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Comparing small scale plasticity of copper-chromium nanolayered and alloyed thin films at elevated temperatures

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Abstract—The yield strengths and deformation mechanisms of Cu–Cr nanolayered and alloyed thin films were studied by microcompression testing at elevated temperatures. The mechanical response of the films with alternating layers of Cu and Cr with sub-100 nm interlayer thicknesses and alloyed films of the same average composition was compared to determine the role of the interfaces on deformation. Higher resistance to plastic flow at elevated temperatures was exhibited by the nanolayered films with smaller interlayer thickness among the layered films, while the alloyed film revealed an anomalous increase in strength with temperature exhibiting a deformation mechanism similar to the pure Cr film.

Keywords: Micromechanics; Nanostructured materials; Transmission electron microscopy; Interfaces; Stress-assisted diffusion

1. Introduction

Nanolayered thin films, which are composed of alternating stacks of layered materials of similar or dissimilar bonding such as metals, ceramics and also polymers with individual layer thicknesses of less than 100 nm, are found in ever increasing numbers of applications due to their superior functional [1–3] and/or structural properties. Nevertheless, the usage of these nanolayered thin films is based on empirical performance and not on scientifically backed design rules, which will assist in engineering optimal micro-/nano-structures desired for the application.

The exciting possibilities at the nanoscale and the difficulty in producing bulk nanostructured materials, especially metals, provide the scientific impetus for studying nanolayered thin films. While several studies have been undertaken to clarify the mechanical behavior of such films at ambient temperature [4–16], few have investigated the deformation response at elevated temperatures [17–22]. These few studies have mostly used the instrumented indentation technique, which despite the ease of testing presents difficulty in direct interpretation of the results due to the complex stress states involved. The micro-compression technique, which is an established technique for studying plasticity in materials exhibiting limited or negligible ductility, offers a near uniaxial stress state and in combination with a microscope allows *in situ* visualization of the deformation sequence [23].

The nano-layered stacking of soft, ductile copper and hard, brittle chromium offers the possibility of studying not only the influence of layer thickness of a *fcc*//*bcc* stacking of nanocrystalline copper and chromium respectively, but also the role of interfaces of these nearly immiscible systems [24] on their mechanical behavior. From a technological perspective, it is desirable to obtain an optimal composition of a Cu–Cr alloy to improve the strength and oxidation resistance of copper used universally in applications exploiting the electrical properties of copper, while demanding high strengths. While a few studies have investigated the extension of miscibility by using rapid quenching and severe plastic deformation and forming metastable Cu–Cr alloys, a more thorough recent study has indicated that an optimal composition is indeed achievable [25]. These ideas and inputs lead to the motivation to study the role of compositional architecture, in other words, design of the nanolayering vis-à-vis nano-scaled alloying of the films of the same overall composition. Hence, the mechanical behavior of a Cu–Cr alloyed film of the same nominal composition was also investigated and compared with the nanolayered Cu–Cr thin films to obtain insights into the plausible advantages of the nanolayering/architecture over the alloyed film. Since the

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nano-scaled alloy films are far beyond the solubility limit, the thermal stability of these systems, which is important for any future applications where exposure to elevated temperatures cannot be avoided (e.g. Joule heating in electronic devices), is an outstanding issue.

Thus, in this study, the strengths and deformation mechanisms of nanolayered and alloyed Cu–Cr thin films of the same nominal composition have been investigated using nanoindentation and micro-compression at ambient and elevated temperatures and correlated with the nanostructure, layer thickness/grain size and internal stresses obtained using transmission electron microscopy and X-ray diffraction.

2. Materials and methods

2.1. Coating deposition

Nanolayered (NL), alloyed (A) and pure thin films of copper and chromium were deposited to total thickness of 2 μm by direct current magnetron sputtering (Mantis Deposition Ltd, UK, Model: QPrep) on Si (100) substrates with a 200 nm thick layer of thermally grown SiO_2 to prevent chemical bonding of the first chromium layer with the bare Si (100) substrate. The films were synthesized by sputtering 99.99% pure copper and 99.95% pure chromium targets (76.2 mm diameter × 3 mm thick) in an Ar atmosphere with a flow rate of 45 sccm and sputtering pressure was 0.3 Pa after achieving a base pressure better than 2×10^{-5} Pa. Currents of 200 mA and 300 mA were used for Cu and Cr respectively for all except the alloyed (synthesized by simultaneous sputtering) film, where currents of 193 mA and 318 mA were used for Cu and Cr respectively. In addition, the substrates were rotated at a constant speed to achieve a uniform deposition.

2.2. Structural characterization

High resolution scanning electron microscope (HRSEM) images of surfaces and cross-sections of the films were obtained at a tilt of 54° by using a Zeiss Auriga cross beam workstation®. The cross-sections were made using the Ga^+ beam operated at 30 kV with currents of 2 nA to mill the rectangular trenches, fine mill the walls with 600 pA and polish using 50 pA. Surfaces of the pure films and the alloyed film were polished using the Ga^+ beam with currents of 50 pA operated at 30 kV before imaging.

X-ray diffraction technique was used to determine the crystal structure and the grain size of the films. The phases present in the films were analyzed from grazing incidence X-ray diffraction (GI-XRD) patterns obtained from a Seifert Type ID3003 diffractometer operated at 40 kV and 30 mA. The patterns were excited by a Co–K_α source grazing the samples at 2° in point focus mode in steps of 0.05° and count time of 40 s per step. The phase analysis was complemented by energy dispersive X-ray spectroscopy (EDS) measurements performed using a Jeol 6490 scanning electron microscope operated at 15 kV to estimate the composition of the films.

Transmission electron microscopy (TEM) of cross-sections of the thin films was carried out using a Jeol JEM-2200FS field emission gun instrument operated at 200 kV. Details of the procedure for preparing the electron transparent cross-section lamellae are provided elsewhere [25].

2.3. Mechanical characterization

2.3.1. Nanoindentation

The indentation response of all the films as a function of penetration depth was studied by using a Berkovich indenter tip in a Hysitron Ubi® nanoindenter in load controlled mode. Twenty-five tests were carried out in each case such that the maximum load was adjusted from 10 mN for the first test to 1 mN for the last indent with a loading rate of 1 mN/s and constant hold time of 10 s. The hardness and reduced elastic modulus were obtained from the load – displacement curves from each test by using the Oliver and Pharr method [26].

2.3.2. Micro-compression

Micro-pillars were machined within all the films using a Zeiss Auriga dual beam FIB workstation operated at 30 kV. Initially, large trenches with diameters of 10 μm were machined using currents of 2 nA to provide sufficient clearance for the flat punch used for compression and allow viewing of the entire length of the micropillar. The desired dimensions of the micropillars with diameters of 800–900 nm and maintaining an aspect ratio of approximately 2.3 were achieved by fine milling using currents of 600 pA and polishing using 50 pA. The compression tests were carried out by using the Alemnis *in situ* SEM indenter [27,28] with a 2.5 μm diameter diamond flat punch in displacement control at rates of 5 nm/s. The load–displacement curves were corrected for instrument and substrate compliances [29] before converting them into engineering stress–strain curves. Stress values at 0.5% strain offsets of the engineering stress–strain curves were considered as the yield strengths of the respective films. The micropillars were imaged after compression with a Hitachi S-4800 high resolution scanning electron microscope (HRSEM).

3. Results

3.1. Nano-/microstructure of the films

While FIB cross-sections and images revealed that all the films were approximately two microns in thickness as desired, the ion beam polishing of the surfaces of the films provided complementary insights into the microstructure of the films (Fig. S1). The pure copper films revealed a bimodal distribution in grain size with sizes ranging as large as 1 μm and agglomerates of twinned sub-300 nm grains. A plate-like morphology with thicknesses of around 50 nm and cavities at their wavy interfaces were characteristic of the pure chromium films, while the alloyed films reveal columns of around 50 nm and cavities at the inter-columnar boundaries (Fig. S1).

FIB cross-sections of the nanolayered films revealed continuous layers of copper (lighter) and chromium (darker) with few pores located irregularly but close to the interfaces of the layers (Fig. S1). Both layered films exhibit interfaces, which were flat initially, but increase in waviness further away from the substrate after approximately 40% of the total thickness of the film. Wavy interface morphologies have been observed in several systems and can be suppressed by optimization of the deposition parameters [30]. TEM of the film cross-sections confirmed the polycrystalline nature of the individual layers, presence of twins within the copper layers and cavities within the chromium layers of the 66Cu//33Cr - NL film (Fig. 1(a)). The presence