanically polishing the specimen on the untreated side until it was about 30 μm thick followed by Ar ion milling at low temperatures. Average grain size of the top surface layer of the SMATed samples was obtained from X-ray diffraction (XRD) line broadening. XRD experiments were performed on a Siemens D-500 diffractometer with CuK α radiation in the range of 30–80° with a step width of 0.02°. Vickers microhardness (HV) tests on the cross sections of the samples were carried out on a Buhler

microtest device with an applied load of 0.1 N for 10 s. The microhardness variation was measured along the depth (up to 600 μm from the top surface), and the distance between any two neighbouring indentations was at least 10 μm . The average surface roughness (R_a) and peak-to-valley (PV) of the copper samples before and after SMAT was measured using a stylus type surface profilometer (Taylor Hobson Surtronic 25) with an accuracy of 0.01 μm .

3. Results and discussion

Figure 2 shows the cross-sectional optical microscopic microstructures of the as-received and SMATed copper samples. As can be seen, the as-received sample has coarse grains with grain size from 50 to 100 μm . After SMAT, the coarse grains disappeared and severely deformed surface layers were produced. Obviously, the plastic deformation along the depth for all SMATed samples is inhomogeneous; i.e. irregular, multiple slips near the top surface were gradually replaced by single slips with increasing depth. During SMAT, the balls provided repeated multidirectional impacts on a surface at a high speed and generated high-density dislocations and deformation twins. The resultant dislocations could be re-arranged under stress to the dislocation networks which led to the formation of nanocrystallites separated by grain boundaries. Furthermore, deformation twins subdivided the original grains efficiently by introducing different boundaries and leading to formation of refined microstructures. The formation of nano-sized grains is mainly due to three factors: a very large strain, an extremely large strain rate and repetitive loading by balls impacts. Mechanism of grain refinement in pure Cu was systematically studied by Wang *et al* (2006). They found

Figure 1. Schematic of the surface mechanical attrition treatment set-up used in this study.

Figure 2. Cross-sectional microstructure of the SMATed samples after different treating times: (a) 10, (b) 30, (c) 60, (d) 120, (e) 180 and (f) 300 min.

that the plastic strain-induced grain refinement in copper closely relates to its deformation modes, and identified two different mechanisms corresponding to different levels of strain rate. In the subsurface layer (thickness $> 25 \mu\text{m}$) of the SMATed Cu, where strain rate is low and deformation is mainly dominated by dislocation activities, grains in the submicron scales are obtained via formation and development of dislocation cells. The grain refinement process includes: (i) formation of dislocation cells in original grains; (ii) transformation of dislocation walls into sub-boundaries with small misorientations separating the original grains into individual subgrains; (iii) evolution of sub-boundaries into highly misoriented

grain boundaries. On the top surface layer (few microns beneath the uppermost surface) of the SMATed Cu, strain rates are much increased so that deformation twinning plays a significant role in plastic deformation. The grain refinement process involves formation of high-density nanometer-thick twins dividing the original coarse grains to twin-matrix lamellae, development of dislocation walls that leads to further division of the twin-matrix lamellae into equiaxed nano-sized blocks, and evolution of these preferentially oriented blocks into randomly oriented grains (Wang *et al* 2006). Grains cannot be observed in the regions near the treated surface (beneath the top surface) with optical microscopy. Figure 3(a) shows a

Figure 3. (a) Bright field TEM image and corresponding selected area diffraction (SAD) pattern (the inset), (b) dark field TEM image and (c) grain size distribution of the top-treated surface layer of the SMATed copper sample (treated for 300 min).

typical TEM plane view observation and selected area diffraction (SAD) pattern (inset) of the top surface layer in the SMATed copper sample (treated for 300 min). It is clear that the microstructure of the top-treated surface layer is characterized by ultrafine equiaxed grains with random crystallographic orientations. As can be seen, the mean grain size in the surface layer is ~ 10 nm. Quantitative analysis of dark-field TEM image shows that the plane-view grain size of the sample ranges from 3 to 30 nm with an average value of 12 ± 3 nm (as shown in figure 3c). XRD patterns of the Cu samples before and after SMAT are shown in figure 4(a). It is observed that

after SMAT, there is an evident broadening of the Bragg reflections relative to the coarse-grained sample. This can be mainly attributed to grain refinement, increase in the atomic-level strain and micro-distortions of the crystalline lattice. Only a slight change can be observed in the XRD patterns with increasing SMAT duration. The average grain size of the surface layer after SMAT was calculated using Scherrer–Wilson equation. Figure 4(b) shows the variation of grain size and thickness of the deformed layer as a function of treating time, which were obtained from XRD and optical microscopy analyses, respectively. Results show that the average grain size of the top

Figure 4. (a) XRD patterns of the copper samples before and after SMAT at different times. (b) Variation of the grain size and thickness of the deformed layer of the SMATed samples as a function of time duration measured from XRD patterns and microscopic observations, respectively.

Figure 5. (a) Variation of hardness with depth from the top surface on a cross section of the SMATed samples. (b) Variation of hardness of the top surface layer of the SMATed samples with treating time.

surface layer of the SMATed samples reduced gradually with treating time. However, the thickness of the severely deformed layer increased obviously with treating time. These realities suggest that at short treating times (up to 120 min), increase in the treatment time leads to more reduction in grain size (from 20 to 8 nm), but further increase in the treating time (from 120 to 300 min) has not shown any significant change in the grain size. Figure 5(a) shows the microhardness variation with the distance from the SMATed top surface to the matrix for samples treated at different times. The hardness value decreases gradually with farther distance from the surface. The diffusion zone depths (defined by the distance from the top surface to the point where the microhardness is same with that of the matrix) are different for SMATed samples, and increase with treatment time, which are also in good agreement with the microscopic observations shown in figure 2. The microhardness values of the top surface of the SMATed sample as a function of grain size is shown in figure 5(b). A sharp increase in the hardness is obtained after treatment for 10 min. However, with further increase in the treatment time, it is found that the hardness values of the top surface of the SMATed samples increase slightly and these values are at least two times higher than that of un-treated copper. According to the well-known Hall–Petch relationship, large grain refinement into nanometer scale that is induced by SMAT can lead to strengthening and hardening of the copper samples. Based on the microhardness results, it can be concluded that the increment in the treatment time did not show significant effect on the top surface hardness. Because the grain size of the top layer of the SMATed samples is more similar in the long period of treatment times (i.e. 120, 180 and 300 min), the hardness values do not show any obvious change. It becomes interesting that nanocrystalline can also be found even for very short duration (i.e. 10 min). This short-treatment duration has

important meaning in engineering applications because it can save time and energy. There is a wide range of numerical parameters and measurement methods available for characterization of surface roughness. However, height-based parameters have been commonly used in basic roughness characterizations because they can easily be determined from stylus-type profilometer. The arithmetic mean roughness (R_a value) is defined as the average of the absolute value of all area values, $y(x)$, contained within a profile length, as shown in (1)

$$R_a = \frac{1}{L} \int_0^L |Z(x)| dx, \quad (1)$$

another parameter used for roughness measurements is the vertical distance between the highest peak and the lowest valley (PV) of the profile. The R_a and PV values were used in this study because they have been used routinely in industrial applications to quantify the changes in the surface morphology and they are reasonable representations of the roughening behaviour of the materials. The relationship between grain size and roughness is often found to be linear (Mahmudi and Mehdizadeh 1998), but some investigations show deviations from the linear behaviour, especially at higher strains (Dai *et al* 2004, 2005). The changes of R_a and PV of the SMATed samples as a function of treating time are shown in figure 6. It should be noted that the data points shown in these curves are the average values of the three traces. Both curves indicate that the grain size has an appreciable effect on the roughening behaviour of the SMATed samples. As can be clearly seen from both the curves, with increase in the treatment duration, the amount of PV and R_a values first sharply increase and then decrease. At first, when the balls are impacted to the smooth surface, the indents created by the impacting balls are separated. Each of these indents generates a pair of the peak and valley,

Figure 6. Variation of R_a and PV as a function of SMAT time.

so the PV value rises as a result of the formation of new indents. But, by increasing the treatment time from 10 to 30 min, the amount of the indents increases and, as a consequence, the PV value decreases because of the reduction of the smooth contact area and the increment of the surface hardness (increased resistance to plastic deformation). By further increasing the treatment duration, the PV value change is small while it keeps its reducing trend. The trend and evolution sequence of the R_a value can be deduced from the investigation of the PV value.

4. Conclusions

Nanocrystalline surface layers were successfully synthesized on pure copper by means of SMAT at different treatment times. Results showed that the treatment time has a significant effect on characterization and properties of surface layers. Thickness of the deformed layer increased from 50 to 500 μm with increasing duration from 10 to 300 min. Average grain size of the top surface layer of the SMATed samples decreased from 20 to 7 nm with time. As a result of grain refinement, the hardness of the SMATed samples increased by a factor of two or so, and the hardness value decreased with increasing depth from the top surface. Surface roughness results showed in a different manner, i.e. the R_a and PV values, first increased sharply and then decreased.

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