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Thermal stability, phase decomposition, and micro-fatigue properties of pulsed electrodeposited nanocrystalline Co-Cu

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Abstract

Nanocrystalline (nc) immiscible Co-Cu alloys system is a promising material where the decomposition of the super-saturated solid solution can be used to obtain nano-structured materials. In this research, homogenous and solid nc Co-Cu thick films were synthesized through the pulsed electrodeposition technique in complex sodium tartrate electrolyte. Annealing procedures were conducted to evaluate its thermal stability and induce phase decomposition of cobalt and copper, which can be utilized to enhance mechanical properties and thermal stability. Initial cyclic micro-bending experiments were also conducted to observe micro-fatigue properties and structural evolution during mechanical loading.

Keywords: nanocrystalline; thermal stability; phase decomposition; cyclic micro-bending

1. Introduction

Nanocrystalline (nc) materials have outstanding mechanical and physical properties (Gleiter (1989); Meyers et al. (2006)). However, these types of materials are thermally and mechanically unstable and improvements are necessary for wide range applications. Many experiments have been conducted to improve the thermal stability of nc materials, for example, through the addition of alloying elements (Bachmaier and Motz (2014)), through the addition of second

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phase or oxide particle (Molonari et al. (2010)), and by studying the effect of impurities (Hibbard et al. (2006)).

Among the promising materials are immiscible Co-Cu alloys, in which the decomposition of the super-saturated solid solution can be used to obtain nano-structured materials. A series of experiment conducted by Bachmaier (Bachmaier and Motz (2014); Bachmaier and Pfaff et al. (2015); Bachmaier and Stolpe et al. (2015)) showed that nc Co-Cu alloys synthesized by the HPT method have improved thermal stability compared to pure nc Co. No significant decrease of HV numbers was observed in nc Co-Cu even after annealing them for 100 hours at the a temperature $\leq$ 400°C. Interestingly, despite the significant grain coarsening that was observed at 600°C, the microstructure of nc Co-Cu could be maintained in the ultrafine grain region. Phase decomposition of solid solution Co-Cu into fcc-Cu and fcc-Co phases at this annealing temperature was also detected by XRD measurement. Furthermore, phase decomposition of Co-Cu was also observed at a lower annealing temperature (400°C) and it is stable for a long annealing period. However, minor grain coarsening was also observed at this temperature, and further work is required to find the optimum condition for phase decomposition.

The synthesis of nanostructured materials by using the HPT method leads to several problems since it depends on the initial size of the copper and cobalt powder. Moreover, the vacancies and residual stresses were also observed in the nanostructured materials. Synthesis of nc materials by using other methods, for example the electrodeposition technique is possible and has been successfully performed and described in some literatures to produce nc Co (Hibbard et al. (2001)), nc Cu (Lu et al. (1999)), and nc Co-Cu ((Bachmaier and Stolpe et al. (2015); Müller (2014)). Moreover, the synthesis of nc materials through the electrodeposition technique is a simple route of production which also provides technological and economic benefits.

It was also found that nc materials are mechanically unstable since their fatigue resistance are lower compared to ultrafine grain and coarse grain (Mughrabi and Höppel (2010)). Moreover, grain coarsening induced by plastic deformation was also observed on ultrafine grain Cu during cyclic micro-bending experiments (Kapp et al. (2017)). This phenomenon indicates that interesting microstructure development or phase transformation on a nano- and very small scale is possibly observed during mechanical fatigue loading.

2. Experimental Procedures

2.1. Deposition of nc Co-Cu

Nc Co-Cu films were synthesized through the pulsed electrodeposition technique at high current density and low duty cycle (i: 100 mA/cm^2; t_{pulse}: 2 ms; t_{off}: 18 ms). Cu disk ($ø_{surface}$: 12 mm) and platinized-Ti rod were prepared as cathode and anode respectively. According to experiments conducted by Müller (Müller (2014)), homogenous and porosity-free deposits were obtained after deposition in complex tartrate electrolyte instead of complex citrate electrolyte, so the deposition in complex tartrate electrolyte was preferred in this experiment. Pulsed electrodeposition was conducted in the electrolyte containing 112.20 g/L $CoSO_4.7H_2O$, 6.38 g/L $CuSO_4$, 56.44 g/L $C_4H_4KNaO_6.4H_2O$, 142.04 g/L Na_2SO_4, 18.55 g/L H_3BO_3, 2.00 g/L Saccharin, and 0.20 g/L sodium dedocyl sulfate. Deposition was conducted for 24 hours to produce approximately 350 µm film thicknesses and the electrolyte's temperature was maintained at 40°C.

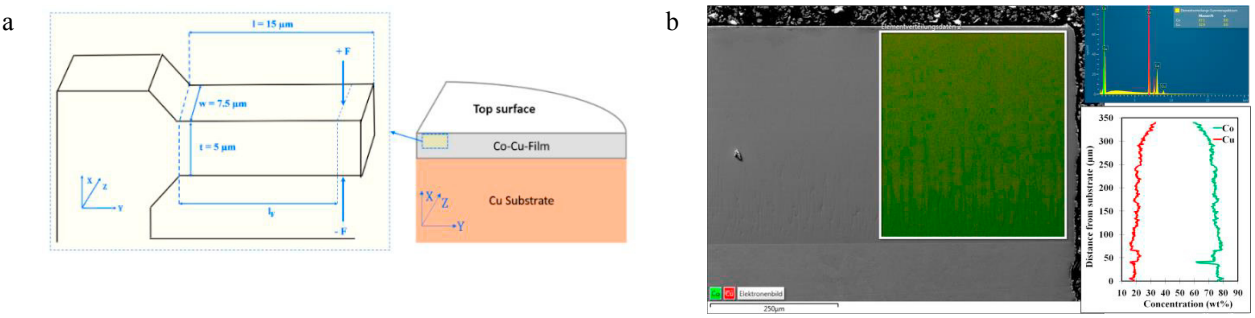

Fig. 1. (a) Schematic drawing of free standing micro bending beam and its position corresponding to the nc Co-Cu film; (a) SEM-EDS observation at the cross section of nc Co-Cu film;

2.2. Characterization and annealing procedures

Deposited nc Co-Cu films were cut in cross-section direction along with Cu substrate. Hereafter, samples were subjected to the subsequent isothermal annealing in the vacuum chamber at different temperatures (300ºC, 400ºC, 450ºC, 600ºC, and 800ºC) and for different periods (1 hour, 5 hours, 24 hours, and 64 hours), then the samples were quenched to the atmospheric air. All as-deposited and annealed samples were surface prepared with a grinding and polishing machine up to a grid of 1 µm and (if required) OPS was also applied. XRD and microhardness measurement were conducted by using non-OPS polished samples, while OPS polished samples were required for SEM observation. TEM samples preparation was conducted by cutting the polished samples to disks of 3 mm and then further processing them with GATAN PIPS for ion milling.

Cu K-alpha radiation (λ: 1.5405980 Å) X-ray diffraction was used to observe the phases of each sample and the scan step size was controlled at 0.013º2θ/s. Microhardness measurements were carried out on the DuraScan hardness testing machine made by STRUERS and then evaluated with the associated ecos WorkflowTM software. The test force of 1.962 N (HV0.2) was applied to the sample surface for 12 seconds. Zeiss SIGMA Scanning Electron Microscope and Oxford-instruments Energy Dispersive Spectroscopy were used to observe both the microstructure and the alloys' composition at an accelerating voltage of between 17-20 kV. TEM JEOL 2011 was also used to obtain better information about at an accelerating voltage of 200 kV.

2.3. Cyclic micro-bending experiments

The free-standing micro bending beam with a dimension of 15 µm x 7.5 µm x 5 µm (lengt x width x thickness) was prepared by Focused Ion Beam (FIB) at the area close to the surface of the deposits. A schematic drawing of micro beams is shown in Fig. 1a. The cyclic micro-bending experiments were conducted inside the Zeiss SIGMA SEM by using Advanced Surface Mechanics (ASMEC) system and a UNAT-SEM2 nanoindenter, then the data were recorded by InspectorX Ver. 2 (UNAT software). A double blade gripper was used to transmit the cyclic loading onto the bending beam and the plastic strain amplitudes were controlled at two different values which are $\varepsilon_{a,pl} = 4.0 \times 10^{-4}$ (stage-I: 1st - 2000th cycle) and $\varepsilon_{a,pl} = 6.5 \times 10^{-4}$ (stage-II: 2001st - 4000th cycle). According to the method used by Kapp et al. (2017), the value of the maximum surface stress σ_s and the maximum surface strain ε_s were taken into account. Based on the elastic bending beam theory, the maximum surface stress σ_s and the maximum surface strain ε_s are calculated from force-displacement data by using equation (1) and (2). The applied displacement is u, the recorded force is F, length of bending is l_F, width of beam is w, and thickness of beam is t.

$$\sigma_s = \frac{6\,F\,l_F}{w\,t^2} \tag{1}$$

$$\varepsilon_s = \frac{u\,t}{2\,l_F^{\,2}} \tag{2}$$

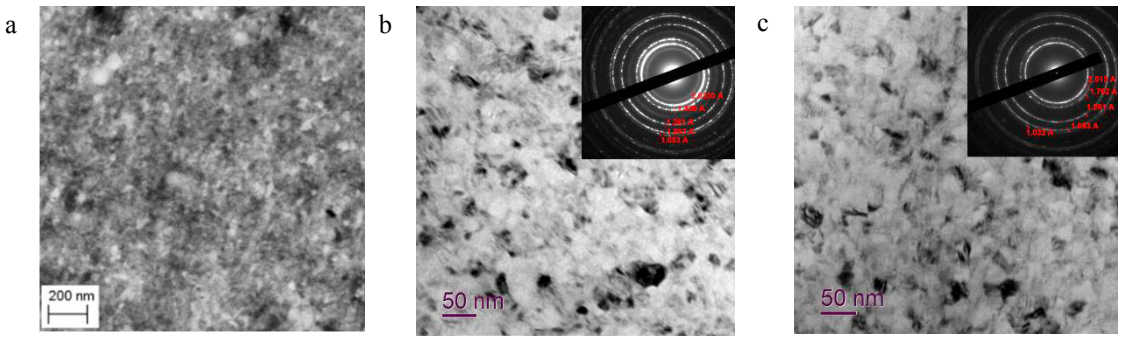

Fig. 2. (a) BSE images of microstructure of as deposited sample; BF TEM micrograph and SAD pattern of (b) as deposited sample and (c) annealed at 300ºC for 64 hrs sample.

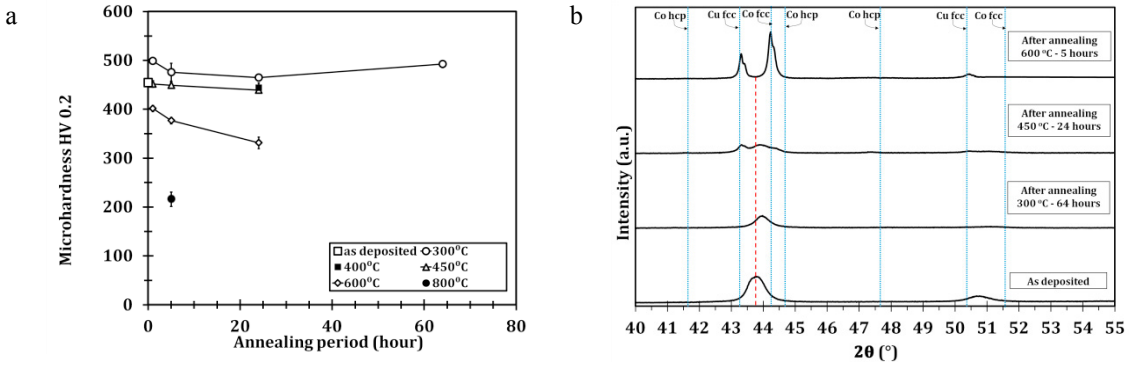

Fig. 3. (a) Microhardness HV0.2 of as-deposited nc Co-Cu and annealed samples as a function of annealing period at different annealing temperatures; (b) XRD patterns of as-deposited and annealed samples. The blue lines represent the diffraction peaks of Co and Cu, whereas the red line is located in the center of diffraction peak of as-deposited sample.

3. Results and Discussion

3.1. As deposited

Fig. 1b shows SE images of as deposited nc Co-Cu at the cross section view. The thick films of nc Co-Cu for up to 350 µm were successfully deposited with no-porosity observed. SEM-EDS measurement shows the typical composition 67wt% Co-33wt% Cu is observed. Interestingly, the Co and Cu atoms are homogenously distributed from the Cu substrate interface next to the surface of the deposit (see Fig. 1b).

Fig. 2b shows a bright-field TEM images and a selected area diffraction (SAD) pattern of deposited nc Co-Cu film. The average grain size for about ~23±8.16 nm is confirmed and the average microhardness for about 455±6.9 HV is measured (see Fig. 3a). The SAD pattern strongly indicates that deposited nc Co-Cu exhibits supersaturated solid solution phase since the diffraction rings are in the between of the fcc Co and fcc Cu Debye-Scherrer rings of {111}, {200}, {220}, and {311} planes. Supersaturated solid solution Co-Cu was also observed in previous researches with this typical alloy composition (Bachmaier and Motz (2014); Bachmaier and Stolpe et al. (2015)). Moreover, the XRD pattern of the as-deposited sample (Fig. 3b) shows a similar result with SAD pattern, where the diffraction peaks are located between the fcc Cu and fcc Co diffraction peaks.

3.2. Thermal stability and phase decomposition

As-deposited nc Co-Cu films were subjected to isothermal annealing procedures to investigate their thermal stability. Fig. 3a shows that these annealing procedures at 300°C which corresponds to ~35% of the melting temperature of the alloy lead to an increasing value of hardness where minor grain coarsening is observed by a bright-field TEM image (see Fig. 2c). The hardness value increases for up to 492±7.27 HV for the sample annealed for the longest period (64 hours) and the measured grain size for this sample is 40±13.24 nm. Interestingly, lattice distortion is also observed in the diffraction pattern of XRD (Fig. 3b) and SAD-TEM (Fig. 2c) compared to the as-deposited sample. This could be an indication of the phase decomposition which was also observed in the experiment carried out by Bachmaier (Bachmaier and Pfaff et al. (2015)) at a higher annealing temperature (400°C) with a different alloy composition. Furthermore, this will be an advantage for the tailoring phase decomposition at low temperature, where nano-sized grain below 50 nm can be maintained.

Minor grain coarsening is also observed in the sample annealed at 400°C for 24 hours, where the hardness value decreases to 444±10.31 HV (see Fig. 3a) and the grain size increases to 82±28.00 nm. A microstructure image of the sample annealed at 400°C for 24 hours is given in Fig. 4a. This could be an upper-limit temperature for the tailoring phase decomposition where nano-sized grain can be maintained below 100 nm, but an annealing procedure at lower temperature will be preferred. Grain coarsening is more pronounced in the samples annealed at higher temperatures (450°C and 600°C), where the hardness values significantly decrease for up to 439±5.18 HV and 331±11.78 HV for the sample annealed at 450°C and 600°C for 24 hours, respectively (see Fig. 3a). However, ultrafine grain structures

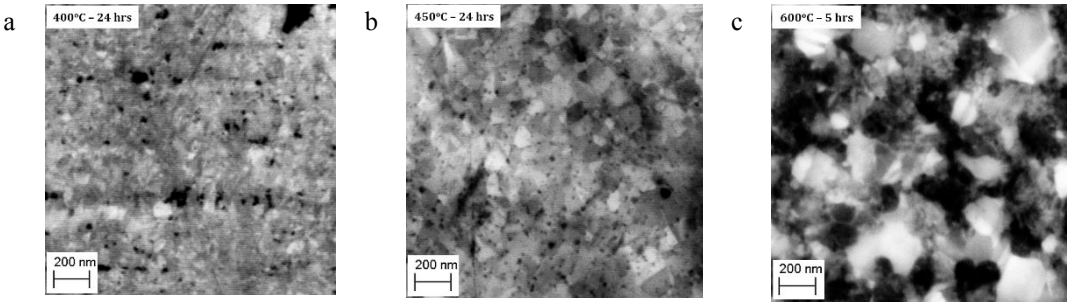

Fig. 4. Microstructure images of (a) annealed at 400°C for 24 hours; (b) annealed at 450°C for 24 hours; and (c) annealed at 600°C for 5 hours taken by BSE detector.

were remained in the sample annealed at 450°C and 600°C, in spite of an annealing period of up to 24 hours. Interestingly, distinct microstructures are clearly observed at the samples annealed at these temperatures (see Fig. 4(b-c)) and the phase decomposition to fcc Co and fcc Cu phases is confirmed by the XRD patterns (see Fig. 3b).

3.3. Initial cyclic micro-bending test

Low cyclic micro-bending tests were conducted to observe initial fatigue properties of as-deposited nc Co-Cu films. Selected surface stress as a function of surface strain data was plotted into cyclic hysteresis loop graph and shown in Fig. 5a. The average stress amplitude ($\sigma_{s,avg,amp}$) of each cycles was calculated by equation (3) and then plotted into a graph as given in Fig. 5b. This graph is very useful to observe softening/hardening phenomena and also to determine at which cycle the crack (if it appears) is initiated.

$$\sigma_{s,avg,amp} = \frac{\sigma_{s,max} - \sigma_{s,min}}{2} \tag{3}$$

The beam was subjected into two stages of the cyclic bending test. Firstly, the beam was induced to the cyclic bending loading with a plastic strain amplitude of $\varepsilon_{a,pl} = 4.0 \times 10^{-4}$ for 2000 cycles and the average stress amplitude values (Fig. 5b) remain constant. Afterwards, the beam was also subjected to 2000 further bending cycles by increasing the plastic strain amplitude to $\varepsilon_{a,pl} = 6.5 \times 10^{-4}$. Selected cyclic hysteresis loops (see Fig. 5a) show that Young's modulus of the beam gradually decrease at a cycle number >3000 and a crack is observed after the end of the test as given in Fig. 6 (a-b). Moreover, Fig. 5b shows that the average stress amplitude significantly decrease after cycle number of 3200 and it is believed that the crack was initiated at this point. The crack with the length of ~1.5 μm is measured from the beam (see Fig. 6b) and grain coarsening is also observed from the area close to the crack (see Fig. 6c). The mechanism of the crack formation, grain coarsening, and their interaction must be studied further.

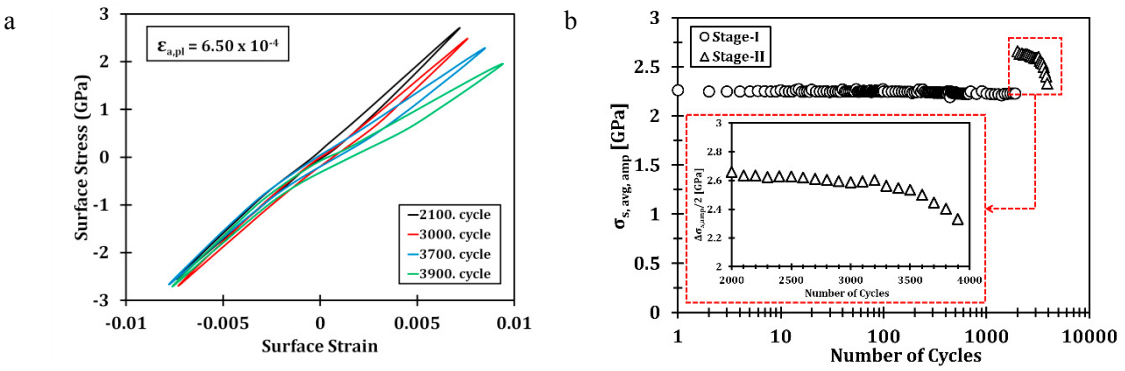

Fig. 5. (a) Selected cyclic hysteresis loop of the beam at plastic strain amplitude of stage-II (6.5 x 10^{-4}); (b) The average stress amplitude values ($\Delta\sigma_{s,amp}$) were calculated as a function of the number of the cycle.

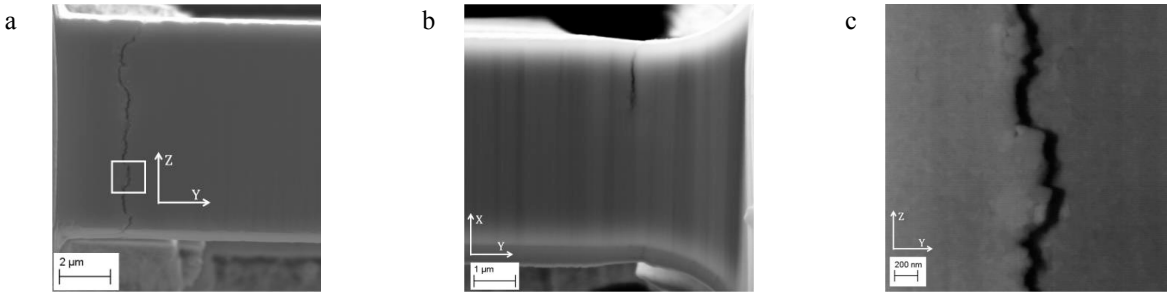

Fig. 6. SE images of the beam after 4000 cycles observed from (a) top view and (b) side view; (c) BSE images of microstructure of the beam after 4000 cycles at the position marked on (a). The axis in all images is corresponding with the axis described in Fig. 1a.

4. Conclussion

The porosity-free and homogenous nc $Co_{67wt\%}$-$Cu_{33wt\%}$ films have been successfully synthesized through the pulsed electrodeposition for up to 350 µm film thicknesses. Nano-sized grain of ~23 nm and supersaturated solid solution Co-Cu are observed in deposited nc Co-Cu films.

As-deposited nc Co-Cu has a good thermal stability at an annealing temperature of 300°C. Phase decomposition is indicated by the increase of hardness and the observed lattice distortion at this annealing temperature (300°C), where the grain size can be maintained below 50 nm. As deposited nc Co-Cu has a good thermal stability for up to 400°C. Annealing at higher temperatures (450°C and 600°C) leads to a more pronounced grain coarsening but interesting microstructure and phase decomposition are reported. Further works are required to study phase decomposition in nc Co-Cu.

Initial cyclic micro-bending tests show that the micro beam of nc Co-Cu has a good fatigue resistance for up to 2000 cycles at the plastic strain amplitude of $\varepsilon_{a,pl} = 4.0 \times 10^{-4}$**.** However, a crack is observed on the micro beam after being subjected to 2000 further cycles at the higher plastic strain amplitude ($\varepsilon_{a,pl} = 6.5 \times 10^{-4}$).

Acknowledgements

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