

# Composite Materials with Metal Matrix Condensed from Vapor Phase: Microlayer Materials

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*The problems of microlayer metal materials, obtained by condensation from vapor phase are discussed. Example of copper-molybdenum materials obtaining was first shown possibility to produce composites having a layer thickness of less than 1 micrometer, condensed at substrate temperature above 0,3 melting point of fusible layer (Cu).*

*Композитни материали с метална матрица, кондензирана от парна фаза: Микрослойни материали (Н. Гречанюк, И. Гречанюк, Е. Хоменко, А. Мелник, В. Гречанюк). Дискутирани са проблемите на микрослойните материали, получени чрез кондензация от парна фаза. Примерът на медно-молибденов материал е първата показана възможност да се произведат композити с дебелина на слоевете под 1 микрометър кондензиран при температура над 0.3 от точката на топене на по-лесно стапящия се слой (Cu).*

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## Introduction

The more and more attention every year have paid to metal matrix composite consisting of components with contrasting physical and mechanical properties. Depending on reinforcing phase shape metal matrix composite can be divided into two large classes: fibrous and layered (multilayered).

Multilayer composite with metal matrix have several advantages over fiber materials, particularly in terms of physical and mechanical properties management, in particular [1]:

- Upon receipt of reinforced fiber is difficult to obtain required external surface of layer, whereas it is known that the state and properties of those play a crucial role in behavior of material under load. Furthermore, by changing the sequence of alternating layers and their thickness, the mechanical properties under a load of various kinds of multilayer composites can be varied;

- Reinforcing phases of multilayer composites provide more uniform deformation, compared with fibrous materials at the same volume fraction

- Technology of multilayer composite is more simple and wide explored than those of fibrous materials.

Industrial multilayer composites are produced by different methods based on principles of joining strips, plates and foils of different metals, in particular hot rolling or pouring molten metal of solid plates with

the subsequent rolling ingots, explosion welding, brazing, directed eutectic crystallization etc. Detailed exposition of these methods, as well as some physical and mechanical properties of multilayer composites are presented in a number of reviews and monographs summarizing [1-6]. Eutectic superalloys multilayer composites are increasingly being used in modern aircraft engines production [6-8]. Above mentioned materials have advantages in comparison with single-layer materials, for example, they are characterized by higher values of strength, heat resistance, fracture toughness, etc. [7]. In most cases, the thickness of layers in fibrous material is greater on 3-4 orders of magnitude than average grain size in multilayer composites.

Exceptionally interest for modern technology development are layered materials, in which grain size is comparable or less than the thickness of alternating layers. In such materials, the tensile strength may reach lower limit of theoretical metal strength [9]. Those layered (multilayer) materials are often called in the technical literature as microlayer materials [10, 11].

## Experimental part

Extensive research of MLCM based on Cu, Pb, Sn, Cr, Fe, Ni, Mg, An, Ag, C, Al<sub>2</sub>O<sub>3</sub> with thickness of layer 0,1 microns or less, obtained by wire beam drawing and foil rolling carried out by V. S. Kopan [11]. He showed that microlayer thickness - one of the

main factors which determine the properties of microlayer materials. Usually such features as microhardness, tensile strength, elasticity and fatigue, thermo electro-dynamic force, induced deformation, electrical resistance, coercivity, continuity and fracture toughness and other properties tend to increase with decreasing microlayer thickness.

Electron-beam technology opens unlimited possibilities in designing microlayer materials. Improvements in methods and techniques of material condensation in a vacuum, mainly, particularly in developments of powerful electron-beam evaporators and magnetron systems, allow to creation of new materials with different structure types and layer thicknesses varying widely.

Today, rather conventionally can be distinct two classes of microlayer materials, obtained material condensation in a vacuum (Fig. 1):

- Microlayer condensates with a thickness of about 0,1-10 microns [10,12-16]. The structure of interface between layers likes to large-angle grain boundary in polycrystalline (Fig. 1a);

- Microlayer condensates with ultrathin layers up  $(6 \dots 8) \cdot 10^{-10}$  to  $(6 \dots 8) \cdot 10^{-8}$  m. Depending on the structure of alternate layers, conjugation of atomic planes of crystal lattices of adjacent layers along coherent boundary occurs [17,18] (Fig. 1b), or creation of unified system of atomic planes [19, 20] (Fig.1, c).

- Technology of evaporation and condensation metallic and nonmetallic materials in a vacuum permit to realize two characteristic principles of microlayer condensates formation:

- 1) Condensation at relatively low temperatures, which allows to high density of crystal lattice defect for each layer.

- 2) Condensation at temperatures above melting point of 0,3 fusible layers, which leads to obtaining microlayer condensates with enough equilibrium structure.

Microlayer condensates, obtained at low temperatures, have been studied in detail under the guidance of L.S. Palatnik in 1964-1966 years in Kharkov Polytechnic Institute [21, 22].

The basic laws of changes of structure and physic and mechanical properties of condensed microlayer materials above-mentioned types were summarized A.I. Ilinskiy [12, 23]. Fundamental research of Cu-Cr and Ni-Si microlayer condensates with a small volume percent of reinforcing layers (up to 10%), with layer thickness does not exceed 0,1 microns, were carried out by the author. Summer thickness of the composites was not more than 50...100 mm. As in the

case of fibrous materials, obtained by conventional methods, there was a significant hardening of condensed microlayer materials with decreasing layer thickness. It is show that this size effect is caused mainly by influence of interfacial surfaces. As shown in [12, 23, 24] the change of total interfacial surface area can be accompanied by doubling the strength, as shown in example of microlayer materials Cu-Cr. Microlayer materials retain structural stability and high mechanical properties until temperatures  $400^{\circ}\dots 500^{\circ}\text{C}$ . At higher temperatures the discontinuity (decomposition) alternate layers into separate blocks, fragments and formation of typical hetero-phase structure take place. Structure and properties of microlayer materials with alternate layer thickness more than 0,1 microns is not enough understood. Research of microlayer composites, are represented in literature fragmentary and concern essentially of materials Cu-Fe [12], Ag-Ni [21], Cu-Cr [25], condensed at substrate temperature not higher than  $300^{\circ}\text{C}$ .

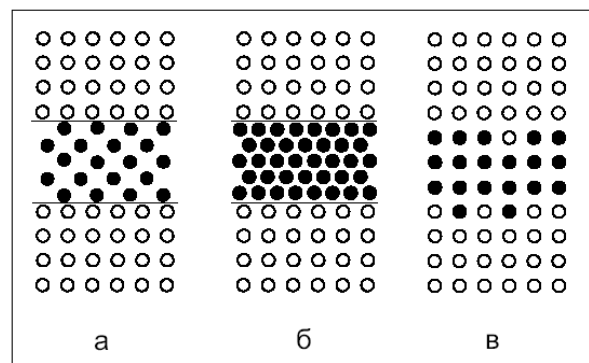


Fig.1. Structural schemes of microlayer materials.

The classification of microlayer materials, shown above, and brief overview of level, achieved in this most important area, indicate that a small part of model microlayer materials condensed at relatively low substrate temperatures ( $300^{\circ}\text{C}$ ) only studied.

Considerable part of research of microlayer materials Fe-Cu, Cr-Cu, Ni-Cu, Mo-Cu, NiCrAlY-NiCrAlY- $\text{Al}_2\text{O}_3$ , NiCrAlY/NiCrAlY-( $\text{ZrO}_2\text{-Y}_2\text{O}_3$ ), Ti-TiAl,  $\text{Ti}_3\text{Al-TiAl}$ ,  $\text{Ti}_4\text{V}_6\text{-AlTi}$ , condensed at substrate temperature  $500 \dots 1000^{\circ}\text{C}$  is presented in [10, 26-30]. Materials with layer thickness up 0,1 to 30 microns were obtained in the form of blanks with dimensions  $250 \times 350 \times (0,5 \dots 1,5)$  mm, with had been cut for mechanical testing, physical and chemical structural studies. Generalization of these studies was done by the author in [31]. It is shown that by choice of alternating layer material and their thicknesses can be obtained a high structural stability, strength and ductility values adaptable in a wide range, low values

of high-temperature creep and low thermal conductivity as compared to those parameters of individual layers. In general, the tensile strength of investigated microlayer materials may be above 1,5 ... 4 times than similar values for individual layers of materials with alternate layers thickness smaller than 2 microns. Microlayer materials elongation tends to decrease and approaches the zero value for the thickness of alternate layers less than 1 micron. The structure, phase composition and mechanical properties of a new class - condensed materials metal/cermet NiCrAlY / NiCrAlY + Al<sub>2</sub>O<sub>3</sub>, NiCrAlY/ NiCrAlY + (ZrO<sub>2</sub> - Y<sub>2</sub>O<sub>3</sub>) in thickness range up 0,2 to 25 micron with oxide content in alternative layers up 0 to 50 % wt were studied. Found that the main factor determining changes of properties is sintered oxide content in microlayer. When oxide concentration is 0,5 ... 4 % wt. and microlayer thickness is 1 ... 25 nm, value of tensile strength and ductility are more than 10 ÷ 20%, and the heat resistance – more than 5 ... 30%, as compared with conventional matrix alloys.

Disintegration of layers with a thickness less than 1 micron of single microlayer in all studied types microlayer materials, condensed at substrate temperatures above 0,3 of the melting temperature of least refractory layer, is observed.

Thus, we can draw a general conclusion that in the literature there is no information about the microlayer materials with a thickness of layers less than 1 micron, condensed at substrate temperatures higher than 0,3 on the least refractory layer melting temperature . At the same time, it is expected that, by analogy with other types for microlayer materials with a layer thickness of less than 1,0 microns, condensed at temperatures ensured equilibrium structure formation (substrate temperature  $\leq 0,3$  least the melting point of refractory layer), can vary structurally sensitive physical and mechanical properties in wide limits by appropriate choice of components in alternate layers and substrate temperature. It is logical to assume that the microlayer materials, obtained at high substrate temperatures have a high level of structure thermal as compared with known materials. Similar materials with lots of layers, the total whose thickness is 100 microns or more may be in accordance with the classification given in [32], attributed to nanostructured systems, i.e. macroscopically homogeneous massive bodies having internal nanostructure. Basic technological conditions for obtaining such microlayer thermo-stable materials were formulated by the author in [33-35]. Practical implementation of these principles was carried out by obtaining of microlayer condensates Cu-Mo [35].

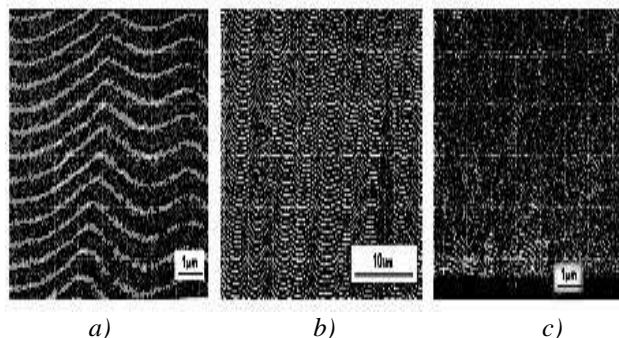


Fig. 2. Typical structure of microlayer condensed materials Cu / Mo: a, b - original state; c - after vacuum annealing at 900 °C for 1 hour.

The typical structure of these microlayer condensates is shown in Figure 2, a, b. Microlayer composites were condensed at substrate temperature  $700 \pm 20$  °C, exceeded 0,6 on the most fusible layer melting temperature (Cu). The copper layer thickness (gray layers) is approximately 500 nm, molybdenum layer thickness (dark layer) is 100 nm. Undulating profile layers repeats profiles substrate on which to condense. Vacuum annealing at 900 °C for 1 hour practically no changes layer continuity (Fig. 2, c). The yield strength and tensile strength of Cu-Mo microlayer materials are 550 and 635 MPa respectively, that are 5 times than the same values for pure copper, and 2 time higher compared with pure molybdenum, whereas elongation those is 2.5 %. After vacuum annealing of 900 °C for 1 hour, mechanical properties of those materials were reduced approximately 10 %, at the same time, the elongation is increased to 7,5%.

## Conclusions

Thus, test mechanical properties results of microlayer materials with internal nanostructure show the great possibilities of the method [33, 34] for layered compositions with controlled structure and properties obtaining.

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