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Annealing Strengthening of Electrically Deposited Metals

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Abstract

The structure of electrically deposited metals was investigated, after low- temperature annealing, with a transmission electron microscope. Electrical deposition with high over-stressing produces dislocation cells which, during subsequent annealing, transforms into subgrains. Structural changes, in that annealing stage, are accompanied by strengthening of the deposited metals. The strengthening can be produced in industrial electroplating and electroforming.

Key words: *electrodeposited metals, annealing, strengthening.*

The structure of electrically deposited Fe was investigated, after low-temperature annealing, with a transmission electron microscope. Electrical deposition with high over-stressing produces dislocation cells which, during subsequent annealing, transforms into subgrains. Structural changes, in that annealing stage, are accompanied by strengthening of the deposited Fe. The strengthening also occurs in electrically deposited Ni, Cu, and Ag, and it can be produced in industrial electroplating and electroforming.

The structure and properties of electrically deposited metals subjected to heat treatment have not been thoroughly investigated. That must be the reason why, in electroplating, the role of heat treatment is limited mainly to degasification and internal stress relief in the electrically deposited metals. However, heat treatment might be used in order to produce desired effects on the structure of such deposits, formed under nonequilibrium crystallization conditions, and thus to obtain the required service properties. The present publication analyzes the effect of precrystallization annealing on structure and mechanical properties of electrolytically produced Fe deposits.

Electrolytic deposition was carried out on polished, stainless steel plates from which the deposits could be easily separated mechanically. Armco iron was used as anodes. Thin foils for transmission electron microscopy were prepared by two-side jet thinning using the known method. Fine structure of the deposits was examined with an EMV-100L transmission electron microscope at an accelerating voltage of 100 kV. Thermogravimetric analysis was carried out with a Q-1500 D derivatograph. Mechanical testing was carried out conventionally. Internal stresses in electrodeposited metals were determined by using the flexible cathode method [1].

Thermodynamic conditions of the electrolytic deposition produce metallic coatings with a high defect density in their crystalline structure and, because of that, characterized by high strength in comparison with the equilibrium state [2]. Such systems are characterized by excess free energy and tendency to transform into an equilibrium state which can be achieved by annealing in a practically affordable time. As the annealing decreases the number of defects, one should expect a decrease of strength, and of hardness in particular. However, experimental data suggested the opposite. It follows from the hardness curves of the deposits Fe that, at 150-250°C, the hardness increases by 50-80% (Fig. 1). The reason for that could be found in the change of the fine structure of electrolytic deposits.

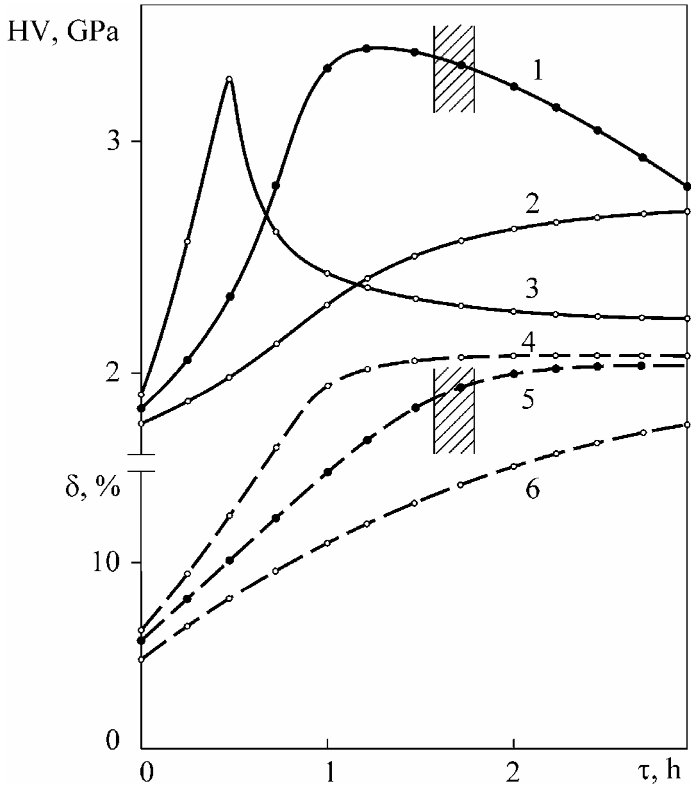

Fig. 1. Hardness (1-3) and ductility (4-6) of Fe deposited under stationary conditions (sulfate electrolyte with additions of hydrazine) as a function of the duration of isothermal annealing at 150 (2,6), 200 (1,5) and 250°C (3,4). The shaded areas represent annealing which results in the optimum combination of properties.

Electron microscope investigation showed that, in the original state, the electrolytic Fe deposits had a typical cellular structure (Fig. 2a). The cellular structure can apparently be explained by tight electrolysis conditions, because the high cathodic polarization causes considerable internal stresses (up to 1 GPa) which promote plastic deformation of the depositing metal. The cells consist of the volumes relatively free of dislocations, separated from one another by either dislocation walls or by high-density dislocation piles. The boundaries between cells are often so wide and blurred that they are comparable with the cells in size.

During low-temperature annealing the blurred, three-dimensional walls of cells become narrower and flatter, while the grains gradually transform into clearly defined subgrains, dislocation free, and with well-developed subgrain boundaries (Fig. 2b). According to gravimetric analysis, in that stage of the annealing the accumulated energy is released. No mass change of, the specimens studied was recorded, which means that the thermal effect is caused solely by structural changes occurring in the deposit. Similarly to cold deformed metals [3], such transformations are characteristic of polygonization, and one can assume that the strengthening of electrolytic Fe deposits in the 150-250°C range can be explained by redistribution and partial annihilation of mobile dislocations and by pinning of the remaining dislocations, inside more stable configurations, by solute atoms which form part of industrial electrolytes (for instance, Mn, Cr, Ni, Cu, etc., are contained in iron-coating electrolytes). Indeed, in deposits produced from pure electrolytes the strengthening effect is much less pronounced and the hardness decreases by only 10-20%, which confirms the above suggestion.

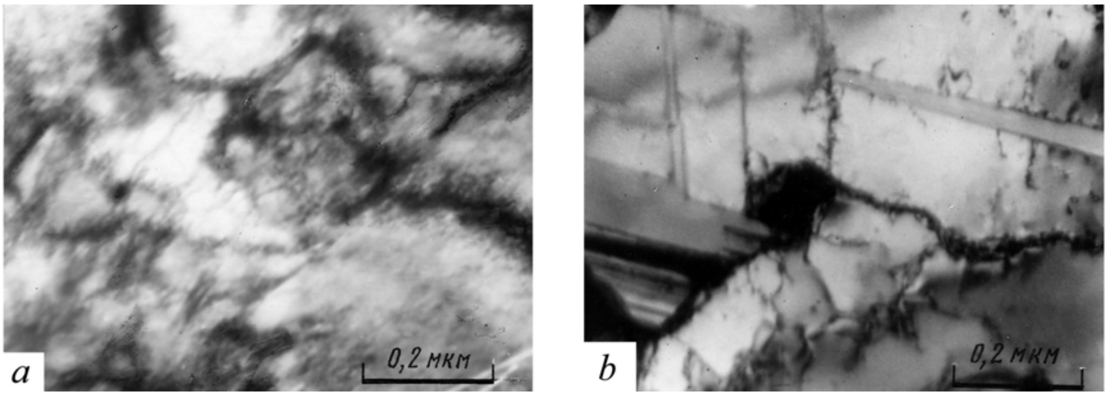

Fig. 2. Microstructure of electrolytic deposits of iron after formation (a) and annealing (b) at 200 °C for 1 hr.

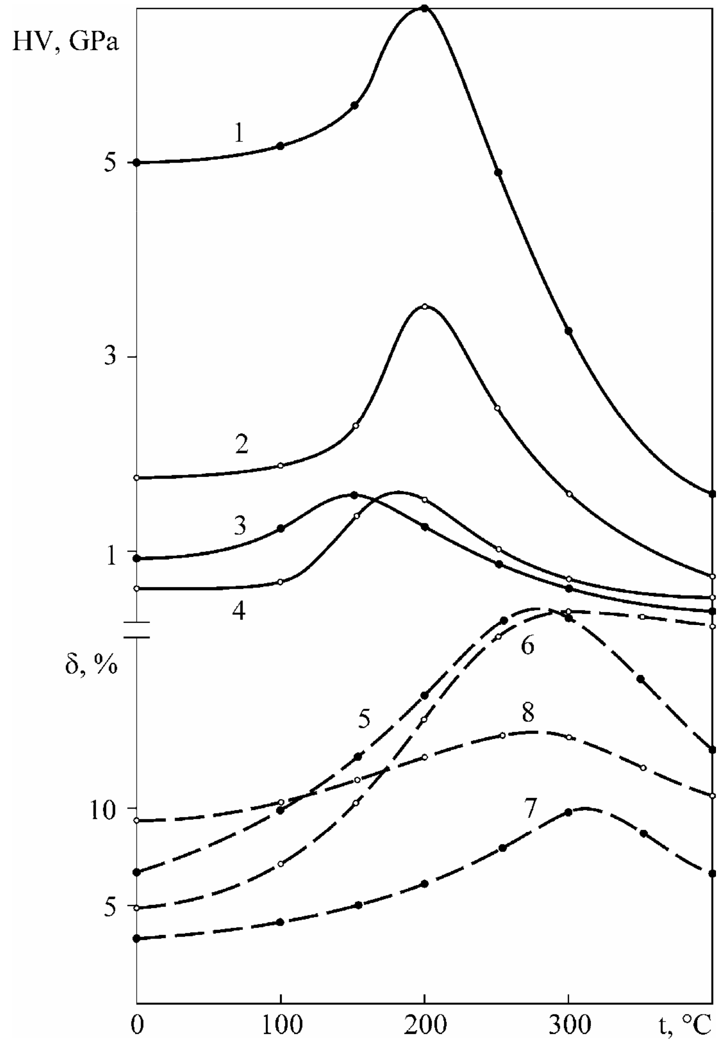

Fig. 3. Hardness (1-4) and ductility (5-8) of Ni (sulfuric acid electrolyte with the addition of saccharine and butynodiol; 1,5) Fe (sulfate electrolyte; 2,6) Cu (ethylendiamine electrolyte; 3,7) Ag (hexacianferrate electrolyte; 4,8) deposited under stationary conditions, as a function of isochronal annealing temperature (1 hr).

Annealing strengthening is observed not only in Fe but also in other metals deposited from industrial electrolytes, for instance in Cu, Ni, and Ag (Fig. 3). The absolute increase of hardness (0.5-1.5 GPa) suggests that low-temperature annealing can be used in electroplating and electroforming for additional strengthening of electrically-deposited metals. Moreover, such annealing results in improved ductility (Figs. 1, 3). The latter can apparently be explained by evolution of the hydrogen introduced into the metal, whose content in the deposits reaches 0.2-3.2 cm^3/g, and by annihilation of excess vacancies, whose concentration was estimated to be 0.1 at.%. Taking into consideration that the processes responsible for the variation of strength and ductility have different kinetics, the optimum annealing conditions can be selected by varying the heating temperature and annealing time (Fig. 1).

Subsequent heating above the hardness peak results in subgrain coarsening and development of recrystallization accompanied by softening of the metal.

References

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