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Structure property correlation of electro-codeposited Cu-Al-V_2O_5 composite coating obtained from Al-V_2O_5 dispersed electrolyte

H.S. Maharana[a,1], S. Bhatnagar[b,1], A. Basu[b,*]

[a] Department of Materials Science and Engineering, Indian Institute of Technology Kanpur, U.P. 208016, India
[b] Department of Metallurgical and Materials Engineering, National Institute of Technology Rourkela, Odisha 769008, India

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ABSTRACT

The present work depicts electro-codeposition of copper along with Al (size ~ 20 nm) and V_2O_5 (size ~ 350 nm) particles as second phase reinforcements on copper substrate. Different compositions of Cu-Al-V_2O_5 composite coatings were formed from acidic electrolyte with addition of 5 g/l Al and 10 g/l V_2O_5 particles in the deposition bath with 8 A/dm^2 current density both in the presence and absence of CTAB. Field emission scanning electron microscope (FESEM) image of non-CTAB added coatings show coarser structure compared to CTAB added coatings. Mechanical characterizations of the coatings portray better hardness and wear resistance of composite coatings compared to unreinforced Cu coated sample. Among the non-CTAB and CTAB assisted coatings, CTAB treated specimens have better mechanical properties in terms of hardness and wear resistance compared to non-CTAB ones due to finer coating matrix and formation of (220) texture. The downgrading of electrical conductivity values of the composite coatings was due to the codeposition of insulating V_2O_5 and finer coating matrix. Aluminum in the coating tends to maintain the electrical conductivity but provides little strengthening effect.

1. Introduction

Copper is a commonly available metal with high electrical as well as thermal conductivity; it has good tensile strength, ductility, creep resistance, corrosion resistance and also has low thermal expansion, apart from that, copper shows unique chemical properties [1,2]. Because of these properties, copper is widely used in electrical and electronic products. There are several necessities for excellent combination of properties required for different applications which alone copper or other material cannot fulfill; therefore alloys and composites are widely used nowadays. Specific applications of copper in electrical switching and windings face various problems such as rapid oxidation even in ambient temperature, corrosion, low hardness and wear resistance. So, there is a need of modification of copper based materials without much deteriorating its original electrical conductivity for the above mentioned applications. Bulk modification by alloying of copper is an effective technique to improve these properties, but it reduces the electrical conductivity to a substantial extent. Moreover, solubility limit of alloying elements in copper restricts this thought. Surface engineering can be an alternate technique, which preserves the original bulk properties of that material. There are several coating techniques such as chemical vapor deposition (CVD), thermal spraying, electro-codeposition, diffusion coatings, laser based techniques etc. [3–6]. But electrodeposition is the most conventional and cost effective method to enhance the surface mechanical properties of materials [7].

Metal matrix nanocomposites containing dispersed second phase nanoparticles have special properties such as dispersion hardening, self-lubricity, high temperature resistance, wear and oxidation resistance [7–12]. Due to various advantages over other coating techniques such as low cost, capability to coat complex shapes and uniform deposition, electro-codeposition creates interest in the field of surface engineering for the development of nanocomposite coatings over the past decades. The second phase ultrafine particles in the electro-codeposition process can be oxides (Al_2O_3, TiO_2, SiO_2, and TiO_2) [13–15], carbides (SiC, WC) or metal particles or combination of one another. These second phase particles got embedded in metallic matrix like Cu, Cr, Ni, Co and various other alloys. These coatings help to improve the properties such as wear and abrasion resistance, self-lubrication, hardness, porosity and corrosion resistance [16–19]. The qualities of the deposits are influenced by certain external variables or process parameters such as current density, particle characteristics, bath composition, and bath agitation etc. [20]. The codeposition of second phase dispersed particles in

* Corresponding author.
E-mail addresses: basua@nitrkl.ac.in, anindya.basu@gmail.com (A. Basu).
[1] Authors contributed equally.

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the coating matrix improves the surface-mechanical properties by grain refinement and dispersion strengthening mechanism. Several parameters such as *pH* of solution, zeta potential of the particles, current density, stirring rate, pulse parameters and particle concentration etc. affect the weight percentage of dispersed particles in the coating [21–24].

Aluminum (Al), having electrical conductivity value next to that of Cu and good oxidation resistance can be added in Cu as alloying by Al can increase both oxidation and mechanical properties of such coatings without much affecting the electrical property. Moreover, addition of V_2O_5 (hard insulating ceramic oxide particle) in the electrolyte can improve mechanical (hardness and wear) properties of the coatings by dispersion strengthening. By reviewing the existing literature, it can be confirmed that existence of Cu based Al and V_2O_5 composite coatings are though very rare, but some literatures related to Al reinforced other metal (Ni, Zn and Mn) based coatings are reported. Out of this, very few have reported about improvement of mechanical and corrosion resistance properties [25–28]. Few years back, Chen et al. published their work based on Al deposition on Cu-W substrate, but they emphasized more on microstructural study [29]. Recently few researchers also published communications on electrodeposited V_2O_5 and V_2O_5 reinforced composite coating on different substrates and studied storage capacity, self-lubricating nature, Li ion battery applications and intercalation properties [30,31]. Therefore, the authors of the manuscript hope the current study will be helpful for the scientific community regarding structural, mechanical (hardness and wear) and electrical properties of electrodeposited Cu-Al-V_2O_5 composite coatings and their possible application in electrical contacts. Moreover, effect of surfactant like CTAB (cetyl trimethylammonium bromide) on such deposition also needs investigation.

The main objective of the present study is to improve the surface-mechanical properties of the Cu based composite coatings by electro-codeposition of both Al and V_2O_5 ultra-fine particles and manipulation of process parameters to maximize the mechanical properties as well as to preserve the original electrical conductivity of Cu.

2. Experimental procedure

2.1. Substrate preparation

In the present study, for electrodeposition of composite coatings, pure Cu was used as substrate material. For the preparation of the substrate, Cu samples of 25 mm × 15 mm × 3 mm size were cut from copper strip and polished by belt grinder in order to remove oxide layer and surface impurities followed by polishing with the series of emery papers starting from 1/0 grade, till 4/0 grade.

2.2. Preparation of ultrafine aluminum powder

As received micron sized Al powder was ball milled to obtain ultrafine powder suitable for electro-codeposition. Al powder was wet milled (toluene as liquid medium) for 15 h in a planetary ball mill (FRITCSCH, Pulverisette-5). The weight ratio of balls to powder was 10:1. After each 30 min of milling operation, the machine was kept idle for another 30 min to control excessive energy formation. The speed of milling machine was maintained at 300 rpm. The milled powder was dried in atmospheric condition followed by heating to 50 °C to remove the traces of liquid left in the powder.

2.3. Deposition

Electrodeposition bath employed in the present study and the deposition parameters are reported in Table 1. In acidic copper sulfate bath, Al and V_2O_5 dispersion was added separately and together with varying concentration as mentioned in Table 1. Total set of experiments were carried out both with CTAB addition and without CTAB addition.

Table 1
Electrolyte bath composition and deposition parameters.

Electrolyte (acidic sulfate bath)	Copper sulfate ($CuSO_4.6H_2O$)·$5H_2O$: 200 g/l Sulfuric acid (H_2SO_4): 50 g/l
Surfactant	Cetyltrimethylammonium bromide (CTAB): 0.5 g/l
Current density	8 A/dm^2
Plating time	20 min
Dispersants	Al and V_2O_5 powder: 5 and 10 g/l each
Temperature	Room temperature
pH	1.5 ± 0.2

The solution containing suspended second phase particles was well stirred using magnetic stirrer at a speed of 200 rpm by placing a cylindrical (20 mm length, 7.5 mm diameter) magnetic bit before and during codeposition process to avoid sedimentation and agglomeration of particles. This also provides a good three dimensional mixing of second phase particles with turbulent flow of the electrolyte [14]. This benefited homogenous deposition of Al and V_2O_5 into copper matrix. Whereas, in case of lamellar and steady flow of the electrolyte, the homogeneous dispersion of second phase particles in the electrolyte is difficult, which can degrade the quality of the composite coating. Deposition was carried out with parallel plate two electrodes configuration in constant current mode and the gap between the electrodes was maintained approximately at 4 cm. The whole deposition process was carried out in a 500 ml cylindrical beaker. The schematic of deposition arrangement for Cu-Al-V_2O_5 system is presented in Fig. 1. Detailed mechanism and model of particle migration and related properties has been explained in separate section (3.11) of the manuscript. The flow rate of the solution was not measured like earlier study [32], but the stirring speed was kept constant for all the samples to maintain the constant flow rate of the solution. For each coating, 200 ml fresh solution was taken for better and uniform coating. Pure copper strip was also as anode. After the completion of deposition process, all the coated samples were washed with distilled water to remove the acidic solution and any loosely bonded particles from the coated surface.

2.4. Characterizations

Powders used in the deposition bath (Al and V_2O_5) were characterized by Malvern Zetasizer (Nano-ZS model) for size distribution and isoelectric point (IEP) calculation. These ultrafine powders were also characterized by high resolution transmission electron microscope (HRTEM) of model TECNAI T30 (FEG). The phase analysis and crystal structure of the developed coatings were analyzed by X-ray diffraction technique using Co Kα (λ = 0.179 nm) radiation at a scanning rate of 10° per minute in a Bruker D8 ADVANCE A25 X-ray diffractometer. From the obtained XRD peaks, relative texture coefficient (RTC) has been calculated for each matrix phase peak of each coating.

The $RTC_{(hkl)}$ determines the fraction of particular orientation present in the phase and the same is calculated by the formula [33,34].

$$RTC_{(hkl)}(\%) = \frac{I_{(hkl)}/Io_{(hkl)}}{\sum (I_{(hkl)}/I_{o(hkl)})} \times 100 \quad (1)$$

where, $I_{(hkl)}$ is the intensity obtained from XRD pattern of textured sample and $I_{0(hkl)}$ is the intensity of the standard oriented sample i.e. from JCPDS data.

The microstructural and elemental composition study of the developed coatings were investigated by a field emission scanning electron microscope (FESEM, NOVA nano SEM-450) attached with an energy dispersive spectroscopy (EDS) detector. Porosity of the obtained coatings was measured by image analysis of the high magnification FESEM images of all coating surfaces using Image-J software. Study was carried out by analyzing the pores present in a square sized area of 80 µm size. Each pore was converted to an equivalent sized circle with equivalent diameter and area of each such circle was measured. Then, total calculated pore area was converted as the percentage of that square sized