Microstructure Analysis of Electroplated Cr-Fe Alloy Deposits on Cu Substrate

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Since a series of health hazard toxic processes in electroplating industry, e.g., Cr^{6+} electroplating, has been banned under RoHS (Restriction of the Use of Certain Hazardous Substance in EEE) regulation, trivalent Cr electroplating has becoming one of the alternatives for Cr^{6+} electroplating. An eco-friendly trivalent Cr-based electroplating bath with high efficiency has recently developed, and believed that Cr-based alloy deposits have better corrosion resistance than pure Cr deposits [1]. This paper reports the morphological/microstructural study of Cr-Fe alloy deposits on Cu rotating cylinder electrodes (RCE) that has electroplated in an eco-friendly Cr^{3+} and Fe^{2+} based solution.

Commercial copper bars were cut/shaped as RCE with an exposure area of 2 cm^2 around the cylinder. RCE surface was mechanically ground, pickled and cleaned with de-ionized water before electroplating taken place. RCE were rotated at 300 rpm and electroplated in the electroplating bath that consisted of 0.8M $CrCl_3 \cdot 6H_2O$, 0.4M $FeSO_4 \cdot 7H_2O$, 0.2M $Na_3C_6H_5O_7 \cdot 2H_2O$, 0.4 M urea, complexing agent and a small amount of conductive and buffer salts with the electroplating current density (EPCD) of 0.2, 0.25, or 0.3 Acm^{-2} for 30, 24, or 20 minutes, respectively. Some of plated specimens were rapidly heated at a heating rate of 3 $^oC/S$ and annealed at 500 ^oC for one second in the RTA (rapid thermal annealing, Model ULVAC RHL-P610CP) vacuum chamber. The Cr-Fe alloy coating/deposits on RCE were examined using a Hitachi SU-70 FEG SEM equipped with a Bruker EDS system.

EDS analysis shows the electroplated deposit/coating was Cr-Fe alloy and homogeneous throughout (Fig. 1). The Cr content in the deposits increased from 30 to 61 wt.% when the EPCD increased from 0.2 to 0.3 Acm^{-2} whereas the Fe content decreased from 63 to 27 wt.% with the increase of EPCD (Fig. 1). Note that C content also increased gradually with the increase of EPCD due to the reduction mechanism. It is believed that the complex-formed Cr ions contain some C and co-deposited onto the cathode simultaneously [2]. SEM images of the as-grown Cr-Fe alloy deposits, as shown in Figure 2, reveal typical nodular (rough bumpy) morphology on the surface of RCE. Although nodular morphology were presented in all electroplating condition, the size of nodular varies with EPCD, ranging between 1 ~ 5 μm in 0.2 Acm^{-2} and 1 ~ 15 μm in 0.3 Acm^{-2}. It is believed that the nodular surface of Cr-Fe alloy deposit was resulted from high EPCD and impurities in the electroplating solution. At high magnification, it appears that the surface roughness reduces with the increase of EPCD in addition to many small pin holes surrounding nodular spots (see upper inserts in Fig. 2). Those small pin holes are believed to be caused by the escape of hydrogen bubbles during electroplating [3]. Cross-section SEM views also reveal some of residual passages created by hydrogen gas. With high EPCD the residual stress was accumulated and led to the network-like cracks on Cr-Fe alloy deposits. The width of cracks was less than 1 μm in as-grown deposits, but it widened to ca. 2 μm and then ca. 3 μm as EPCD increased from 0.2 to 0.25 and then 0.30 Acm^{-2}, respectively (Fig 2). The number of cracks also increased with the increases of EPCD from ~ less 5 to about 15. Thus, the width and the amount of surface cracks increase with the increases of EPCD. Cross-sectional SEM images (lower inserts in Fig. 2) depicts the thickness of Cr-Fe alloy deposits varies with EPCD, i.e., the higher the current the thicker the deposit. The thickness of Cr-Fe alloy deposits was 9.4, 13.2 and 18.9 μm which were formed with EPCD at 0.2, 0.25 or 0.3 Acm^{-2}, respectively. Although the total electroplating charge could be the same (720 Coulomb), electroplating efficiency may vary with different EPCD. Thus, the Cr-Fe alloy deposit with 0.2 Acm^{-2} has the worst efficiency as it formed the smallest thickness and the

largest amounts of pinholes among those deposits.   During the rapid annealing, the Cr-Fe alloy deposits and Cu substrate were heated (500 ^{o}C) at the same time.   Due to the moderately different coefficient of thermal expansion (CTE) between Cr-Fe alloy ($6\sim12\times10^{-6}$) and Cu ($17\sim19\times10^{-6}$), extra residual stress was built up at the interface between deposits and substrate.   In addition, annealing also created additional thermal stress.   The widening and creating more cracks in the annealed Cr-Fe alloy deposits was attributed from the release of part of residual stress (Fig. 3).

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[4] SEM work performed at NISP Lab was partially supported by NSF-MRSEC (DMR 05-20471, Shared Experimental Facility) and UMD.
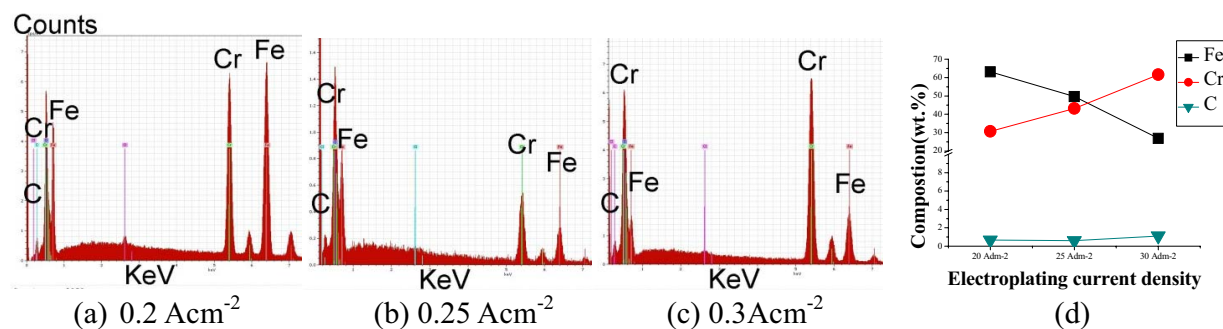
| (a) 0.2 Acm^{-2} | (b) 0.25 Acm^{-2} | (c) 0.3Acm^{-2} | (d) |

Fig. 1.   EDS spectrum Cr-Fe alloy deposits formed with EPCD at (a) 0.2, (b) 0.25 and (c) 0.3 Acm^{-2} as well as the relation between EPCD and elemental composition of Cr-Fe deposits
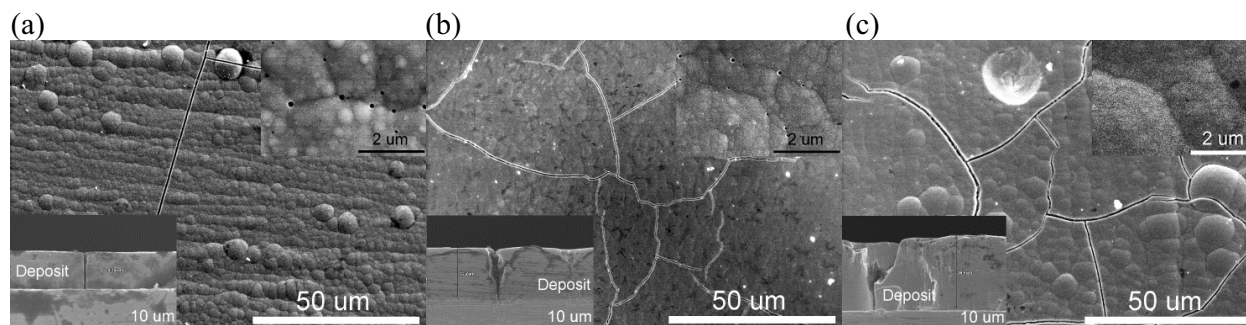

Fig. 2.   SEM images showing surface morphology of as-grown Cr-Fe alloy deposit electroplated with EPCD at (a) 0.2, (b) 0.25 and (c) 0.3 Acm^{-2}
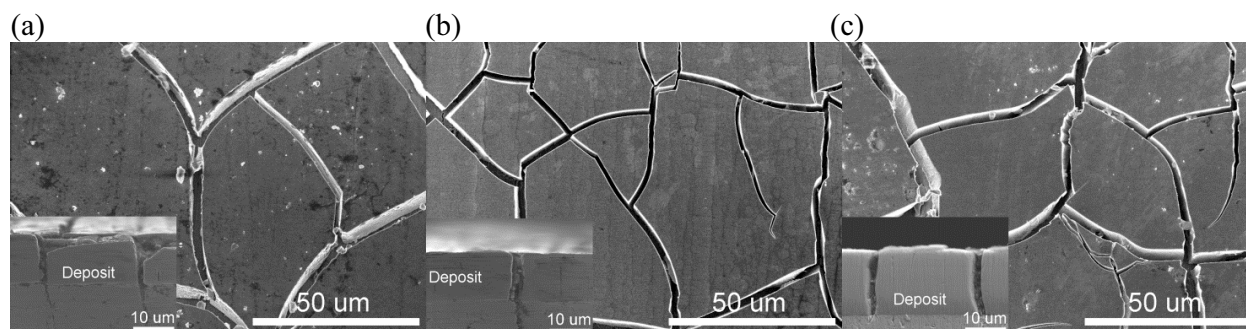

Fig. 3.   SEM images revealing surface morphology of anneald Cr-Fe alloy deposits electroplated with EPCD at (a) 0.2, (b) 0.25 and (c) 0.3 Acm^{-2}