JOURNAL OF NANO- AND ELECTRONIC PHYSICS
Vol. 8 No 3, 03015(3pp) (2016)
ЖУРНАЛ НАНО- ТА ЕЛЕКТРОННОЇ ФІЗИКИ
Том 8 № 3, 03015(3cc) (2016)

The Influence of Copper Condensates Doped with Co, Mo, Ta Transition Metals on the Structure and the Hall-Petch Dependence

M.A. Glushchenko*, E.V. Lutsenko, O.V. Sobol', A.E. Barmin, A.I. Zubkov

National Technical University "Kharkiv Polytechnic Institute", 21, Kyrpychova St., 61002 Kharkiv, Ukraine

(Received 21 April 2016; published online 03 October 2016)

The structure and strength properties of two-component copper-based Cu-Co, Cu-Mo and Cu-Ta vacuum condensates are investigated. It is shown that cobalt, molybdenum and tantalum disperse the grain structure of the copper matrix to submicron and nanometer dimension, form supersaturated solid solutions in the copper fcc lattice and heterophase structures. A decrease in grain size of condensates is explained by the formation of adsorption layers by the atoms of doping elements on the surface of the copper matrix metal growing grains. The Hall-Petch dependences for the yield strength are built. The dependences for Cu-Mo and Cu-Ta condensates have greater slope than a similar function for the single-component copper. The observed effect is explained by the influence of monolayer grain boundary segregation of molybdenum and tantalum atoms and multilayer segregation of Co atoms.

Keywords: Cu-Co, Cu-Mo, Cu-Ta, Yield strength, Grain size, Grain boundary segregation, Hall-Petch dependence, Supersaturated solution, Vacuum condensates.

DOI: 10.21272/jnep.8(3).03015 PACS numbers: 64.75.St, 68.35.Fx, 68.37.Lp, 81.07.Bc, 81.15.Ef.

1. INTRODUCTION

The ability of modifying substances, doping elements or impurities, to focus on the interfaces can significantly, and in some cases decisively influence the crystallization processes from various media, disperse the grain structure of matrix metals, change the physical-mechanical properties of the obtained metals. This also refers to the size dependences of the strength properties, in particular, the empirical Hall-Petch relation, to which a large number of theoretical, experimental, review articles and monographs are devoted, for example [1-11], containing an extensive bibliography dedicated to different aspects of this problem. As follows from the mentioned publications, the behavior of this dependence is caused by a number of factors, such as, the grain size [1-4], the technology of metal production [9], the chemical purity and the state of grain boundaries [2, 5], etc. At the same time, individual articles [12, 13] are devoted to the effect of grain-boundary segregations, their structure, physical-chemical properties of segregating substance. In this connection, the aim of this work was to study the influence of grain-boundary segregations by cobalt, molybdenum and tantalum atoms on the structural state of the copper-based formed condensates and on the Hall-Petch dependences for these objects.

2. OBJECTS AND METHODS OF STUDY

The objects of study were single-component Cu and two-component Cu-Co, Cu-Mo and Cu-Ta condensates in the form of foils up to 50 μm thick, which were produced by evaporation of the components from different sources followed by condensation of the vapor mixtures on non-orienting substrates in vacuum of ~ 10^{-3} Pa. The concentration of alloying elements (C) varied in the range from 0.1 to 2 wt. % and monitored by X-ray spectroscopy. It should be noted that molybdenum and tantalum do not have solubility in copper either in liquid or solid states; cobalt is limitedly soluble in the solid state and infinitely – in copper melt. The chemical compounds are absent in all binary systems. The structure was investigated by X-ray diffractometry on the setup DRON-4 and by transmission electron microscopy on the PEM-100 and JEM-2100. The strength properties were determined in the active stretching mode.

3. RESULTS AND DISCUSSION

In Fig. 1 we present the concentration dependences of the average grain size of the copper matrix (*L*) of the specified objects obtained under similar technological conditions. As seen, the functions *L* – *f*(*C*) have two regions. At concentrations of cobalt, molybdenum and tantalum up to ~ 1.5, 0.55 and 0.4 wt. %, respectively, there is a sharp decrease in the grain size with subsequent attainment of a plateau. The minimum grain size achieved in Cu-Co condensates is approximately equal to 400 nm, in Cu-Mo – ~ 100 nm, in Cu-Ta – ~ 50 nm. These results indicate differences in the processes of grain structure formation of Cu-Co and Cu-Mo, Cu-Ta condensates.

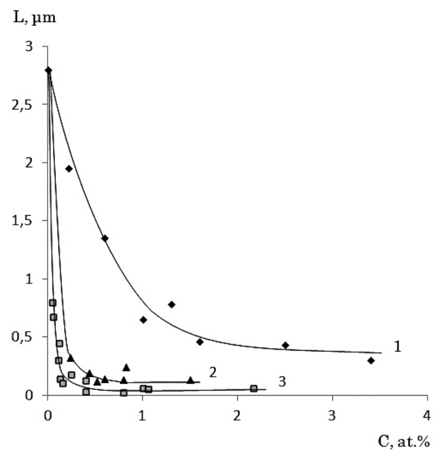

Fig. 1 – Dependences of the copper matrix grain size (*L*) on the concentration of alloying elements (*C*): 1 – Cu-Co, 2 – Cu-Mo, 3 – Cu-Ta

* maglushchenko@gmail.com

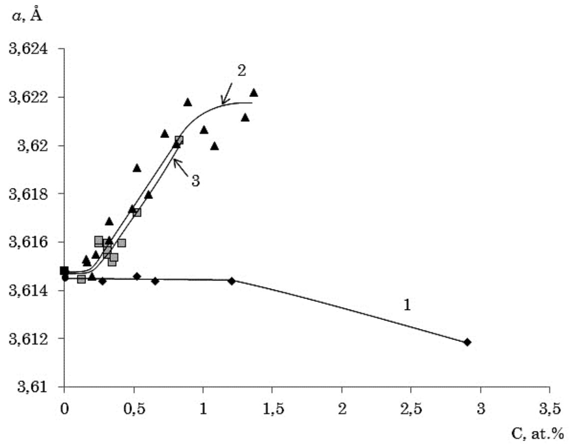

Fig. 2 – Dependences of the lattice constant of copper (a) on the concentration of alloying elements (*C*): 1 – Cu-Co, 2 – Cu-Mo, 3 – Cu-Ta

Analysis of the X-ray diffractometry and transmission electron microscopy data implies that the condensates structure is single-phase in the falling branches of the dependences *L* – *f*(*C*) (Fig. 3). The electron and X-ray diffraction patterns contain only the diffraction reflections belonging to the fcc crystal lattice of copper, and there are no signs on the bright-field and dark-field images indicating the presence of the second phase in the structure of these objects.

It should be noted that there is no noticeable solubility of cobalt, molybdenum and tantalum in the copper matrix metal in this concentration range (Fig. 2). These results and the data of [14, 15] allow to conclude thatthe atoms of cobalt, molybdenum and tantalum are concentrated in the copper grain boundaries in the form of segregations.

The structure of condensates with a concentration of alloying elements corresponding to the plateaus of the dependences *L* – *f*(*C*) is two-phase (Fig. 4). At first, the particles of cobalt, molybdenum and tantalum appear at the grain boundaries, and then – in the bulk of copper grains as the concentration of alloying elements increases. Moreover, an increase in the lattice constant of copper is also observed that indicates the formation of supersaturated solutions of cobalt, molybdenum, and tantalum in copper (see Fig. 3).

The refinement of the grain structure of the copper matrix, the formation of supersaturated solutions and highly dispersed particles of the second phase in the bulk of the matrix metal leads to a significant increase in the strength properties of alloyed condensates. The maximum strength properties are demonstrated by Cu-Ta condensates, the minimum ones – by Cu-Co.

In Fig. 5 we show the Hall-Petch dependences for the yield strength (σ_y) of single-component copper and Cu-Co, Cu-Mo and Cu-Ta condensates obtained under the same technological conditions

$$\sigma_y = \sigma_0 + kL^{-1/2},$$

where σ_y is the yield strength, σ_0 is the resistance to the motion of dislocations in a single crystal, *k* is the Hall-Petch coefficient, *L* is the grain size.

It is important to note that these dependences are plotted for samples with concentrations of alloying elements corresponding to the descending sections of the functions *L* – *f*(*C*) (see Fig. 1). Thus, the grain size was changed by varying the content of alloying elements,

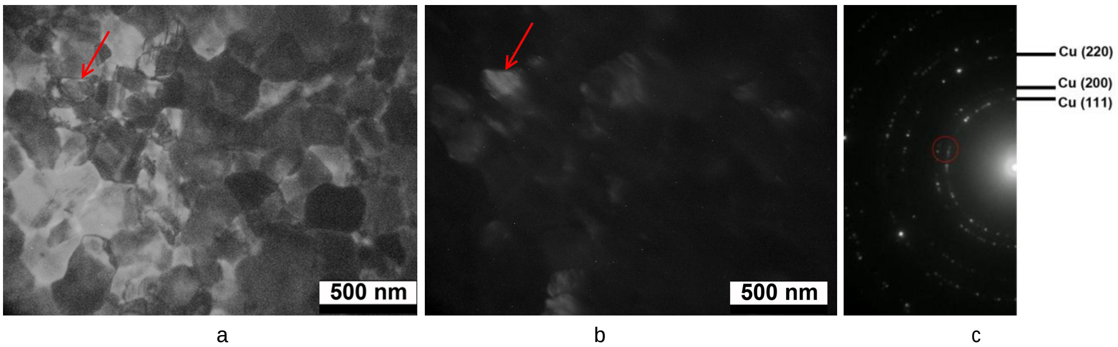

Fig. 3 – Electron microscopic images of the structure of Cu-0.25 wt. % Ta condensates: a) bright-field image, b) dark-field image, c) electron diffraction pattern

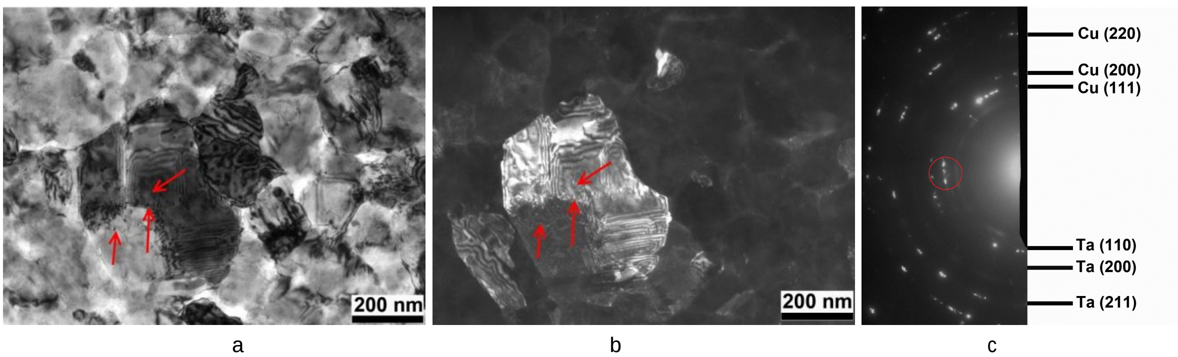

Fig. 4 – Electron microscopic images of the structure of Cu-1.3 % wt. % Ta condensates: a) bright-field image, b) dark-field image, c) electron diffraction pattern (arrows indicate tantalum particles)

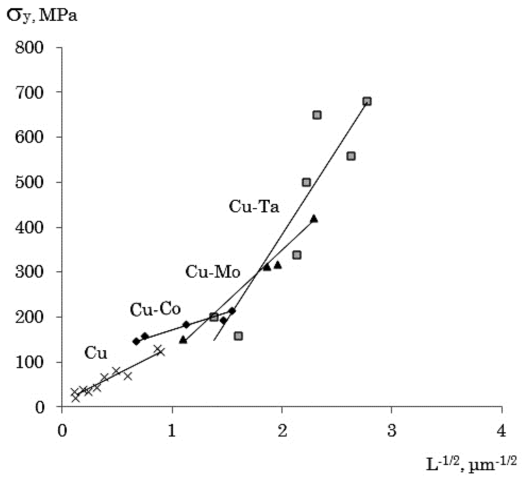

Fig. 5 – Hall-Petch dependences for Cu, Cu-Co, Cu-Mo, Cu-Ta condensates

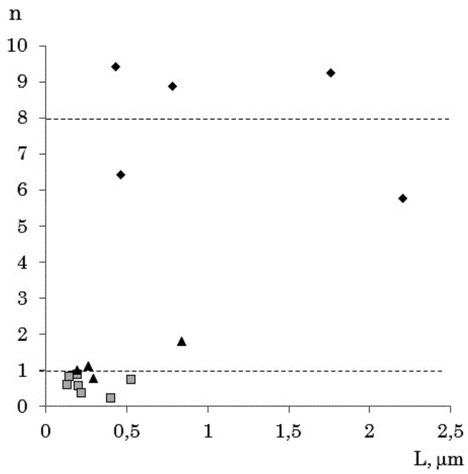

Fig. 6 – Adsorption capacity of grain boundaries of the copper matrix for ♦ – Co,▲ – Mo, ▫ – Ta (in monolayers of segregating element)

which are necessary and sufficient to completely block the growth of the matrix metal grain in the crystallization of vapor mixtures. At that, the behavior of grain-boundary segregations and the intragranular structure of the matrix metal (copper) remain. The estimation of the specified number of atoms of alloying elements concentrated in the grain boundaries of the copper matrix implies that for tantalum and molybdenum this makes ~ 0.5-1 monolayer (*n*), for cobalt this value is an order of magnitude larger (Fig. 6) [14, 15]. This result indicates a stronger interaction of tantalum and molybdenum atoms with copper grain boundaries than cobalt atoms.

For copper condensates, the value of the coefficient *k* is equal to 0.117 MPa·m$^{1/2}$ and of σ_0 – 20 MPa that is in a good agreement with the literature data [2]. Alloying of copper condensates increases the values of this parameter for Cu-Mo and Cu-Ta to the values of 0.21 and 0.37 MPa·m$^{1/2}$, respectively, and for Cu-Co this value is equal to 0.09 MPa·m$^{1/2}$.

Thus, the fact of an increase in the Hall-Petch coefficient for copper by such elements as molybdenum and tantalum has been established in this paper.

The results obtained are an experimental confirmation of theoretical concepts [6] predicting an increase in the cohesive strength of grain boundaries of the matrix metal with increasing melting temperature of the segregating substance as well as the difference in their atomic dimensions with the matrix metal.

4. CONCLUSIONS

1. It is established that alloying of copper condensates with cobalt, molybdenum and tantalum reduces the grain size of the copper matrix to submicron and nanometer dimensions. The efficiency of dispersion of the grain structure of copper condensates increases with increasing melting temperature of the alloying element.

2. It is found that cobalt, molybdenum and tantalum form supersaturated solutions in the fcc crystal lattice of copper during condensation of a two-component vapor.

3. It is shown that depending on the concentration of alloying elements, the condensates of Cu-Co, Cu-Mo, Cu-Ta binary systems can have different structural state, namely, single-phase, two-phase, supersaturated solution based on copper, etc.

4. The slope of the Hall-Petch dependence for Cu-Mo and Cu-Ta condensates increases and remains constant for Cu-Co compared with the same function for single-component copper.

5. An increase in the Hall-Petch coefficient for Cu-Ta and Cu-Mo systems is explained by a monolayer behavior of segregations of tantalum and molybdenum atoms at the grain boundaries of the copper matrix and, correspondingly, by the formation of strong bonds between copper atoms and tantalum or molybdenum atoms.

REFERENCES

1. S.A. Fyrstov, T.H. Rahul', O.A. Shut, *Fyzko-khimichna mekhanika materialiv*, No 6, 5 (2009).
2. E.V. Kozlov, N.A. Koneva, A.N. Zhdanov, N.A. Popova, *Fizicheskaya mezomekhanika* 7 No 4, 93 (2004).
3. E.V. Kozlov, A.N. Zhdanov, N.A. Koneva, *Fizicheskaya mezomekhanika* 9 No 3, 81 (2006).
4. O.A. Shut, *Dopovidi NAN Ukrainy* 9, 70 (2014).
5. R.A. Andriyevskiy, A.M. Glezer, *Phys.-Usp.* 52, 315 (2009).
6. S.A. Firstov, Yu.F. Lugovskoy, *Elektronnaya mikroskopiya i prochnost' materialov. Ser.: Fizicheskoye materialovedeniye, struktura i svoystva materialov*, No 15, 83 (2008).
7. V.Ye. Panin, T.F. Yelsukova, Yu.V. Grinyayev, *Fizicheskaya mezomekhanika* 6 No 3, 63 (2003).
8. O.Yu. Kuzina, T.F. Yelsukova, V.Ye. Panin, *Fizicheskaya mezomekhanika* 8 No 4, 13 (2005).
9. A.I. Gusev, *Nanokristallicheskiye materialy: metody polucheniya i svoystva* (Yekaterinburg: UrO RAN:1998) [in Russian].
10. R.Z. Valiyev, I.V. Aleksandrov, *Nanostrukturnyye materialy, poluchennyye intensivnoy plasticheskoy deformatsiyey* (Moskva: Logos: 2000) [in Russian].
11. Ying Wang, Jianqiu Zhou, T.D. Shen, David Hui, Shu Zhang, *Comp. Mater. Sci.* 58, 175 (2012).
12. T.D. Shen, R.B. Schwarz, S. Feng, J.G. Swadener, J.Y. Huang, M. Tang, *Acta Mater*. 55, 5007 (2007).
13. T.D. Shen, S.W. Xin, B.R. Sun, *Mat. Sci. Eng. A-Struct.* 627, 139 (2015).
14. A.Ye. Barmin, O.V. Sobol', A.I. Zubkov, L.A. Mal'tseva, *Phys. Metal. Mettalog.* 116 No 7, 706 (2015).
15. E.V. Lutsenko, O.V. Sobol', A.I. Zubkov, *J. Nano- Electron. Phys.* 7 No 3, 03042 (2015).
16. M.P. Sean, *Acta Metall. Mater.* 28 No 7, 955 (1980).