

Localized Electrospray Impacts on Thin Metal Films

A.P. Kuzmenko¹, A.E. Kuz'ko¹, D.I. Timakov¹, L.I. Roslyakova¹, M.B. Dobromyslov²

¹ South-West State University, 94, 50 LetOctyabrya Str., 305040 Kursk, Russia

² Pacific National University, 136, Tikhookeanskaya Str., Khabarovsk, Russia

(Received 19 May 2014; revised manuscript received 05 July 2014; published online 15 July 2014)

The investigation results of nanoscale phenomena and structural changes due to shock localized impacts at electric discharges on thin metal films from copper and chrome are given. Mechanisms of shape-formation of concentric circles within discharge area and ordered nanoparticle aggregates on film surfaces are provided.

Keywords: Electrospray impacts, Nanostructurization, Metal films, Ordered nanoparticle aggregates.

PACS numbers: 52.80.Dy, 52.80.Wq

1. INTRODUCTION

Electrophysical effects are widely used for the synthesis of nanomaterials. Among them are: formation by adsorption on the surface of Si (111) at 500 °C in a high vacuum of copper nanoislets, which serve as current-operated devices [1]; explosion of copper wires in nitrogen under reduced pressure, laser ablation of copper with the action of laser pulse of 1.4 MW/mm² on a target put in polysoloxane, to avoid oxidation and aggregation of particles [2]; grinding of copper at cryogenic temperatures, which makes it possible to obtain copper particles with gradient structure and the size of crystal grains on the surface on the order of 20 nm and rigidity of 2.1 GPa, and some others. Also, nanostructured state of copper may be created by plasma of electric discharges, including low-voltage ones, influencing on its surface. It was established in [3] that with the action of single electric discharges on an annealed copper foil with a thickness of 50 μm recrystallization of metal occurs, with the result that the size of the copper grain decreases as one goes to the discharge center, varying from 150 μm to 10 nm at distances of 3000 and 50 μm, respectively. Such structurization of copper in the melting and thermal action area was explained by the great cooling rate (of order 10⁶ K/s), which increases as one goes to the discharge center.

2. EXPERIMENTAL SECTION

The present work deals with localized electric effects of rectangular pulses on thin metal films. The originated structural rearrangements were studied with atomic-force (SmartSPM) (AFM), scanning electron (Quanta 200 and Quanta 600) (SEM) and confocal microscopy (OmegaScope) (KM).

Generator with interface for programmed control of shape and pulse duration supplied to the discharge area was used as a pulse source. The generator was implemented on Arduino Uno computing platform with output power amplifier. Both optic control of the discharge start time and registration with digital accelerometer of excited acoustic vibrations traveling in the film were done. A keen copper rod with a polished surface treated in a weak solution of hydro-

chloric acid was used as anode [3]. Film (cathode) was fastened in micron positioning device, which secured accurate and optically controlled relative position of anode and cathode, and also visualization of the current processes. Figure 1 gives a schematic of anode and cathode of real physical sizes. The increase in structure granularity to 150-200 μm and removal of textural stresses was achieved by annealing of all samples during 1 h at a temperature of 800 °C in 10⁻⁵ mmHg vacuum. With consideration for chosen current parameters, size and shape of anode the intensity of electric impact (current density) was 3 × 10⁵ A/cm². Under these conditions beginning from even minimum pulse duration (~ 50 μs), big specific effect was achieved $h > 3.1 \times 10^9$ A²c/cm⁴ with an energy release of up to $w = 5 \times 10^3$ J/g, i.e. an electric explosion happened described for the first time by academician A.G. Mesyats [4].

3. RESULTS AND DISCUSSION

Obviously, at such powerful effects melting, evaporation, and plasma formation were initiated. The optic control data revealed that throughout discharge, due to the evaporation of apex the cathode-anode distance increased following to empirical dependence $h \sim C\tau^{1/3}$, where τ – the discharge duration, and C – the evaporation rate of anode. The experimentally found increase in this distance was equal to 0.2-0.6 mm.

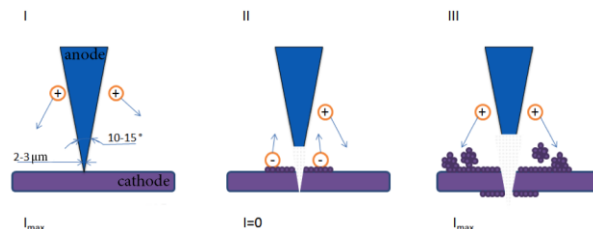


Fig. 1 – Schematic of anode and cathode position with characteristic sizes and stages in nanostructuring at an electric discharge

According to SEM and CM data at film surfaces concentric structural formations after electrodischarge treatment were appeared being radially

symmetric, having radius linearly dependent on duration and power of the discharge. Centrally symmetric circles appeared, as a rule, at top, and at melting through at bottom surfaces of samples. Observed sizes of the melting area and a through hole are dramatically greater than predicted sizes of the emission centers – ectons (several μm) according to [4]. This is likely due to the fact that duration of current pulses is 10^3 times greater than the existence time of ectons (10^{-9} – 10^{-8} s) and also multiple repetitions of discharges. As shown in [4] the energy released at the explosion besides heating the cathode to the depth of tens of μm (comparable in the order of magnitude with the film thickness) causes evaporation of atoms from its surface and explosive emission excites the shock wave.

AFM and SEM data (Fig. 2a, b) reveal that in the central part of the discharge area nonuniformly distributed nanoparticles originated with sizes of up to 30 nm combined in blocks of a random shape and with a height difference of up to 50 nm. In the middle part of the melting area a clearly defined structure of ordered nanoparticle aggregates of (ONAs) was observed. Spherical shape of nanoparticles with sizes of 30 nm was a proof that melting happened at discharges. The estimation of melting temperature for copper nanoparticles for the experimentally determined size of 30 nm $T_{\text{melt}}(r) = T_{\text{melt}}(1 - 2 / (\rho_s L r) [\sigma_s - \sigma_l (\rho_s / \rho_l)^{2/3}]) = 900$ K, where K – melting temperature, L – melting heat, σ_s, σ_l – surface tension of solid and liquid phase, ρ_s, ρ_l – density of solid and liquid phase for volume copper, respectively. At motion of ablated particles wetting occurs at their collisions under the influence of shock waves. Also ONAs for chrome and agglomeration of nanoparticles for copper (Fig. 2a, b respectively) and average size distribution of nanoparticles from the discharge center took place.

Several stages may be highlighted in the shape formation of the observed microstructure (Fig. 1) following [4]. The first is characterized by the maximum current, intensive heating (to the temperature greater than the melting temperature) of cathode and anode and the generation of a shock wave. At the second stage the anode material evaporates, the anode-cathode distance increases up to 200–600 μm , exchange of sign on the electrodes and quenching of the discharge current take place. The origination of ONAs (at both sides of the film) found in the work characterizes the third stage at which fractal structures appear from clusters owing to shock-wave mechanism. As it follows from this scenario all set of the observed structural shape formations in the process of a single pulsed discharge between the keen anode and the metal film cathode may be in a consistent way theoretically described within thermoelastic mechanism.

Let us analyze the dispersion equation of capillary waves $\omega = (\sigma k^3 / \rho)^{1/2}$. For example, for liquid-phase copper considering that the wave number $k = 10^7$ rad/s is dictated by the size of ONAs and taking into consideration of liquid-phase copper values of σ and ρ (surface tension and density) the estimation of the melt vibration gives the value of $\sim 1.5 \cdot 10^{-8}$ c. According to [4] the

velocity of explosive emission products may reach 10 km/s. Coincidence of propagation fronts for the shock wave and discharge products leads to blocking and quenching of the discharge current, corresponding to the second stage of nanostructurization (Fig. 1). Duration and intensity of current pulses cause the repetition of explosive emission, which explains fly-away of copper particles and the formation of concentric circles (with the center coinciding with the discharge point) at both foil surfaces well over the melt with increasing radii that follow the arithmetic progression. The radius of the first circle formed due to the shock wave propagation (several km/s) made it possible to pinpoint its origination time, being equal to 50 ns, which was in line with the time of secondary breakdown at an explosion in air of copper wire [5].

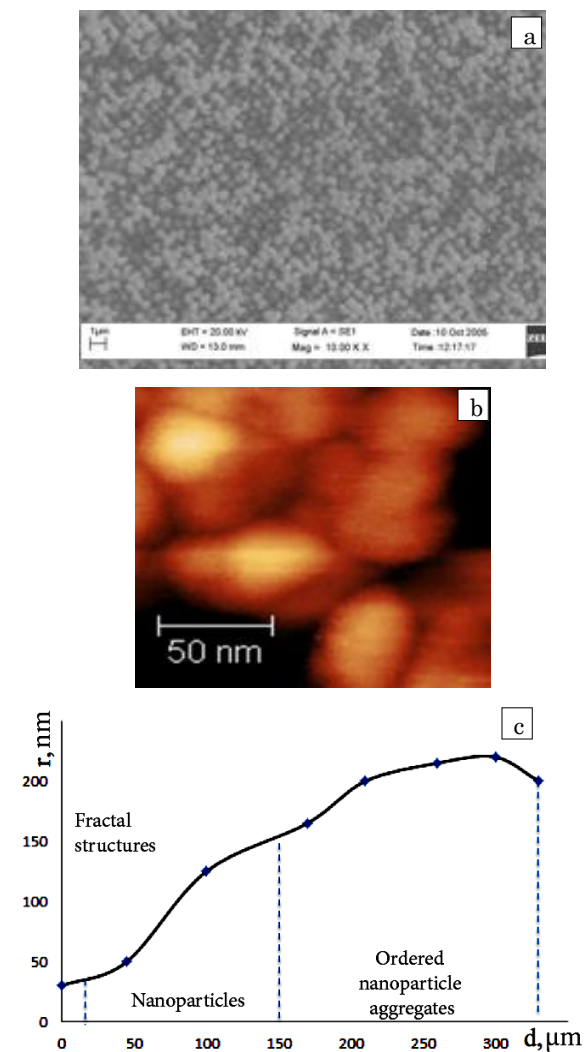


Fig. 2 – Nanoparticles on chrome film – a; ordered aggregates as clusters from copper nanoparticles – b; characteristic average size distribution of nanoparticles from the discharge center – c

Physical nature of those structural formations can be established from the Marangoni criterion. According to it the value of the Bond number $\rho g \beta h^4 / \sigma$ turns out to be much less than unity, as it follows from its estimation if known are film thick-

ness h (several μm), ρ – density, β – thermal conductivity, and σ – surface tension of melted copper. Thus, we may speak of a dominant role of thermocapillary phenomena in microstructurization, which is in accord with conclusions in [6]. The observed origination of microscale wave-like formations at the film

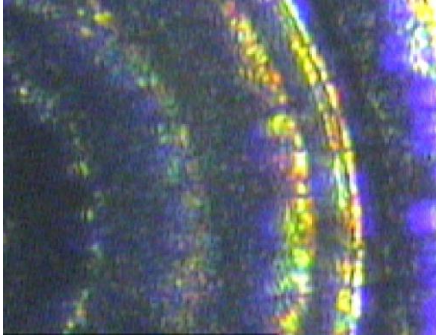


Fig. 3 – Fragment of concentric circles near the edge of the melt area

surface (size of order $\lambda \sim 20 \mu\text{m}$, Fig. 3) makes it possible to calculate the propagation velocity of thermo capillary waves $V^2 = (2\pi\sigma / \lambda\rho)th(2\pi / \lambda)$, whose value coincides with transverse sound wave velocity for copper – $V \sim 3.8 \times 10^3 \text{ m}$. This fact indicates the pos-

sibility of excitation by shock waves under such conditions of symmetric Lamb plate waves, at least of zero order, which coincide with bulk transverse acoustic wave.

Shock waves are responsible for the modulation of thermo capillary waves, as is illustrated in Fig. 3. A twofold decrease in length of thermo capillary wave structure (arithmetic progression step) may be explained by the fact that after the first breakdown there was at least another one. It was caused by the voltage pulse increasing to the peak value. The second breakdown was at the point situated at even nonuniform surface of the film cathode and that corresponds to the minimum cathode-anode distance, which is in accord with data of real-time studies of explosive evaporation of thin metal wires [5].

4. CONCLUSIONS

Nanostructured surfaces of metal electrodes can be used for produce contact pairs, which increases the intensity of the charge injection and provides advanced electroconvection. This is due to the high aspect ratio and the density of charged elements, their regular arrangement and reduction of the distance between the anode and the cathode [7].

REFERENCES

1. A. Anders, *J. Phys. D: Appl. Phys.* **40** 2272 (2007).
2. M. Saito, K. Yasukawa, T. Umeda, Y. Aoi, *Opt. Mater.* **30**, 1201 (2008).
3. S.A. Pyachin, V.G. Zavodinsky, A.P. Kuz'menko, M.A. Pugachevsky, A.A. Burkov, D.I. Timakov, *Tech. Phys. Lett.* **36** No 7, 652 (2010).
4. G.A. Mesyats, *Phys. Usp.* **38**, 567 (1995).
5. S.A. Pikuz, S.I. Tkachenko, D.V. Barishpol'tsev, G.V. Ivanenkov, A.R. Mingaleev, V.M. Romanova, A.E. Ter-Oganes'yan, T.A. Shelkovenko *Tech. Phys. Lett.* **33**, 651 (2007).
6. A.L. Zuev, A.G. Kostarev, *Phys. Usp.* **51**, 1027 (2008).
7. D.I. Timakov, P.V. Abakumov, A.I. Zhakin, *Izvestiya of South-West State University* No 1 (34), 38 (2011) [In Russian].