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Iron–tungsten alloys electrodeposited under direct current from citrate–ammonia plating baths

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ABSTRACT

Fe–W alloys containing ~23–30 at.% tungsten were electrodeposited from citrate–ammonia solutions at different cathodic current densities. A characterization of the structural properties of these coatings is reported.

The 8 to 15 μm thick Fe–W coatings obtained are smooth and nano-crystalline. The structure of such as-electrodeposited coatings evolves slightly with increasing cathodic current densities. Above 5 A dm^{-2}, micro-cracks appear in electrodeposited Fe–W coatings, and the oxygen content in the coatings increases. A nano-crystalline structure and a high tungsten content result in nanohardness of 13 GPa. The electrodeposited Fe–W alloys remain "nanocrystalline" after annealing up to 800 °C. After heating at 1000 °C, the nano-crystalline structure transforms into a microcrystalline one, and up to three phases are formed, namely $FeWO_4$, Fe, and possibly Fe_2W.

1. Introduction

The electrodeposition of pure tungsten and molybdenum coatings from tungstate solutions is hindered by the formation of an oxide layer on the cathode during electrodeposition. That oxide cannot be reduced to metallic tungsten directly because of the very low over-voltage for hydrogen evolution on tungsten. Hence, a further reduction to metallic tungsten does not proceed, and the entire current is consumed for hydrogen evolution [1–2]. Very thin films of metallic tungsten electrodeposited from alkaline aqueous solutions containing WO_3 (pH 13) were reported by Azhogin et al. [3]. On the contrary, tungsten and molybdenum ions do co-deposit with iron group metals so that alloys containing a high content of refractory elements are obtained [4–7]. This phenomenon is called by Brenner "induced co-deposition" [7]. Electrodeposited tungsten alloys possess attractive corrosion and tribological properties [6–11]. Therefore such coatings were considered recently as an alternative to electrolytic chromium coatings. The electrochemical synthesis of W and Mo-based alloys has essential advantages compared to the electrodeposition of chromium in terms of ecological and health risks [12,13].

At least four processes take place during the electrodeposition of Fe–W alloys, namely the reduction of both iron complexes and tungstate ions, the evolution of hydrogen, and the formation of products resulting from the incomplete reduction of iron ions [14–16]. Moreover, the current efficiency, the structure, and the morphology of such electrodeposited alloys depend on the cations presented in the electrolyte, namely NH_4^+, K^+, and Na^+ [16]. Recently, the mechanical properties of Fe–W coatings deposited from various electrolytes at current densities varying from 1 to 35 A dm^{-2} at plating temperatures between 40 and 90 °C, were reported [6,12,14]. The maximum microhardness was obtained for Fe–W coatings electrodeposited from citrate–ammonia baths operated at 70 °C. An important feature of such alloys was their amorphous or nanocrystalline structure [6,14–18]. The corrosion behavior of such Fe–W coatings was reported by Kublanosky et al. [18]. In order to improve stability and buffer capacity of the plating solution, the electrodeposition of tungsten containing alloys should be done at higher temperatures (70 °C) and relatively high concentrations of ammonia (1.2–1.5 M) at pH 7–9 [19].

The aim of this work is to study the electrodeposition of Fe–W alloys coatings over a wide range of cathodic current densities from environmentally friendly citrate–ammonia solutions containing high amounts of ammonia. The changes in structure and composition caused by an annealing up to 1000 °C were investigated.

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2. Experimental

2.1. Electrodeposition of W-containing alloys

Fe–W alloys were electroplated from aqueous solutions containing 0.2 M ferric sulfate, 0.33 M sodium citrate, 0.4 M sodium tungstate, and 0.17 M citric acid. A pH of 8.0 was maintained by adding ammonia or sulfuric acid. The thickness of the electrodeposited coatings varied between 8 and 15 μm. The thickness was calculated based on gravimetric and elemental analyses of the electrodeposited alloys. ST3 steel was used as substrate, except for XRD analyses where copper was used as substrate. Prior to electrodeposition, the ST3 substrates were mechanically polished using diamond paste followed by

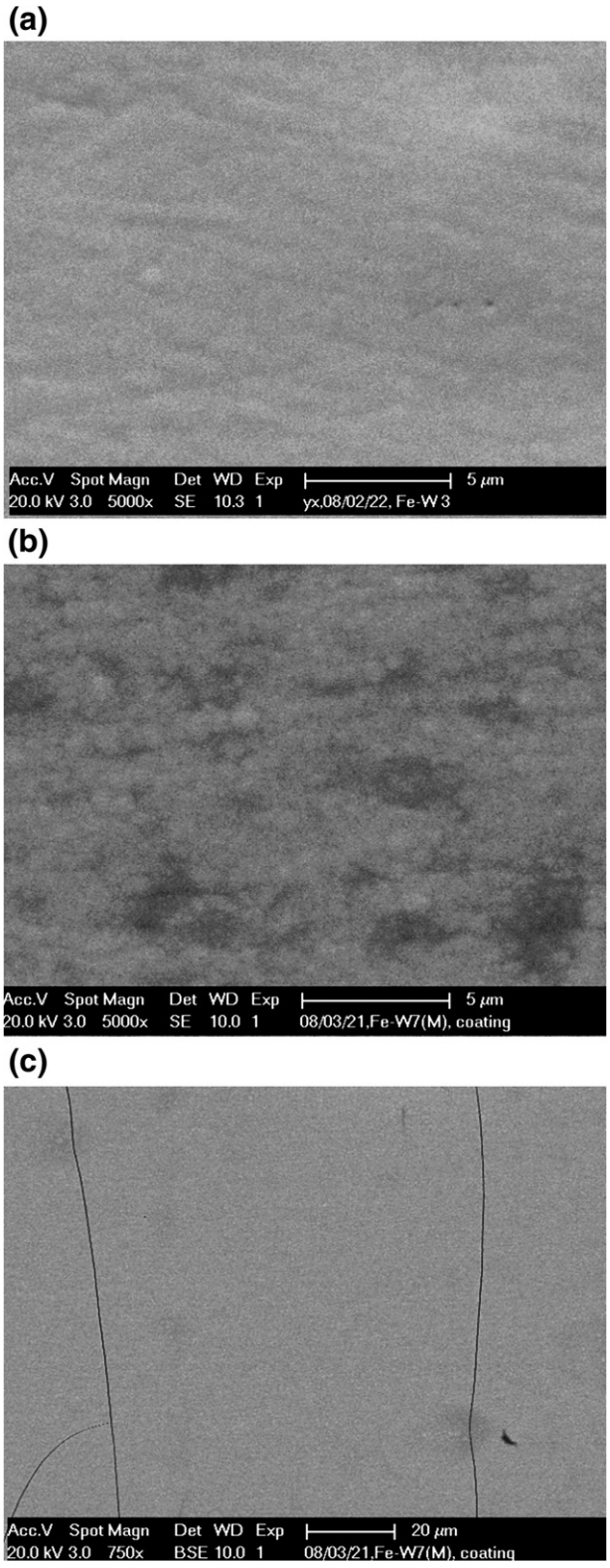

Fig. 1. SEM morphology of as-deposited FeW coatings electrodeposited at different current densities: (a) 1 A dm^{-2}; both (b) and (c) 10 A dm^{-2}. Fig c was taken at lower magnification. Thickness of the coatings was 11.5 ± 3.5 μm.

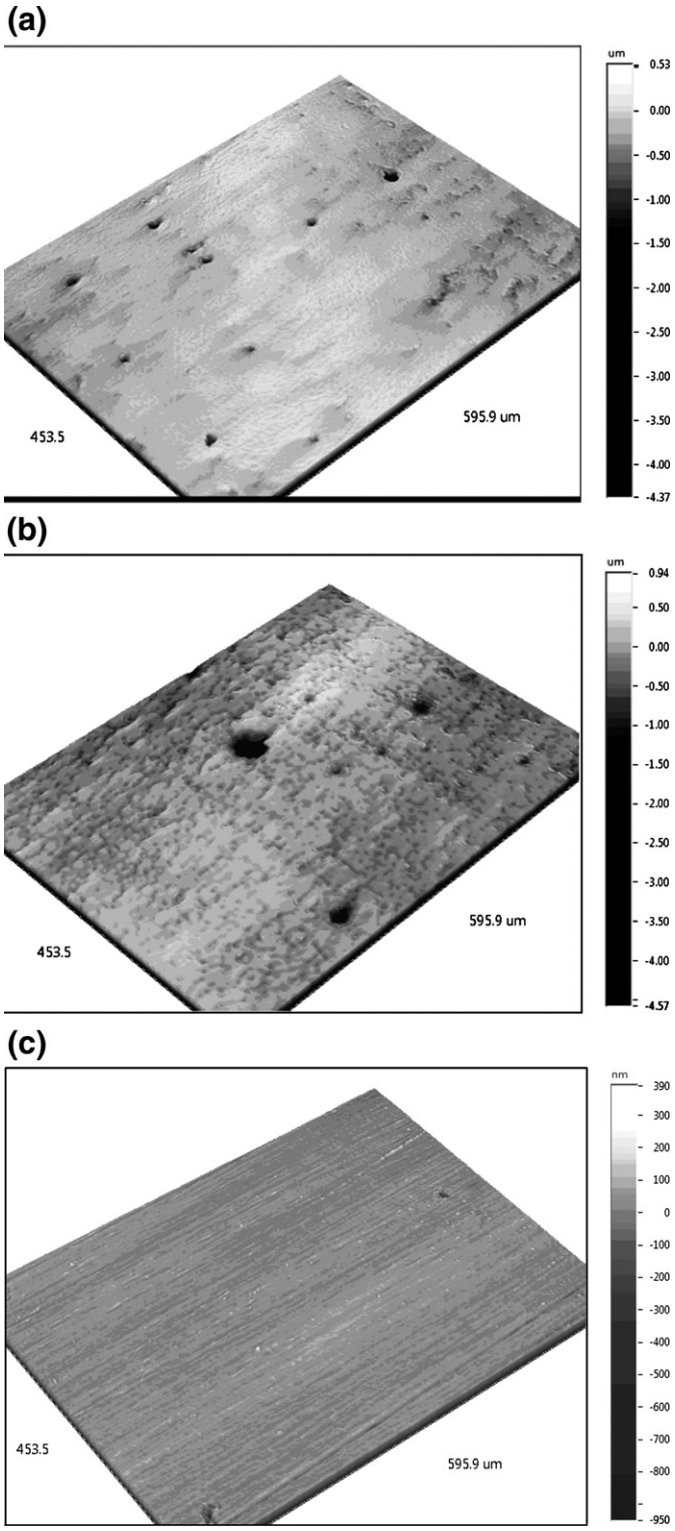

Fig. 2. Surface scan images obtained by white light interferometry of Fe–W coatings electrodeposited at: a) 3 A dm^{-2}, b) 10 A dm^{-2} and c) 2 A dm^{-2} under ultrasound stirring. Thickness of the coatings was 11.5 ± 3.5 μm.