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Massive Dispersion-Strengthened Composition Materials with Metal Matrix Condensed from the Vapour Phase

M. I. Grechanyuk¹, V. G. Grechanyuk², A. M. Manulyk³,
I. M. Grechanyuk², A. V. Kozyrev², and V. I. Gots²

¹*Institute for Problems in Materials Science, N.A.S. of Ukraine,
3, Krzhizhanovsky Str.,
UA-03142 Kyiv, Ukraine*

²*Kyiv National University of Construction and Architecture,
31, Povitroflotsky Ave.,
UA-03037 Kyiv, Ukraine*

³*Synergy ANTECH Services Corp.,
32, Bill Hutchinson Crescent,
ON L1C 7E1 Bowmanville, Ontario, Canada*

This article presents the results of a study of the condensed dispersion-reinforced materials (CDRM) obtained from the vapour phase. The mechanical properties of materials depending on their reinforcement are studied in systems based on metals and alloys, with reinforcing additives of oxide, carbide or boride. Mechanical properties are evaluated as a complex of tensile strength, deformation limit, and relative elongation. As a result, it is shown that the mechanical properties of materials obtained from the vapour phase depend on the following factors: type of matrix, type of dispersed particles, temperature and roughness of the substrate, purity of the initial materials, and the rate of their evaporation. As found, the achievement of high mechanical properties due to the formation of a specific structure can be realized by regulating the temperature of the substrate. A decrease in the temperature of the substrate during the fabrication of the dispersion-reinforced material leads to a coarsening in the structural grains. Outstanding properties are obtained in the Cu–1 wt.% Mo CDRM with coarseness of matrix grains of 1.45–3.25 μm and characteristic diameter of reinforcing particles of 12–25 nm. As shown by evaluating the interaction of the matrix and dispersed particles at the interface and using high-speed evaporation, it is easy to develop the new CDRM with predefined properties.

У статті наведено результати дослідження конденсованих дисперсно-армованих матеріалів (КДАМ), одержаних з парової фази. Досліджено

механічні властивості матеріалів в залежності від армування їх у системах металів і сплавів з добавками оксидів, карбідів і боридів. Механічні властивості оцінювали комплексно, враховуючи міцність на розрив, межу деформації та відносне видовження. В результаті було показано, що механічні властивості матеріалів, одержаних з парової фази, залежать від наступних чинників: типу матриці, типу дисперсних частинок, температури та шерсткості підкладки, чистоти вихідних матеріалів, швидкості їхнього випаровування. Встановлено, що досягнення високих механічних властивостей через формування специфічної структури уможлиблюється шляхом зміни температури підкладки. Пониження температури підкладки під час виготовлення дисперсно-армованого матеріалу приводить до збільшення розміру зерен. Високі значення властивостей було одержано для КДАМ системи Cu–Mo (1 мас.% Mo) з розміром зерен матричної фази у 1,45–3,25 мкм і діаметром армувальних частинок у 12–25 нм. Було показано, що, враховуючи взаємодію матриці та диспергованих частинок на межі поділу фаз, використовуючи високошвидкісне випаровування, можна доволі легко створити нові дисперсно-армовані матеріали із заздалегідь визначеними властивостями.

Key words: condensed dispersion-reinforced materials (CDRM), condensation, vapour phase, composition materials, metal matrix.

Ключові слова: конденсовані дисперсно-армовані матеріали (КДАМ), конденсація, парова фаза, композиційні матеріали, металева матриця.

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1. INTRODUCTION

The emergence of new technologies in the middle of the 20th century, such as plasma arc, electron-beam radiation and laser, posed new challenges for developers in the field of new technologies for material processing and welding. First, why does a freely burning electric arc melt metals mainly on the surface, and the depth of the melting zone is less than its width? The search for an answer led to a new understanding of the energy torrents concentration (ETC). It became clear that if the energy of the power source (electron beam, plasma arc, and laser) reaches the value $E \geq 10^5\text{--}10^6 \text{ W/cm}^2$, the material heating process turns into a self-propagating one (synergistic). Moreover, when the power threshold-value changes, the heat transfer conditions in the object have directed for heating.

Overcoming this threshold opens up new opportunities for technologists. Extensive scientific and technical experience with ETC has shown that the most efficient source of energy for material processing is an electron beam [1].

The E. O. Paton Electric Welding Institute and Scientific-

Production Enterprise 'Eltehmash' developed new multifunctional electron-beam installations with two, three, and five crucibles to create dense molecular beams. The intensity of those beams reaches 10^{23} particles cm^3/s [2]. Beams are quasi-molecular rays, which are characterized as molecular beams with spatial orientation according to cosine law. On the other hand, such beams arise because of internal collisions of vapour torrents in a laminar flow.

The productivity of the installations reaches 10–15 kg of vapours per hour. It is possible to manufacture 100 kg of condensate for eight hours of uninterrupted work, and sometimes even more.

Academician B. Movchan and his group investigated the basic physical and mechanical foundations of thick (0.01–2 mm) condensates at the E. O. Paton Electric Welding Institute of the National Academy of Sciences of Ukraine [2, 3]. They revealed the main physical-mechanical properties of condensers as a function of condensate parameters and their composition.

The possibility of obtaining the dispersion-reinforced, microporous and microlayer materials by condensation from the vapour phase is an effective way to create new materials with advanced desired properties.

Composite materials condensed from the vapour phase have a thickness of 0.1 to 5 mm. The grain size of the matrix phase in depending on the condensation temperature and the content of the reinforcing particles and ranges from 0.5 μm to 10 μm , whereas the size of reinforcing nanophase particles varies from 1 to 4 nm. The same method was used to obtain bulk nanocrystalline microlayer materials based on copper and molybdenum with a grain size of 80–90 nm for copper and of 20–40 nm for molybdenum. Thus, condensate dispersion-reinforced materials should be considered as nanostructured composites. The study of the structure and properties of such materials is the purpose of this work.

Condensed dispersion-reinforced materials (CDRM) are materials consisting of a polycrystalline matrix and an even volume of dispersed particles of another phase (Fig. 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 dispersion-reinforced condensed materials are studied at the E. O. Paton Electric Welding Institute. These materials include iron-carbide systems, iron-boride, iron-iron oxide, nickel-oxide, copper-copper oxide, tungsten-oxide systems [4]. All our previous works embedded the study of dispersion-reinforced materials based on nickel, chromium, copper and titanium [5]. In our days, studies of other systems continue [6].

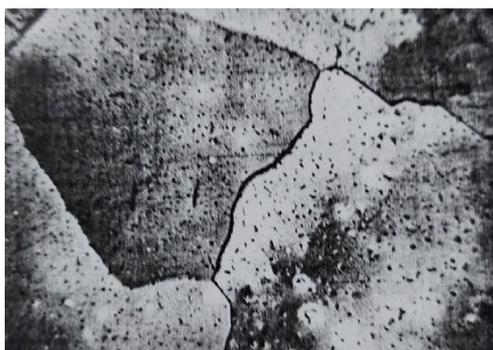


Fig. 1. Typical structure of disperse-reinforced material obtained from the vapour phase.

Analysis of the obtained results allows concluding that the mechanical properties of condensed dispersion-reinforced materials depend on the following factors:

1. type of metallic matrix (pure metal or alloy);
2. technological parameters for obtaining condensers (temperature of deposition, vacuum level, deposition rate of the initial components, chemical purity of initial components, substrate surface roughness).

The main factor affecting the structure and the following mechanical properties is the contact between the reinforced particles and the metal matrix. The criterion for the value of this contact is the contact angle between the molten metal and the particles of the refractory material [7]. This angle depends on the environment in which the molten state interacts with high-temperature particles, the purity of the molten metal and the particle itself, the temperature of the melt, and exposure time. There are well-known research data in the literature that determine the contact interconnection in the systems: $Me(\text{alloy})-MeO$, $Me-C$, $Me-B$ in the vacuum or gaseous environments [8].

Two-phase simple condensed $Me-MeO$ systems, where Me are pure metals such as iron, nickel, copper, and ceramic particles such as yttrium oxide, aluminium oxide, and zirconium dioxide are currently the most studied. Dispersion-reinforced materials with good mechanical properties can be obtained at a concentration of the reinforced part of 0.6 wt.%.

2. EXPERIMENT

The mechanical properties of the CDRM depending on their reinforcement have been studied in systems based on metals (Ni, Cu)

and alloys ($MeCr$, $MeCrAl$, $MeCrY$, where Me was Fe, Ni or Cu) with reinforcing additives of oxide, carbide or boride (Al_2O_3 , TiC, NbC, ZrC, TiB_2 , ZrB_2 and other). Mechanical properties were evaluated as a complex of tensile strength, deformation limit and relative elongation.

The condensed composite materials from the vapour phase were deposited on a carbon steel substrate with dimensions of $220 \times 250 \times 10$ mm and heated to the required temperature. The roughness of the substrate after polishing was $R_a = 0.63$. For further separation of the finished condensate from the substrate, a CaF_2 separating layer with a thickness of 10–15 μm was applied in advance. The evaporation of metallic and ceramic components was performed from two separate crucibles with a diameter of 70 mm and a liner distance between crucibles of 150 mm. As already mentioned, this technological approach makes it possible to gradient condense of materials along the substrate with a wide concentration range of the high-temperature phase with a high-temperature melting point. The material with thickness of 1–1.5 mm was separated from the substrate and cut into strips of $20 \times 220 \times 1-1.5$ mm in size. These strips were used as samples for the research. The estimation of porosity for each concentration was carried out on 7–10 samples. The porosity was estimated from the results obtained as an average value.

3. RESULTS AND DISCUSSION

The ultimate tensile strength (σ_B), the deformation limit ($\sigma_{0.2}$), and relative elongation (δ) as the function of Al_2O_3 weight fraction in the condensed Ni- Al_2O_3 obtained at the substrate temperature of 700°C and $1000 \pm 20^\circ C$ are shown in Fig. 2, *a*, *b*. Analysis of these data shows that a slight increase in the concentration of dispersed Al_2O_3 particles leads to a dramatic decrease in plasticity.

Maximum plasticity is observed in a very narrow range of Al_2O_3 concentrations of 0.25–0.4 wt.%. Structural circumstances, such as the average grain size of the metal matrix equal to the space of free movement between two reinforced particles, explain the increase in ductility [2].

It should be noted that the maximum of the curves with an increase in temperature shifts towards a higher concentration of aluminium oxide (Fig. 2, *b*). The values of absolute plasticity in two materials of the $Me-MeO$ phase-type with an optimal concentration of dispersed particles increase with an increase in the condensation temperature. For example, at a substrate temperature of 1000°C, Ni- Al_2O_3 with 0.35–0.4 wt.% Al_2O_3 has a higher relative elongation than pure nickel.

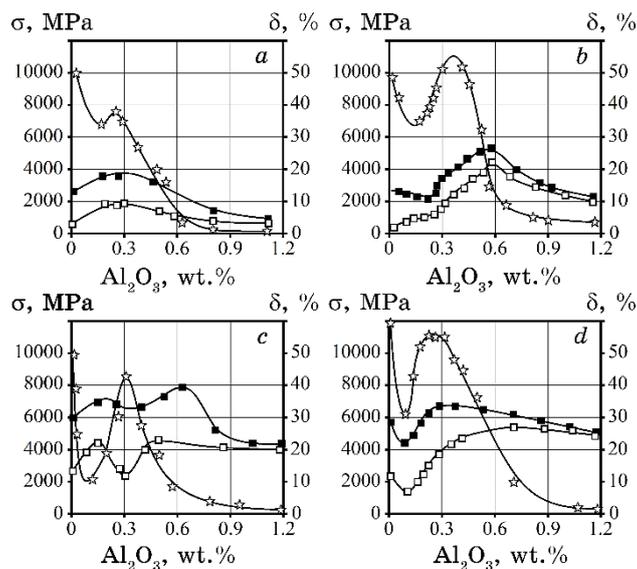


Fig. 2. Tensile strength, deformation limit, and relative elongation as the function of Al_2O_3 weight fraction in the Ni- Al_2O_3 (a, b) and Cr(Ni)- Al_2O_3 with 20 wt.% Ni (c, d) CDRM obtained at the substrate temperature of 700°C (a, b) and 1000°C (c, d); ☆— δ , %; ■— σ_B , MPa; □— $\sigma_{0.2}$, MPa.

Similar changes in mechanical properties are observed in more complex two-phase condensed systems based on compositions $MeCr$, $MeCrAl$, $MeCrY$, where Me is Fe, Ni, or Cu.

The increase in strength is noticeable in a wider range of Al_2O_3 concentrations (up to 1 wt.%). However, at such concentrations of high-temperature particles in condensed materials, they have low plasticity. This change in mechanical properties is explained by the complete absence of interphase interactions at the particle-matrix interface. The contact angle Al_2O_3 with nickel within the range 150–115° depends on the experimental conditions. As a result, porosity appears in the condensate without interaction, which leads to a weakening of strength and flexibility.

An increase in the phase interaction in the Ni(Cr)- Al_2O_3 system (contact angle of 85°) leads to an increase in strength and deformation values in a wider range of Al_2O_3 concentration as compared to Ni- Al_2O_3 compositions.

For the two-phase systems $Me-MeC$ and $Me-MeB$, the curve changes direction towards a more significant concentration of reinforced carbide or boride particles in comparison with oxide phases. Such a shift in the curve occurs, when the fraction of reinforced particles is of 3–7 wt.%. This trend extends to condensed materials

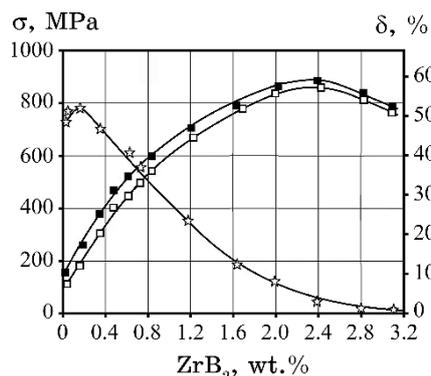


Fig. 3. Tensile strength, deformation limit, and relative elongation as the function of ZrB_2 weight fraction in the Cu- ZrB_2 CDRM obtained at the substrate temperature of $700^\circ C$; ☆— δ , %; ■— σ_B , MPa; □— $\sigma_{0.2}$, MPa.

based on nickel, iron and copper in the case of using reinforcing particles TiC, NbC, ZrC, TiB₂, and ZrB₂.

Figure 3 shows the change in mechanical properties in the Cu- ZrB_2 system.

An increase in the ZrB_2 up to 0.8 wt.% allows increasing the strength and deformation up to 560–600 MPa. With an increase of up to 2.4 wt.%, the strength reaches 950 MPa.

The plasticity of Cu- ZrB_2 condensates sharply decreases in the region of low ZrB_2 concentrations, but remains satisfactory in the content of reinforcing phase up to 1 wt.%. The Cu- ZrB_2 composition keeps pick of plasticity at a ZrB_2 content of 0.1 wt.%, same as the CDRM with oxides. Receive results is very well correlated with wetting of zirconium diboride by molten copper. The contact angle is in the range $123-36^\circ$ at the temperature of $1100-1400^\circ C$ [8].

The copper CDRM reinforced with molybdenum have similar mechanical properties (Fig. 4). At the increasing percentage of molybdenum up to 2 wt.%, the plasticity of the copper matrix drops for 45–15%, and the limits of strength and deformation increase twice, accordingly, to 270 MPa and 350 MPa. With an increase in the content of molybdenum to 6 wt.%, the strength increases to 500 MPa that is more than four times higher than that of pure copper. The deformation limit reaches 410 MPa that is more than eight times higher than pure copper. The relative elongation of the materials is kept at a fairly high level of 10–12% and does not depend on the concentration of molybdenum within the range 2–6 wt.%. A gradual decrease in the mechanical properties of the Cu-Mo CDRM is observed when the concentration of dispersed molybdenum particles exceeds 12 wt.%.

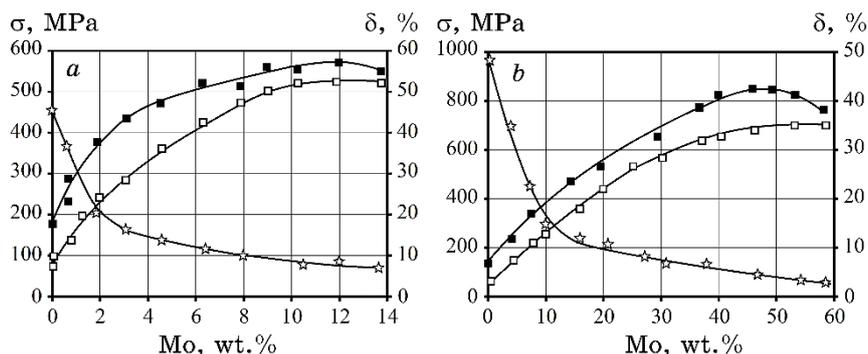


Fig. 4. Tensile strength, deformation limit, and relative elongation as a function of molybdenum concentration in the copper CDRM obtained at substrate temperature of 700°C (a) and 900°C (b); \star — δ , %; \blacksquare — σ_B , MPa; \square — $\sigma_{0.2}$, MPa.

The higher level of reinforcement by molybdenum concentration in the condensates makes the material outstanding in its mechanical properties. Such mechanical properties of the aforementioned materials are a consequence of the structure with the actual grain sizes and the specific sizes of the reinforcing particles.

These dimensions are determined by the temperature of the substrate. A decrease in the temperature of the substrate during the manufacture of the dispersion-reinforced material leads to a coarsening in the structural grains. For example, in the case of Cu–Mo (1 wt.%) at a substrate temperature of 700°C, the coarseness of matrix grains is $D_g = 1.45\text{--}3.25\ \mu\text{m}$ with a characteristic diameter of reinforcing particles $d_p = 12\text{--}25\ \text{nm}$. Tensile strength increases to 270–428 MPa, deformation limit up to 140–400 MPa, and elongation up to 7%.

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

The standard deviation of the results obtained was about $\pm 5\%$.

At a substrate temperature of 500°C, the tensile strength increases to 498 MPa, the deformation limit up to 420 MPa, and the relative elongation up to 9%. Further deformation leads to coarsening of the grain of the copper matrix to 1 μm .

The higher deposition temperature of the CDRM in all cases reduces the strength and increases the plasticity of the materials. For example, in Fig. 4, b shows the mechanical properties of Cu–Mo obtained at substrate temperature of 900°C. The strength increases with the concentration of molybdenum up to 25 wt.%, then remains almost unchanged up to 50 wt.%. The beginning of the degradation of mechanical properties is observed when the concentration of mo-

lybdenum is more than 15 wt.%. The plasticity of this material initially decreases at a molybdenum concentration of 1 wt.% and tends to decrease further with an increase in the concentration of reinforcing particles.

The depth of vacuum, the purity of the initial materials, and the roughness of the substrate surface have a strong influence on the mechanical properties of the CDRM.

The possibility to supply oxygen or nitrogen at the deposition process allows creating the oxides and nitrides, which strengthens the matrix and improves mechanical properties, but reduces ductility, electrical conductivity and thermal conductivity.

Many CDRM defects (microdroplets, non-metallic inclusions) depend on the purity of the evaporated components. The best options are metals and alloys obtained after electron-beam smelting and refining. All the electron-beam treated compositions contain much less fusible additives, oxygen, nitrogen and hydrogen compared to standard commercially pure metals and alloys.

As the evaporation rate increases, the possibility of removing additives from the evaporation bath is high. After electron-beam purified of metals and alloys, the deposition rate of pure metal and alloys is in the range 3–60 $\mu\text{m}/\text{min}$, and, for the dispersion-reinforced materials, it is of 0.5–10 μm .

The better surface roughness of the substrate improves the mechanical properties of the CDRM. It is experimentally proved that the surface roughness of the substrate should be $R_a = 0.63\text{--}1.2$.

3. CONCLUSION

It has been experimentally confirmed that the dispersion-reinforced condensed materials obtained from the vapour phase have excellent mechanical properties. These properties depend on the type of metal matrix, types of dispersed inclusions, substrate temperature, interphase interaction at the interface between the matrix and reinforced particles, substrate roughness, and evaporation rate.

By evaluating the interaction of the matrix and dispersed particles at the interface and using high-speed evaporation, it is easy to develop the new CDRM materials with predefined properties.

REFERENCES

1. I. V. Zuev, *Obrabotka Materialov Kontsentrirrovannymi Potokami Ehnergii* [Materials Processing by Dense Energy Torrents] (Moscow: MEI: 1998) (in Russian).
2. B. A. Movchan and I. S. Malashchenko, *Zharostoikie Pokrytiya, Osazhdenyye v Vakuume* [Heat-Resistant Coatings Deposited in Vacuum] (Kiev:

- Naukova Dumka: 1983) (in Russian).
3. B. A. Movchan, *Suchasne Materialoznavstvo XXI st.* [Modern Materials Science in the 21st Century] (Ed. I. K. Pokhodnya) (Kyiv: Naukova Dumka: 1998), p. 318 (in Ukrainian).
 4. A. V. Demchishin, *Struktura i Svoistva Metallicheskih i Nemetallicheskih Plotnykh Vakuumnykh Kondensatov i Nauchnyy Podkhod k Ikh Polucheniyu* [Structure and Properties of Metallic and Nonmetallic Thick Vacuum Condensates and Scientific Approach towards Obtaining Them] (Thesis of Dissert. for Dr. Tech. Sci.) (Kiev: E. O. Paton Electric Welding Institute: 1981) (in Russian).
 5. N. I. Grechanyuk, *Novyye Konstruktsionnyye Materialy, Poluchennyye v Vakuume iz Parovoi Fazy dlya Novykh Tekhnicheskikh Detaley* [New Construction Materials Obtained in a Vacuum from the Vapour Phase for New Technical Parts] (Thesis of Dissert. for Dr. Tech. Sci.) (Kiev: E. O. Paton Electric Welding Institute: 1988) (in Russian).
 6. N. I. Grechanyuk, V. A. Osokin, P. P. Grechanyuk, R. V. Kucherenko, M. E. Golovkova, and G. E. Kopylova, *Modern Electrometallurgy*, 2: 9 (2006) (in Russian).
 7. Yu. V. Naidich, *Kontaktnyye Yavleniya v Metallicheskih Rasplavakh* [Contact Phenomena in Metal Melts] (Kiev: Naukova Dumka: 1972) (in Russian).
 8. G. V. Samsonov and A. P. Ehpik, *Tugoplavkie Pokrytiya* [Refractory Coatings] (Moscow: Metallurgiya: 1973) (in Russian).