

## Part 1

# Composition Materials with Metal Matrix Condensed from the Vapor Phase

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**Abstract:** The data of condensed from vapor phase disperse reinforced materials design is presented. It is shown that the material's mechanical properties depend on matrix type, types of dispersed particles, temperature and roughness of the substrate, purity of initial materials, and its evaporation speed.

**Keywords:** Electron-beam evaporation, Condensed materials from the vapor phase, Disperse reinforced materials.

## INTRODUCTION

The appearance of new technologies such as Plasma-Arc, Electron-Beam, and Laser in the middle of the XX century put new challenges before developers in new technologies of materials processing and welding. Why the freely burning electric welding arc performed metals melting on the surface (the ratio of the molten zone's deepness to the width of this zone  $< 1$ )? That initiated a new meaning of energy torrents concentration (ETC). If the energy power source (electron-beam, plasma-arc, laser) reaches the value of  $\geq 10^5 - 10^6 \text{ W/cm}^2$ , the process of the material heating turns into self-propagated (synergetic). And when the threshold power value changes, the heat transfer conditions in the object directs to heating up.

An overcoming of this threshold opened new opportunities for technologists. A substantial scientific and technological experience working with ETC showed that the most effective energy source for materials processing is the electron beam [1].

Electrical Welding Institute, named after E.O. Paton and Scientific Production Enterprise Eltehmash, developed new multifunctional electron beam production units with two, three, and five crucibles to create dense molecular beams. The intensity of those beams reaches  $10^{23}$  particles  $\text{cm}^3/\text{s}$  [2]. Beams are qazi-molecular rays, which are characterized as molecular beams with space orientation of them according to cosine law. From the other side, such beams result from internal collisions of vapors torrents in laminar flowing.

The efficiency of the installations gives 10-15 kg of vapors in one hour. It is possible to get 100kg of condensate and sometimes even more for eight hours of uninterrupted work.

Academician B.E. Movchan and his group researched primary physic-mechanical principles of thick (0.01-2 mm) condensates in Electrical Welding Institute named after E.O. Paton Ukrainian National Academy of Science. [2,3]. The main physical-Mechanical properties of condensers were detected as a function of condensate parameters and their composition.

An ability to get dispersed-reinforced, miro-porous, and micro-layered materials through condensation from the vapor phase is an effective way in new materials creation within advanced programming properties. Studying the structure and properties of such materials is a goal of this work.

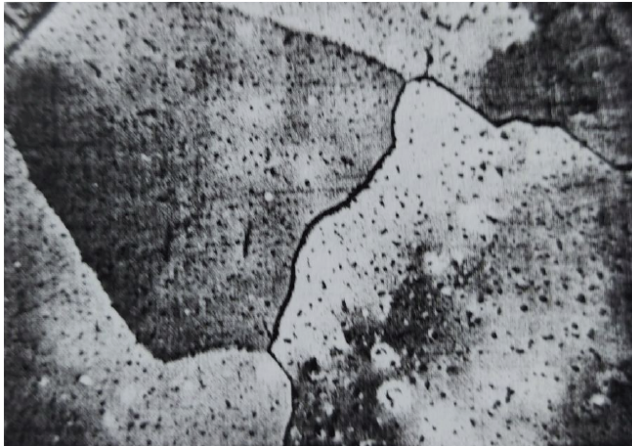
## EXPERIMENTAL PART

Condensate dispersed-reinforced materials (CDRM) are materials consisted of a poly-crystal matrix and an even volume of disperse particles of another phase (Figure 1). It is possible to change the average sizes of matrix crystals from hundreds of microns to several thousands of angstroms and reinforced particle sizes from tens of angstroms to several microns.

The structure and physical-mechanical properties of dispersed-reinforced condensed materials are studied in Electrical Welding Institute named after E.O. Paton. It includes iron-carbide systems, iron-boride, iron-iron oxide, nickel-oxide, copper-copper oxide, tungsten-oxide systems [4]. All previous works embraced the study of dispersed-reinforced materials on the nickel,

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chromium, copper, and titanium base [5]. In our day's research of other systems is continuing [6].



**Figure 1:** Typical structure of disperse-reinforced material obtained from the vapor phase.

Analyze of the obtaining results allows concluding that mechanical properties of condensed dispersed-reinforced materials depend on such factors:

- By type of metallic matrix (pure metal or alloy);
- Technological parameters of getting condensers (temperature of deposition, vacuum level, speed of initial components deposition, chemical purity of initial components, substrate surface roughness)

The main factor influencing the structure and following mechanical properties is the contact between reinforced particles and metallic matrix. The value criteria of that contact are the wetting angle between molten metal and refractory particles [7]. This angle depends on the environment where the molten state interacts with high-temperature particles, the pureness of molten metal and particle itself, melt's temperature, and exposure time. There are much-known research data in the literature, which determine contact interconnection in the systems: Me(alloy)- MeO, Me-C, Me-B in vacuum or gaseous environments [8, 9].

Two phases, simple condensated systems Me-MeO, where "Me" is pure metals such as iron, nickel, copper, and ceramic particles such as yttrium oxide, aluminium oxide, and zirconium dioxide most studied present day.

It is possible to get dispersed-reinforced materials with good mechanical properties when the reinforced part concentration is 0.6 % weight.

The strength limit ( $\sigma_b$ ), the deformation limit ( $\sigma_{0.2}$ ), and elongation as the function of the condensed Ni- $\text{Al}_2\text{O}_3$ , obtained at the substrate temperature 700 °C and  $1000 \pm 20^\circ\text{C}$ , shown in Figure 2a and Figure 2b. Analysis of these dates shows that small concentrations of disperse  $\text{Al}_2\text{O}_3$  particles increase leads to abrupt reduction of ductileness.

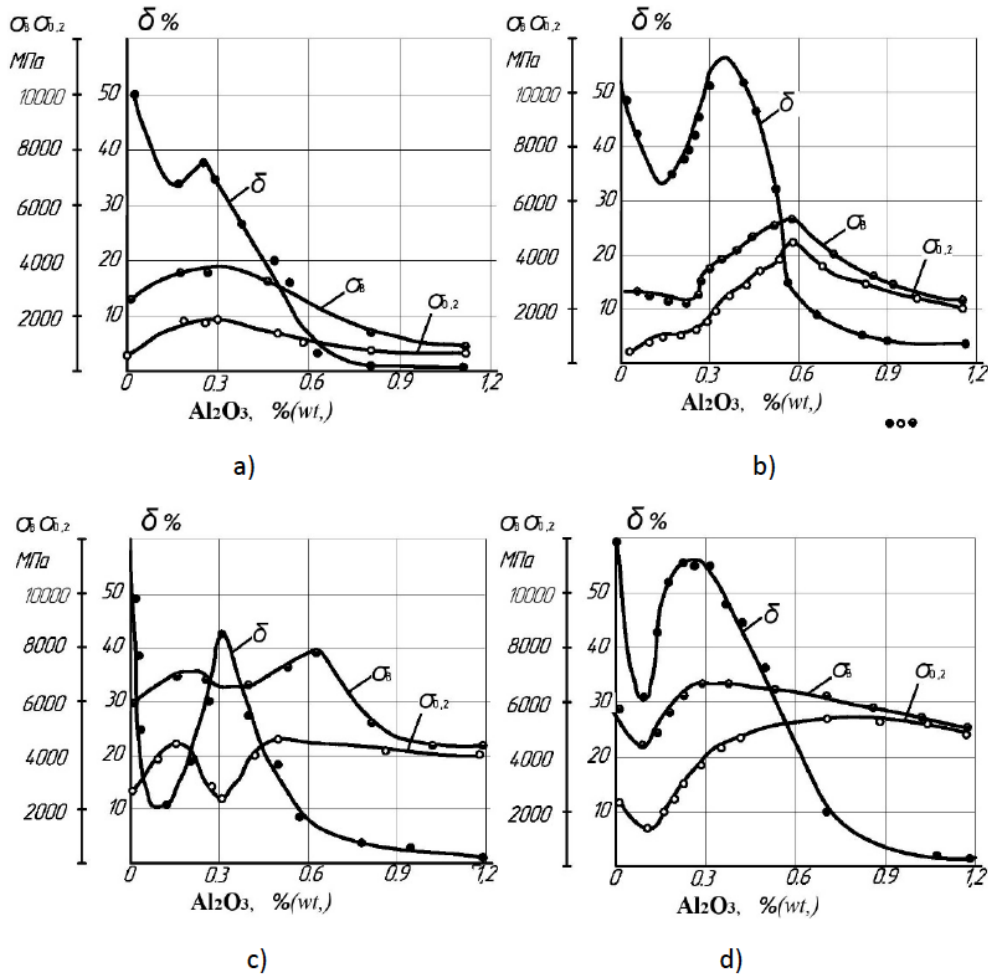
The maximum plasticity is visible at a very narrow concentration interval  $\text{Al}_2\text{O}_3$  (0.25 – 0.4 % weight. The structural condition, such as the average grain size of the metallic matrix equal to the space of free movement between two reinforced particles, explains the ductility increasing [2].

The condensed composite materials from the vapor phase were deposited on a carbon steel substrate with 220 x 250 x 10 mm sizes and heated up to the necessary temperature. The substrate roughness after polishing was  $R_a = 0,63$ . For further separation of ready condensate from the substrate, the separation layer of  $\text{CaF}_2$  was painted in advance with a thickness of 10-15  $\mu\text{m}$ . Evaporation of metallic and ceramic components was performed from two separate crucibles with diameters of 70 mm, with liner distance between crucibles of 150 mm. As mentioned here, the technological approach allows gradient condensed materials along the substrate with a wide interval of high-temperature phase concentration with the high-temperature melting point. The material with a 1-1.5 mm thickness was separated from the substrate and cut to the strips with 20 x 220 x 1-1.5 mm. These strips serve as samples for the investigation. The porosity estimation on each concentration was done on 7-10 pieces. The porosity was estimated based on getting results as an average value.

It is necessary to mention that curves maximum on (Figure b) with temperature increase shifts to the side of more aluminium oxide concentration.

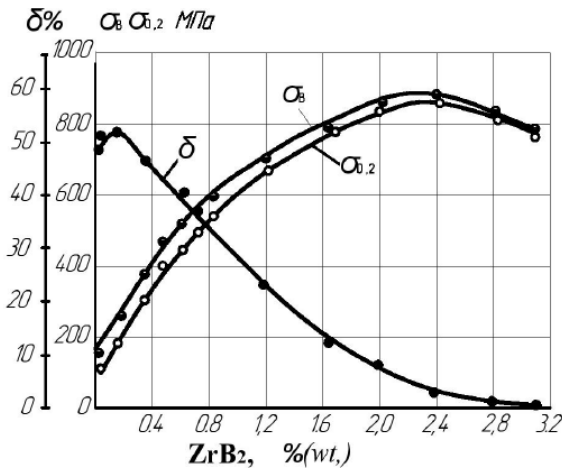
Absolute ductileness values in two Me-MeO phase-type materials with optimum concentration of dispersed particles increasing when the condensation temperature rises. For example, at substrate temperature 1000 °C Ni - (0.35 -0.4 % weight)  $\text{Al}_2\text{O}_3$  has relative elongation more significant than a pure nickel.

Similar mechanical properties changes observe more complex two-phase condensed systems based on complicated compositions MeCr, MeCrAl, MeCr Y,



**Figure 2:** Strength, deformation, and relative elongation as a function of Al<sub>2</sub>O<sub>3</sub> concentration in CDRM Ni-Al<sub>2</sub>O<sub>3</sub> (a,b) and (Ni-20 % weight) Cr-Al<sub>2</sub>O<sub>3</sub> (c, d) obtained at the temperatures 700 °C (a,b) and 1000°C (c,d).

Me = Fe, Ni, Cu Figure 3 concentration in CDRM Cu-ZrB<sub>2</sub>, dispersed condensates obtained at 700°C on a substrate.



**Figure 3:** Strength and deformation and relative elongation as a function of ZrB<sub>2</sub>.

The strength increase is visible at a more wide concentration interval of Al<sub>2</sub>O<sub>3</sub> (up to 1 % of weight). But at such concentrations of high-temperature particles, in the condensed materials, they have low plasticity. Such mechanic properties changing explain by the complete absence of interphase interactions on the particle-matrix border. The wetting angle of Al<sub>2</sub>O<sub>3</sub> by Nickel varieties at 150° – 115° depends on experimental conditions [9]. As a result, when the interaction is absent in condensate, the porosity appears that leads to strength and flexibility slackening.

The growing of phase interaction in Ni(Cr) - Al<sub>2</sub>O<sub>3</sub> system [9] (wetting angle is 85°) is following in strength and deformation values expanding in the broader interval of Al<sub>2</sub>O<sub>3</sub> in compering with Ni- Al<sub>2</sub>O<sub>3</sub> compositions.

For two-phase systems, Me – (MeC, MeB), the curve changes the direction to the more considerable

concentration of reinforced particles of carbides or borides in compare to oxide phases. This curve shifting happens at 3%-7 % weight of reinforced particles.

Such tendencies belong to condensed materials on Nickel, Iron, and Copper base in the case of TiC, NbC, ZrC, TiB<sub>2</sub> ZrB<sub>2</sub> reinforced particle application. Figure 3 shows mechanical properties changing in the Cu-ZrB<sub>2</sub> system

An increase of ZrB<sub>2</sub> up to 0.8 % of weight can enhance the strength and deformation to the 560 – 600 MPa. For a percentage increase up to 2.4 % weight, the strength reaches 950 MPa.

The elasticity of Cu-ZrB<sub>2</sub> condensates sharply declines within the range of small concentrations of ZrB<sub>2</sub> but stays satisfactory at the reinforced phase containing up to 1 % of the weight.

Cu-ZrB<sub>2</sub> composition keeps pick of ductileness at ZrB<sub>2</sub> = 0.1 % weight, same as CDRM with oxides.

Receiving results is very well correlated with wetting of zirconium diboride by molten copper. The wetting angle is in a range of 123° – 36° at the temperature of 1100 °C – 1400 °C [8].

Similar mechanical properties correspond to CDRM copper reinforced by Molybdenum (Figure 4). At the increasing percentage of Molybdenum up to 2 % weight, the elasticity of the copper matrix drops to 45 % - 15 %, and the limits of strength and deformation increase twice, accordingly to 270 MPa and 350 MPa. Following growing, Mo content up to 6 % of weight improves strength, up to 500 MPa that is more than

four times higher than pure copper. The limit of deformation reaches 410 MPa that is higher than pure copper more than eight times. Relative elongation of materials keeps a considerably high level and equal to 10% - 12% and doesn't depend on the molybdenum concentration in the range 2% - 6% of the weight.

Gradual diminishing of mechanical properties of Cu-Mo CDRM is visible at Molybdenum disperse particles concentration higher than 12 % weight.

The higher level of reinforcement by molybdenum concentration in the condensates makes the material's mechanical properties outstanding.

Mechanical properties of materials mentioned above have a structure with actual sizes of grains and specific dimensions of reinforced particles. The values of these sizes detect by substrate temperature.

The substrate temperature decreasing in the dispersing reinforced material manufacturing leads to structural grains coarsening. For example, for Cu-Mo(1%w) at substrate temperature, 700 °C matrix grains coarsening is  $D_g=3.25 \mu\text{m} - 1.45 \mu\text{m}$  with characteristic reinforced particles diameter is  $d_p=12 \text{ nm} - 25\text{nm}$ .

The strength limit increases to  $\sigma_b=270 \text{ Mpa} - 428 \text{ Mpa}$ , deformation limit to  $\sigma_{0,2}=140 \text{ Mpa} - 400 \text{ MPa}$ , and elongation to 7%.

Additional cold forging with 30 % deformation improves mechanical properties of disperse-reinforced materials even more.

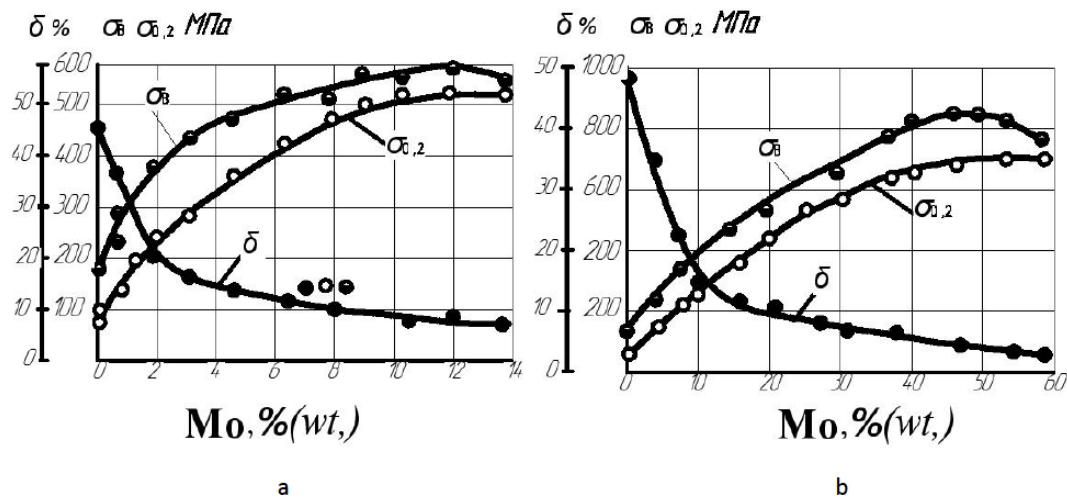


Figure 4: Strength, deformation, and relative elongation as a function of Molybdenum concentration in copper, obtained at substrate temperature a- 700°C, b – 900 °C.

The standard deviation of obtained results was around  $\pm 5\%$

The limit of strength is going up at substrate temperature  $500\text{ }^{\circ}\text{C}$ , and equal to  $498\text{ MPa}$ , the limit of deformation raises to  $420\text{ MPa}$ , and relative elongation is up to  $9\%$ . Further deformation making grain coarsening of the copper matrix more coarse up to  $1\text{ }\mu\text{m}$ .

Higher deposition temperature for CDRM in all cases decreases the strength and increases the elasticity of the materials. For example, Figure 4.b shows the mechanical properties of Cu-Mo condensers made at substrate temperature  $900\text{ }^{\circ}\text{C}$ . Strength increases in Mo concentration before  $25\%$  w than its unchangeable up to  $50\%$  w of Molybdenum. The beginning of mechanical properties degradation is observed at molybdenum concentration above  $15\%$  w. The ductileness of mentioned material initially is going down from Mo concentration of  $1\%$  w and tending further declining with reinforced particles concentration growth.

Vacuum deepness, purity of initial materials, the roughness of substrate surface have a strong influence on the mechanical properties of CDRM.

The possibility of supplying oxygen or nitrogen at the deposition process creates oxides and nitrides, reinforcing matrix and increasing mechanical properties but ductility, electro-conductivity, and thermo-conductivity decreasing.

Many defects in CDRM (micro-droplets, nonmetallic inclusions) depend on evaporated components' purity. The best options are metals and alloys obtained after electron-beam smelting and purification. All electron-beam processed compositions contain much less low melting additives, oxygen, nitrogen, and hydrogen compare with standard technically pure metals and alloys.

As far as the evaporation speed increases, additives' probability of removing from the evaporated pool is high. After electron-beam purified metals and

alloys, the rate of deposition of pure metal and alloys is in the range of  $3\text{ }\mu\text{m}/\text{min} - 60\text{ }\mu\text{m}/\text{min}$  and for dispersing reinforced materials  $0,5\text{ }\mu\text{m} - 10\text{ }\mu\text{m}$ .

The better surface roughness of the substrate makes better mechanical properties of the CDRM. It is experimentally proved that the surface roughness of the substrate should be  $0.63 - 1,2\text{ Ra}$ ,

## CONCLUSION

Experimentally confirmed that disperse reinforced condensed materials got from the vapour phase have superior mechanical properties. These properties depend on the type of metallic matrix, types of dispersed inclusions, the substrate's temperature, interphase interaction on the border of matrix-reinforced particles, and the substrate's roughness and speed of evaporation.

With the estimation of the matrix dispersal particle interaction on the borderline and application of high-speed evaporation, it is easy to design new CDRM materials within advance programmed properties.

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