

MECHANICAL PROPERTIES OF METALLIC FILMS

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INTRODUCTION

AMONG the new materials marking the progress of modern science and technology are the films obtained by condensation in vacuo. One of the highly interesting and poorly-studied properties of films is their high strength. Besides, as we know, one of the most pressing problems of modern solid state physics is to raise the actual strength of materials close to the theoretical value calculated from the interatomic interaction forces.

Strengths close to the theoretical have been attained in recent years in filamentous crystals, or whiskers.^[1,2] Study of condensed films, which have a small dimension h in only one direction, rather than two as in whiskers, may prove very promising in searching for new high-strength materials. Furthermore, as we shall see below, the small dimension h in films can exceed h in whiskers by several orders of magnitude.

Finding the reasons for the high strength of films is of considerable scientific and applied interest. In addition, condensates contain practically all the known crystal lattice defects. Owing to their small thickness h , they are a very convenient object for getting direct information on the interaction of various defects, and on the effect of the free surface of films and the substructure on the process of movement of dislocations and other defects, etc.

Data on mechanical properties are needed in connection with the wide use of films in modern technology.

For example, among the studies on physics of ferromagnetic films we can single out a group of studies on the effect of stresses on the magnetic characteristics and domain structure of films.^[44] Naturally, one requires information on the mechanical properties of the studied films in planning such studies. This problem is also of interest from the engineering standpoint, since ferromagnetic materials in the form of films are widely used in designing new microminiature devices (in radioelectronics, telemetry, etc.) Here they often provide for the possibility that these devices are to operate under working conditions of vibration, high acceleration, etc.

The first information on the high strength of vacuum condensates appeared in a monograph by S. A. Vekshinskiĭ.^[5] According to his data, the breaking strength of Al films considerably exceeded that of a foil of the same thickness prepared by ordinary rolling. Several tens of studies have been published thus far on the mechanical properties of films over the very wide range $h \cong 0.02-70 \mu$. The greatest number of these studies have appeared in the last 5-6 years.

The classification of films into "thin" and "massive" (thick) films is provisional, and acquires a distinct physical meaning only when we examine the definite structural state and concrete physical properties. The criterion of the thin-film state for mechanical properties can be taken to be the critical thickness h_c (or range of h_c) below which the parameter h directly affects the structure of the condensates. As we shall see below, h_c

is close to $0.2\text{--}0.4\ \mu$ for the studied metal films.

In this review we shall try to systematize the known studies in this country and abroad on the mechanical properties of thin and massive films. We shall preface the presentation of the experimental results with a brief review of the methods of mechanical testing of films. In conclusion, we shall discuss the possibilities of practical use of high-strength condensed films.

1. MECHANICAL TESTING METHODS

We shall briefly discuss below the currently known methods of estimating the mechanical strength of thin and massive films. We note that the given problems as applied to thin films have been discussed in detail in [105].

1.1. Abrasion Method^[4,5]

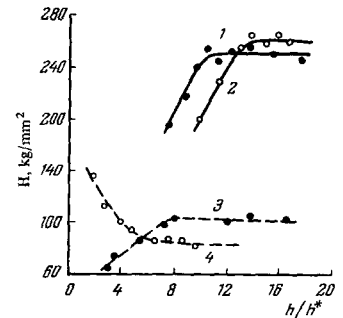
This was historically the first method of estimating the strength (implying the hardness and adhesion of films) of condensed coatings not stripped from their substrates. In order to compare the strength of different films, they determined the amount of abrasion by an abrading element (rubber or chamois) required to rub off the coating under a given pressure. We note that hardness and adhesion of films are often contradictory properties, which can distort the results of such studies.

1.2. Microhardness Method

In line with the difficulties of mechanical testing of the specific objects (condensed films), the role of measuring the microhardness H is increasing. It is related in a definite way to the ultimate strength, and can be used to estimate the mechanical properties.^[6,33] An essential fact in studying vacuum condensates is that one is no longer measuring the hardness of individual grains here, but some integral quantity that should be treated as a macrohardness, since the diagonal dimension of the indentation usually considerably exceeds the dimensions of the crystallites.^[6] In order to obtain the true hardnesses in studying films (and also thin sheets, surface coatings, etc.) the ratio of the thickness h of the specimen to the depth h^* of the indentation must exceed some number n ($h/h^* > n$). The most varied and contradictory pieces of information exist on the size of this very important parameter.^[6,33]

The first systematic study of this problem was made in [6], where different combinations of layers (films of Cr, Bi, and Cu) and substrates (glass, steel, Al) were studied. The obtained results made it possible to explain the reason for the discrepancy in the determinations of n . It turned out that the value of n is smaller for soft films on hard substrates (Bi on glass or steel) than for hard films on soft substrates (Cr on steel). The values of n amounted to 4–9. Studies^[33] were later performed to create the groundwork of a technique of measuring H of high-strength Cu and Al films condensed over a broad temperature range on different substrates. Figure 1 shows a typical calibration curve. As we see, the curves have two characteristic regions, inclined and horizontal. The course of the former is governed by the effect of the substrate, since the H of a film measured in this re-

FIG. 1. The microhardness H as a function of the ratio h/h^* for Cu films on aluminum (1–3) and steel (4) substrates $P = 50\text{g}$ (1) and 20g (2–4).



gion depends on the H of the substrate. The horizontal region corresponds to the true H measured when $h/h^* > n$, i.e., when the substrate exerts no influence. The critical value of n was determined from the place where the inclined region of the curve joined the horizontal region, and it varied from 5 to 13. The most unfavorable situation (with respect to the influence of the substrate) was shown to be the combination hard film—soft substrate. For example, while the effect of the substrate began to appear at $14\ \mu$ in measuring H of Cu films on “hard” steel or glass, it happened only at $22\ \mu$ on “soft” aluminum.^[33] Methodological problems of measuring H of films are also discussed in [43]. The existing method of measuring H in instruments of the PMT-3 type permits one to test films starting with h about $10\ \mu$. We note that it becomes possible to test films about $1\ \mu$ thick with more refined apparatus, e.g., by using an instrument for measuring submicrohardness (SMH).^[7]

The above-discussed method can also be used to study the microhardness of electroplated coatings, etc.

1.3. High-speed Rotor Method

The method was developed by Beams and his associates,^[12] and used to measure the breaking and adhesive strength of films deposited by electroplating on a steel cylinder. The films failed under centrifugal forces produced by rapid rotation of the rotor in a vacuum. The rotor was set in motion by a rotating magnetic field. A uniaxial stressed state was produced in the test.

1.4. Curvature Method (“Bulging”)

The method was first described by Beams and his associates.^[13] The film to be tested is attached to the open end of a tube of round or rectangular cross-section. “Bulging” is carried out by creating a regulated pressure differential on the two sides of the specimen. If we assume that the film acquires a spherical shape on bending, the stress σ and the strain ϵ are calculated by the formulas

$$\sigma = \frac{Pa^2}{4hd}, \quad \epsilon = \frac{2}{3} \frac{d^2}{a^2},$$

where P is the pressure differential, a is the radius of the aperture of the tube, d is the deflection, and h is the thickness of the film. The films are in a biaxially stressed state while being tested.

In distinction from the rotor method, this method permits one to get information on the stress-strain diagram of films. Among the defects of the method, we should mention the insufficiently grounded assumption

on the shape of deflection of the film,^[41] which can lead to appreciable errors in calculation.

The above-described methods (except for the microhardness method) have been used for testing films having $h \cong 0.01-0.3 \mu$.

1.5. Tension Method

Testing films in tension differs considerably from analogous tests on massive materials. The difficulties of studying films are aggravated by the fact that the problems of mechanical strength of foils obtained by rolling massive materials are still very little studied.^[64] It is important to note that the surface-volume ratio of the specimen is sharply increased in films, as compared with massive specimens. Hence, the role of surface defects, which act as stress sources, is increased. Here their influence on the strength and plasticity increases with decreasing h . The edges of the specimen film play an especially marked role, acting as the sources of the dislocations that arise in deformation.^[11] The experiments of Orowan^[10] on tension in cut mica plates 10μ thick are highly indicative. Using grips that freed the edges of the mica from stresses (the grips were somewhat narrower than the specimen), Orowan obtained an almost tenfold increase in strength, from 35 to 320 kg/mm².

The films to be tested are usually cut in the form of rectangular strips. Using special masks^[22] makes it possible to prepare films of a required shape with undamaged edges. The role of the masks becomes more important when testing brittle films, in which surface defects exert an especially large influence.^[37]

Edge effects are enhanced with decreasing h , and wrinkles arise from inhomogeneous application of the load to the film, etc. This results in considerable divergence of the strength values.^[15,16] In this regard, we should consider the tube ("scroll") method used in testing films having $h = 0.07-0.4 \mu$.^[26,29] The condensed films were deposited on a substrate over a lower layer of collodion. When the latter was dissolved, the residual macrostresses rolled the films up into cylindrical tubes, or "scrolls" (see Sec. 2.5). Using specimens of this form made it possible to eliminate the drawbacks mentioned above (see also^[34]).

In tension tests, the films are attached to the grips of a micromachine. One of the grips is fixed, while the other is moved by the forces of a weight,^[15] an electromagnetic field,^[18,26,28,29] or the elastic pull of a wire.^[15,17] The displacement of the movable grip, e.g., measured optically, is proportional to the total elongation. We note that, as a rule, films have been tested in micromachines designed to study the strength of whiskers. This method has been used for films in the h range from several microns down to 0.06μ . An original method has been proposed^[31,38] for even thinner films ($0.015-0.05 \mu$): stretching on a water surface. Here the overall friction in the instrument and surface tension forces were small in comparison with the breaking load. We note that one can't eliminate the influence of "edge effects" even in this case.

Thicker films have been tested on refined micromachines^[22,27,33] normally used to study the strength of polymer and plastic films, and also on a beam-balance

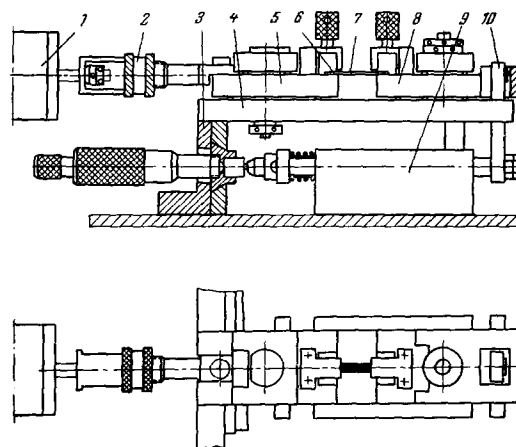


FIG. 2. Diagram of a micromachine for testing films with automatic recording of the stress-strain diagram: 1—inductive transducer, 2—screw coupling, 3—wedge assembly, 4—base, 5, 8—movable carriages, 6—grip, 7—film specimen, 9—crossbar drive, 10—crossbar.

type micromachine with automatic loading^[34] similar to a machine for testing alloy whiskers.^[9] The strain was measured with a dial gauge, and the stress-strain diagram determined point-by-point.

The fundamental defects of these designs include the lack of automatic recording of the stress-strain diagram, and also their very low rigidity. The latter characteristic becomes especially important because of the low absolute deformation of films up to the failure point (for details, see^[8]). Along this line, we have built a rigid micromachine for testing films with automatic recording. Figure 2 is a drawing of it. The loading device consists of an electric motor with a reducing gear, attached to a wedge. The latter makes it possible to regulate the rate of displacement of the movable grip over the range 0.002–1 mm/min, depending on the inclination angle of the wedge, which is regulated with a micrometer. A supporting rod is in constant contact with the wedge, and imparts the stress to the grips of the machine through a cross bar. The grips are mounted on carriages moving on ball bearings lying in grooves in the motionless base. The stress is recorded by an inductive differential transducer having a beryllium bronze disk as its force element. The range of measurable loads amounts to 0.05–5 kg. This permits one to test films (and foils) over a large range of h . The machine is distinguished by very great rigidity: about 3×10^{-5} mm/g. The stress-strain diagram is recorded by a recording potentiometer in coordinates P and Δl (P is the load, and Δl is the absolute deformation, which is equal to Vt , where V is the rate of displacement of the movable grip and t is the time of testing). Tests at low velocities on the rigid micromachine have made it possible to get valuable information on neck formation, the intrinsic strength, and the limiting plasticity of films (see Sec. 3.1).

Analysis of studies on the mechanical properties of films shows that most of them have been done by the bulging and tension methods, which give the fullest information on the stress-strain diagram. Here tension is the generally accepted method of testing. It permits one to compare the results for films and for massive

Table I. "Bulging" method

Metal	Temperature of substrate $T_s, ^\circ\text{C}$	Thickness h, μ	Ultimate strength, $\sigma_u, \text{kg/mm}^2$	Variation in σ_u with decreasing h	Reference	σ_u of the ordinary metals [66, 68]	Remark
Ag	Near room temperature	0.2–0.02	20–60	Increase	13	14	Single crystal films
Au	"	0.2–0.02	12–58	"	13	12–13	
Au	375°	0.3–0.1	12–25	"	19	12–13	
Ag	Near room temperature	0.06–0.01	65–120	"		14	
Al	"	0.07–0.04	50–120	"		6	
Cu	"	0.07–0.02	110–165	"	30	20	
Ge	"	0.08–0.04	50–120	"		7	
Ni	300°	0.07–0.02	80–110	"		33	
Fe	300°	0.08–0.02	About 90	Invariant		18–25	
Ni	220°	0.26–0.02	138–90	Decrease		33	
Fe	Not stated	0.2–0.02	92–74	"	36	18–25	

materials, e.g., foils. The difficulties of testing for small h have fostered the development of the bulging method, which has a number of advantages (absence of edge effects, homogeneous stress application, etc. As we shall see below, the two methods give a considerable scatter in the strength values. It is hard to distinguish here the effect of the methods of testing and preparation.

The above-described difficulties have led to the development of direct methods of measuring mechanical characteristics: determining elastic deformation from the variation in interplanar spacings of films having $h \cong 0.01$ – 0.1μ , directly stressed in an electron microscope^[58] or electron-diffraction apparatus.^[30, 61] We note that one can also perform such measurements on thicker films by using X-ray diffraction.^[63]

2. STRENGTH OF CONDENSED FILMS

2.1. Effect of Thickness

Most studies on the mechanical properties of condensates have been concerned with thin films of thickness $h \leq 1 \mu$. There are a number of reasons for interest in studies in this h range. First of all, the very first tests of thin films revealed anomalously high strengths. This attracted attention immediately to these objects. Furthermore, problems of interaction of dislocations with the free surface are of great interest in the modern theory of hardening. Here the role of the surface increases greatly with decreasing dimensions of the objects under study. Finally, films having $h \leq 1 \mu$ are very widely used in modern technology (radioelectronics, computing technology, etc.).

The existing information on the relation between strength and thickness of films is very contradictory. Even the initial studies of Beams and his associates,^[12] which treated electroplated Ag and Au films by the rotor method, showed an appreciable increase in strength for $h < 0.2 \mu$.

Most of the results on the effect of film thickness have been obtained by the curvature and tension methods.

a) Curvature method (bulging). The summary Table I gives the experimental results obtained in testing films (mainly polycrystalline). The highest strengths are indicated here (the scatter was as high as 100%).

We note the following upon analyzing the studies by the curvature method. Most of the authors think that the

strength of films increases with decreasing h . Here the highest strengths far exceed the corresponding characteristics of ordinary metals of metallurgical production. However, the attained strengths differ considerably in magnitude. For example, the highest values of σ_u for Ag films having $h \cong 0.02 \mu$ prepared under similar conditions amounted to 50 – 60 kg/mm^2 ^[13] and 90 kg/mm^2 ^[30]. In addition, tests of Ni films showed a directly opposite thickness effect (cf. ^[30] and ^[36], Fig. 3). The cited discrepancies indicated first of all that the purity of the metal and the conditions of preparation and testing considerably affect the obtained results. Furthermore, continuity breaks can appear in very thin films having $h \leq 0.02$ – 0.03μ , and can lead to an anomalous relation of σ_u to h (see, e.g. ^[36]). Surface tension can contribute substantially in testing very thin films.^[30] Finally, according to the data of ^[41], calculations in tests by the bulging method can involve considerable errors, since the film does not deform into a sphere, as is erroneously assumed.

b) Tension method. Information on the mechanical properties of films has been obtained in tension tests over the very wide thickness range from 0.06 to 75μ (Table II). Table II gives the highest strength values. As we see, the films are several times as strong as the annealed massive metals (or even the cold-worked metals; see Fig. 4).

We began a systematic study of the mechanical properties of films in 1960. We performed first studies on specimens several tens of microns thick. The choice

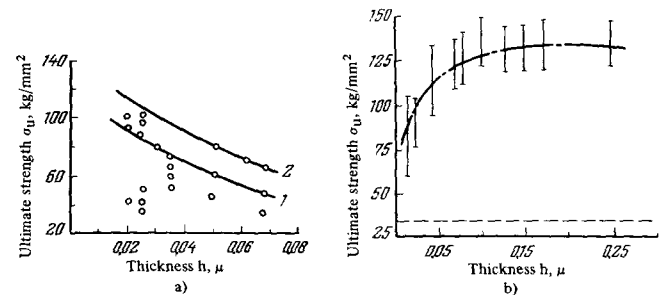


FIG. 3. Strength of Ni films as a function of the thickness ("bulging method). a) curves for the mean (1) and maximum (2) strength;^[30] b) curve for the mean strength. The vertical lines indicate the scatter in σ_u , and the dotted line indicates the strength of ordinary massive Ni.^[36]

Table II.

Metal	$T_S, ^\circ\text{C}$	h, μ	$\sigma_u, \text{kg/mm}^2$	Variation in σ_u with decreasing h	Reference	σ_u of the ordinary metals [66, 68]	Remark
Au	About 100 300°	7—0,7	37—79	Invariant	15	12—13	Mono- and polycrystalline films
Au	Not stated	12,5—0,5	23—51	Invariant	16	12—13	
Au	< 150, 300°	1,5—0,06	20—48	Invariant	18	12—13	» »
Au	About 40° 300°	5—0,2	20—35	Invariant	28	12—13	» »
Ni	About 50°	0,4—0,07	160—225	Increase	26, 29	33	See Fig. 4
Cu	Not stated	4,6—1,7	45—90	Increase	27	20	
Ag	Near room temperature	0,05 0,015	54 69	Increase	31	14	Tension on a water surface
Ag	100—140°	50—1	20—50	Increase	Our data	14	See Fig. 6
Cu	120—160°	75—0,5	50—90	Increase	34	20	See Fig. 5
Ni	240—270°	30—3	100—130	Invariant	Our data	33	
Au	110—150°	20—10	30—44	Invariant	32	12—13	
Al	180—220°	50—25	14—22	Invariant	24	6	
Fe	400—420°	30—10	66—74	Invariant	33	18—25	

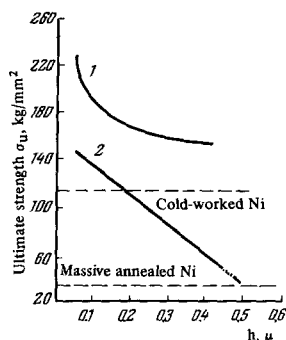


FIG. 4. Strength of Ni films as a function of the thickness (in tension). [29] 1—freshly condensed, 2—annealed films.

of h values was dictated by a number of technical considerations: $h \geq 10 \mu$, it becomes possible to measure the microhardness (see Sec. 1.2), and development of methods of mechanical testing and diffractometric study of the substructure, etc., are facilitated. We subsequently undertook a complex study of the mechanical properties and substructure of considerably thinner films (Table II; [24, 34]).

Analysis of the data obtained by the tension method reveals not only contradiction in the information on the effect of h , but also a wide spread in the attained strengths. Besides the above-mentioned role of the conditions of preparation (see also Sec. 2.3), specific features of the mechanical tests of thin films can also manifest themselves, especially "edge effects" (see

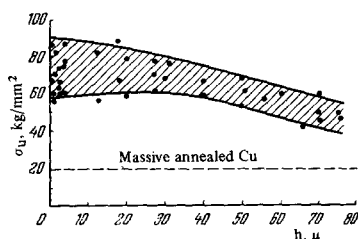


FIG. 5

FIG. 5. Ultimate strength of Cu films of different thicknesses [34] $H = 200\text{--}250 \text{ kg/mm}^2$, $T_S = 120\text{--}160^\circ\text{C}$.

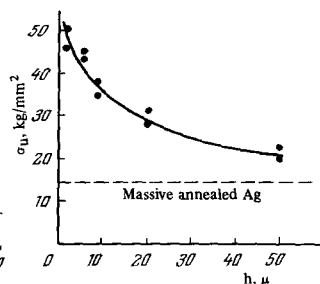


FIG. 6

FIG. 6. Ultimate strength of Ag films of different thicknesses.

Sec. 1.5). The role of the latter increases with decreasing h . The scroll method is worth considering in this regard for thin specimens ($h \leq 1 \mu$). [26, 29] It involves less buckling under tension and reduced influence of the cited effects. Indeed, inhomogeneous residual stresses in the scroll film may exert a certain influence in this case. [40]

2.2. Effect of Substrate Temperature and Rate of Condensation

One of the important parameters governing the mechanical properties of condensates is the temperature T_S of the substrate during condensation. The effect of T_S has been studied in detail in [24, 32, 33, 42]. As an example, Fig. 7 gives the results of tests on Ni films about 20μ thick. As we see, raising T_S from 140 to 300°C lowers σ_u by a factor of two.

All the metals that we have studied show analogous patterns.

The information on the effect of T_S on the strength of thinner films is very limited. Such data are given only in [36], where they found a relation between the strength of Ni films 0.07μ thick tested by the bulging method and the parameter T_S (Fig. 8). These data resemble the results of tension tests on Ni films two orders of magnitude thicker (see Fig. 7).

Annealing also leads to considerable weakening. This happens in different ways in thin and thick films. For

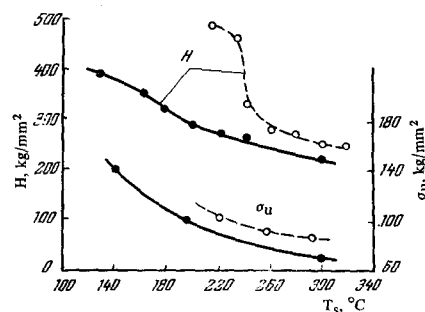


FIG. 7. The microhardness H and the ultimate strength σ_u of Ni films as functions of T_S ($h = 20 \pm 5 \mu$). \circ —crucible condensates, \bullet —crucible free condensates.

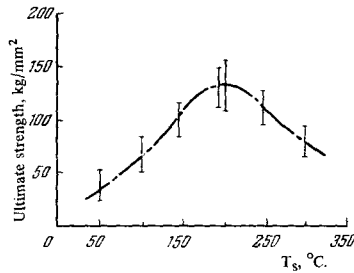


FIG. 8. Effect of the substrate temperature T_s on the strength of Ni films having $h = 0.07 \mu$.^[36]

example, according to our data, annealing high-strength Cu films in vacuo at 300°C reduces the strength by a factor of two ($\sigma_u = 32\text{--}36 \text{ kg/mm}^2$). Here the thickness shows no appreciable effect over the range $h = 5\text{--}50 \mu$. According to the data of ^[29], annealing Ni films 0.07–0.5 μ thick at 650–700°C gives an almost twofold decrease in σ_u . However, the strength-thickness relation remains the same throughout (see Fig. 4). When $h > 0.4\text{--}0.5 \mu$, the strength does not depend on the thickness, and it approaches the values of σ_u for massive annealed Ni.

On the other hand, measurements by the bulging method^[38] have shown that the strength of Au and Ge films at constant thickness (0.025–0.035 μ) practically does not vary as the annealing temperature is raised to 400–500°C.

The rate of condensation ω_c is among the most poorly studied parameters. The existing information on the effect of ω_c on mechanical properties deals with thick films.^[33,34]

For example, when ω_c is reduced by a factor of 4–5 (from 1.5–2 to 0.3–0.5 μ/min) the strength of copper condensates is reduced by about 15%. Here, the smaller ω_c is, the more the strength depends on the thickness.^[34] As was shown in ^[24], under certain conditions of preparation, the strength of films practically does not depend on h even over the range 15–150 μ .

2.3. Effect of Degree of Vacuum and Method of Evaporation

As we know, the residual gases are absorbed by the condensed films during the process of evaporation and condensation of metals in vacuo. This is governed by the pressure of gases, and also by chemical reaction with the film being prepared. This absorption decreases with higher vacuum and increasing rate of condensation.

The information on the effect of the degree of vacuum on the mechanical properties of films is very limited. A study of vacuum distillates of Cr^[45] condensed at different degrees of vacuum has shown that the microhardness falls with higher vacuum (Table III).

In the opinion of the authors of ^[45], this phenomenon is due to the alloying effect of the residual gases.

Table III^[45]

Pressure, Torr	10^{-4}	10^{-5}	10^{-6}	10^{-7}
Microhardness, kg/mm ²	200	180	140	120

It was noted in ^[27] that poorer vacuum, over the range $10^{-5}\text{--}10^{-4}$ Torr, reduces the tensile strength of Cu films.

Experiments of recent years have shown that the method of preparation exerts an especially great influence on the properties of condensates. In preparing films, one usually uses heaters in the form of filaments or foils of refractory metals (Ta, Mo, W). Here the metal to be evaporated is either put directly on the heater, or in a crucible made of heat-resistant material (Al₂O₃, BeO, etc.).^[46] These methods are called the crucible methods, in distinction from the crucible-free methods, in which the metal to be evaporated does not directly contact a heater or crucible, e.g., evaporation by the methods of electronic bombardment or high-frequency heating of a metal in the suspended state.^[48,51,55] One of the fundamental requirements on the heater material is that it should not react with the metal being evaporated. As recent experiments have shown,^[49,50,54,55] in a number of cases one has to reexamine the known recommendations^[46] on choice of heater material.

The greatest effect was obtained in measuring the microhardness of Al films, which show very high chemical activity. Crucibles made of Al₂O₃ and BeO,^[54] a tungsten heater,^[33] and the crucible-free method^[55] have been used for evaporation. Table IV gives a selection of data from measurements on films having $h = 20\text{--}50 \mu$ condensed at $T_s = 200^\circ$.

Table IV

Evaporation method (reference)	54		33	45
	Al ₂ O ₃	BeO		
Microhardness, kg/mm ²	330	200	90	16

As we see, Al condensates alloyed with aluminum oxides by reaction of the metal with the refractory are hardest.^[55] This interaction is also manifested when one uses tungsten heaters,^[33] and especially BeO crucibles.^[54] This is not in accord with the known literature data.^[46,55]

Among the new results is also the discovered reaction^[55] of copper being evaporated with an Al₂O₃ crucible. Here the microhardness of crucible-free Cu condensates was less by a factor of 1.5–2 at comparable T_s . The processes of this reaction are complex in nature, and haven't yet been studied sufficiently. For example, it has been shown by the radioactive-isotope method^[50] that when permalloy is evaporated from a tungsten coil, the films are contaminated by the evaporator metal (about 0.01%). The contamination is reduced with repeated experiments and also with higher vacuum.

We have studied the effect of the evaporation method on the mechanical properties of Ni films 3–30 μ thick. The condensates were prepared by two methods: from aluminum crucibles in a 5×10^{-5} Torr vacuum, and also by electron bombardment of a crucible-free rod of metal of the same purity (99.99%) in a 5×10^{-7} Torr vacuum. The rate of condensation $\omega_c = 0.1\text{--}0.2 \mu/\text{min}$. Figure 7 shows the results. As we see, adopting crucible-free

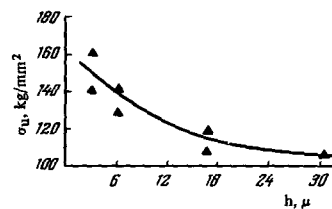


FIG. 9. Strength of crucible-free Ni films as a function of the thickness.

evaporation lowers σ_u and especially H . However, crucible-free films can be prepared at lower values of T_S (see Sec. 2.5). This makes it possible to attain a high strength, of about 140 kg/mm^2 . In contrast to crucible condensates, crucible-free condensates show an explicit dependence of the strength on h (Fig. 9). Thus, the values of σ_u rise from 110 to 160 kg/mm^2 as h decreases from 30 to 4μ (cf. data of Sec. 2.1 for crucible films). The scatter in σ_u due to increase in plasticity is also appreciably reduced.

Thus, under comparable conditions of condensation, Ni films alloyed with products of reaction between the crucible and the molten metal are stronger than crucible-free films. However, if one lowers T_S and reduces h , one can prepare stronger and more plastic crucible-free films, for which $\sigma_u \approx 160 \text{ kg/mm}^2$. We should note that this value of σ_u agrees well with the data^[29] for Ni films having $h \approx 0.4 \mu$.

We have also conducted analogous studies on permalloy condensates (80%Ni–20%Fe) prepared under the conditions described above. Owing to the great brittleness of crucible films, the tension tests were performed only for $T_S > 390^\circ\text{C}$. As we see (Fig. 10), the strength of crucible-free films at comparable T_S hardly varied, in spite of the considerable decline in H . The reason consists in the great brittleness of crucible films, which reduces the value of σ_u . The plasticity is greater for crucible-free films, and this decreases the spread in σ_u to 15%.

The highest strength realized in tests of crucible-free permalloy films attained the extremely high values of 220 kg/mm^2 . This exceeds the strength of the massive alloys by a factor of 3–4.^[67]

2.4. Alloy Films

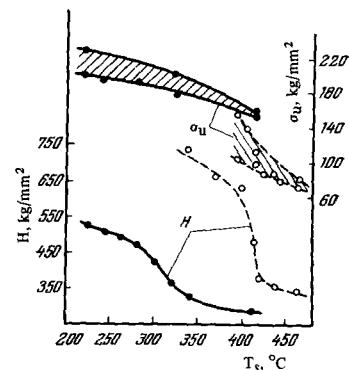
The information on strength of alloy films is very limited. The first results^[25] were obtained on condensates of chromium bronze having $h = 2\text{--}30 \mu$. The method we developed permitted us to prepare alloys of constant composition over the T_S range from 140° to 360°C . We showed in^[25] and in later experiments that the strength of the films is practically independent of h , and declines with increasing T_S . Table V gives the fundamental results. The table indicates that alloying

Table V

Material	H_{max} , kg/mm ²	σ_u , max kg/mm ²
Bronze films (0.3–0.4 % Cr)	270	70
Bronze films (0.8–2 % Cr)	420	420
Massive bronze (0.7–1.2 % Cr) after aging ^[69]	150	55

FIG. 10. H and σ_u of permalloy films as functions of T_S .

○—crucible condensates, ●—crucible free condensates.



of copper films with chromium strengthens them considerably, the alloy condensates being twice as strong as massive aged chromium bronze. A very important advantage of alloys, as compared with films of metals, is that the high-strength state is stabilized at elevated temperatures.

In^[36] they measured the strength of permalloy films by the bulging method over an h range of $0.02\text{--}0.2 \mu$. The highest values of σ_u amounted to $70\text{--}120 \text{ kg/mm}^2$. The authors ascribed a certain decline in σ_u with decreasing h to inhomogeneity of the films in thickness, which was especially marked in the thinnest films.

Permalloy films, which are widely used in modern microelectronics, were also the object of study in^[52]. Here they studied the magnetic as well as the mechanical properties. Deformation was carried out both by bending the metallic substrate bearing an unstripped film and by ordinary tension. The strength of the films at $T_S = 200\text{--}270^\circ$ amounted to 180 kg/mm^2 at $h = 0.1\text{--}0.3 \mu$, and 140 kg/mm^2 at $h = 1.5\text{--}3 \mu$, as compared with $53\text{--}63 \text{ kg/mm}^2$ for the massive alloy.^[52]

They attained even higher strengths in permalloy films prepared under "clean" conditions by the method of electron-beam heating in a 5×10^{-7} Torr vacuum (see above, Fig. 10). The greatest strength of films having $h = 15 \mu$, condensed at T_S about 230°C , was 220 kg/mm^2 . This is 3–4 times the strength of the massive alloys.^[52]

Thus, alloy films are much stronger than the massive alloys of metallurgical production. As is the case with the metals, contradictory information has been obtained here on the highest values of σ_u and on the conditions for attaining them. Apparently this is due to the methods of preparation and testing. This is confirmed by the results of the three studies discussed above on permalloy films of similar composition (80–85% Ni, 20–15% Fe).

2.5. Internal Macro stresses in Films

In presenting the experimental data on mechanical properties of films, we must mention that they contain appreciable internal macro stresses. Without spending time on these problems, which have been discussed in detail in the review,^[56] we shall only note that the stresses that arise can appreciably exceed in size the yield point of the massive material. For example, the tensile stresses in films $0.1\text{--}0.3 \mu$ thick condensed at T_S near room temperature amounts to $10\text{--}20 \text{ kg/mm}^2$ for Cu, Ag, and Au, and about 100 kg/mm^2 for Ni, Fe, and permalloy.^[56] This gives evidence of the high

strength of films, and indicates that one must take into account the effect of stresses on the mechanical properties of condensates not stripped from their substrates.

The increase in tensile stresses with decreasing T_S leads to spontaneous failure of films. In line with this, there is a T_S below which one can't prepare undamaged films not stripped from their substrate. The value of T_S^* for each metal depends on h and on the conditions of preparation (these problems are discussed in [57] for Be films). For example, T_S^* drops from 200 to 100–130°C in going from crucible to crucible-free condensates of nickel (see Fig. 7). This indicates that the tensile stresses are lowered in the crucible-free films.

2.6. Fatigue Resistance of Condensed Films

Insofar as we know, there is no information in the literature on this very important mechanical characteristic of films.

We present below the first results that we have obtained in fatigue tests of vacuum condensates by alternating beam bending. The objects of study were Ni films having $h = 20\text{--}30\ \mu$, loaded at a frequency of 1300 cycles/min. The testing base was $N = 10^6$ cycles. Figure 11 gives some typical fatigue curves.

As we see, the endurance curves show a sharp break indicating that the films possess a sharply marked fatigue limit σ_f . The values of σ_f were 42 kg/mm² ($T_S = 260^\circ$) and 28 kg/mm² ($T_S = 400^\circ$). They considerably exceed the corresponding characteristics of massive annealed (18 kg/mm²) and even of cold-worked Ni (28 kg/mm²), the static strengths of which are $\sigma_u = 50$ and 117 kg/mm². [100] Just like the massive metals, [8] films obey the relation $\sigma_f \cong 0.35\text{--}0.4\ \sigma_u$.

As we know, the scale factor substantially affects the fatigue strength of materials: σ_f increases with decreasing specimen dimensions. [8] In order to elucidate the effect of this factor, we tested annealed Ni foils of comparable thickness (20–30 μ) obtained by rolling massive material and then annealing it. As we see (see Fig. 11), the σ_f of the films considerably exceeds that of the foils, for which the fatigue strength is about 13 kg/mm² ($\sigma_u = 30\ \text{kg/mm}^2$).

Thus, the very high fatigue strength of condensed films is not due to the scale factor, but to their great static strength.

3. DEFORMATION AND FAILURE OF FILMS

3.1. Tensile Stress-strain Diagrams

The fullest information on the strain behavior of films has been obtained with stress-strain diagrams. Let us examine the fundamental experimental results.

a) A characteristic feature of the stress-strain diagrams of high-strength films is their considerable strengthening,* whereby they withstand stresses far exceeding the ultimate strength of a massive cold-worked foil (Fig. 12).

The parameter h greatly influences the stress-strain diagram (Fig. 13). The greater h is, the lower the stress at which appreciable plastic deformation sets in, and the

*We note that considerable strengthening is also observed when one tests massive films for resistance to compression. [37]

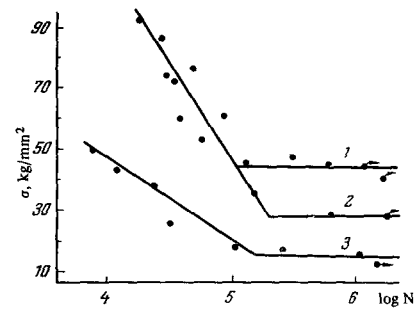


FIG. 11. Fatigue curves of films (1, 2) and foils (3). $T_S = 260^\circ$ (1) and 400°C (2); $h = 20\text{--}30\ \mu$.

lower the yield point $\sigma_{0.2}$. [34] Increase in T_S has an analogous effect. [23, 24, 32, 33]

Mono- and polycrystalline films show similar stress-strain curves, but the former have no region of easy slip. [15, 28, 35]

b) The stress-strain diagrams show an "inelastic effect" even under small loads: [15, 18, 20] the lines for unloading and reloading have different slopes (Fig. 14, curve marked with arrows).

Maintaining the specimen under a constant load below the yield point gives rise to plastic deformation (Fig. 15). Mono- and polycrystalline films show this type of creep at room temperature over a wide range of thicknesses. [15, 18, 23, 24, 27] It is fundamentally due to structural features, [24] rather than to the specific details of the mechanical testing of these objects. [15]

c) Estimates of the elastic modulus E of films from the slope of the unloading curves, [15, 18, 24, 29, 33] and also from x-ray tensometric data [62] gives values close to the tabulated data for the massive materials. Elevated E values found in testing very thin films by the bulging method [19, 30, 31] are explained by an initial stressed state in these objects. [30, 31]

d) Films are characterized by a considerable elastic deformation ϵ_e , which amounts to as much as about 0.6–0.8% for $h < 0.1\ \mu$. [26] The value of ϵ_e falls with increas-

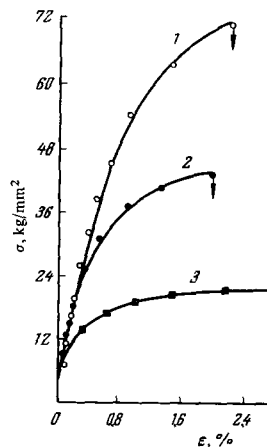


FIG. 12

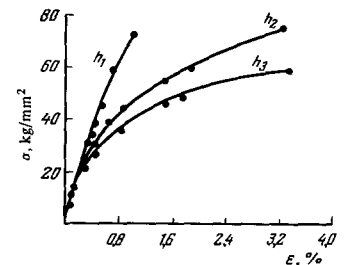


FIG. 13

FIG. 12. Tensile stress-strain diagrams of a condensed film (1), a cold-worked foil (2), and an annealed foil (3) of Cu. $H = 250$ (1), 130 (2), and 50 kg/mm² (3); $h \cong 20\ \mu$.

FIG. 13. Tensile stress-strain diagram of high-strength Cu films of different thicknesses. [34]

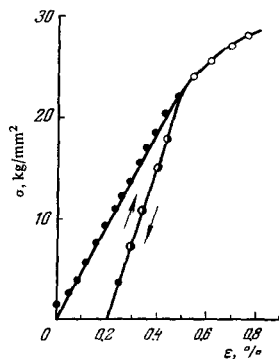


FIG. 14

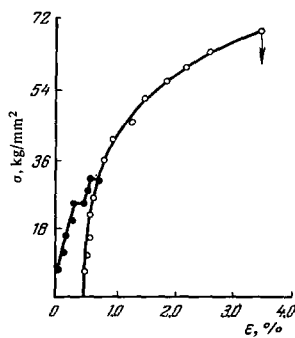


FIG. 15

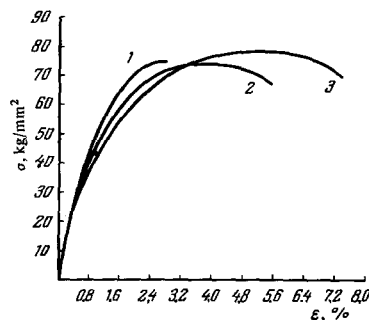
FIG. 16. Tensile stress-strain diagram of high-strength Cu films on a rigid micromachine. $h = 17$ (1), 30 (2), and 60μ (3).

FIG. 14. Tensile stress-strain diagram of a monocrystalline Au film ($h = 1.7\mu$).^[15]

FIG. 15. Tensile stress-strain diagram of Cu films ($h = 22\mu$) showing creep.^[24] ●—loading; ○—unloading and reloading.

ing h , but remains at a very high level. For example, ϵ_e is as much as 0.2–0.3% for Au films at $h = 0.5$ – 3μ ,^[15,16] and about 0.2% for Ni films at $h \approx 20\mu$.^[32] The method of evaporation affects ϵ_e considerably. For example, ϵ_e is less than 0.1% for crucible-free Ni films ($h = 16\mu$).

Alloy films show high elasticity. Thus, $\epsilon_e \approx 0.3\%$ for the films of permalloy and chromium bronze having h of about 20μ that we have tested. For comparison we note that ϵ_e of high-strength alloy steel after thermo-mechanical treatment amounts to about 0.2%.^[103]

Just as the tensile method does, the bulging method shows very high values of ϵ_e . For example, at $h = 0.02$ – 0.2μ , the highest values of ϵ_e amount to 0.5–0.6%.^[30,38] These measurements refer to the macroscopic deformation, which arises not only from the structure and properties of the crystallites themselves, but also from their interaction, to the boundary structure, etc. It is of interest to determine the limiting elastic deformation of the crystal lattice, which depends on the interatomic interaction forces and the degree of perfection of the crystal structure. The first measurements of this type to measure variation of interplanar spacings were performed on monocrystalline Au films deformed within an electron microscope.^[15,58,59] The values of ϵ_e for $h = 0.05\mu$ were as much as 1%. However, these results may be affected by the low accuracy of measurement of interplanar spacings from uncalibrated single-crystal electron-diffraction patterns. Subsequent measurements have been performed on polycrystalline Al and Ag films deformed in an electron-diffraction apparatus, taken simultaneously with a standard.^[60,61] The highest values of ϵ_e amounted to 0.4–0.5%. Analogous results have been obtained in electron-diffraction measurements of ϵ_e in thin films of Al, Ni, Ge, and Fe.^[30]

X-ray tensometric studies have shown^[62] that the highly elastic properties of the crystallites are maintained as we increase h of the films by two orders of magnitude. Thus, the values of ϵ_e for condensates of Cu and Ni for h about 20μ were as much as 0.2 and 0.4%, respectively.

Thus, the elastic deformation of thin films is an order of magnitude higher than in massive specimens. Appropriate stress calculations using the tabulated

values of E give results agreeing with the above-discussed data from mechanical tests.

e) Failure of the films is preceded by plastic deformation ϵ_p , along with the elastic deformation. The former increases as we increase h ,^{*}^[24,30,34] or raise T_s ,^[23,24] or when we change from crucible to crucible-free evaporation. The existing data show a large spread, since the testing method and especially the rigidity of the micromachines (see Sec. 1.5) have a considerable effect on ϵ_p , along with the effects of purity of the films and the conditions of preparation. The less the flexibility of the machines, the more accurately one can measure the overall deformation ϵ up to the breaking point.^[8,28]

Let us present some data on the effect of h and the method of evaporation on the deformation of films. For example, the tests that we have made on high-strength Cu films on a rigid micromachine have shown that the values of ϵ_p increase from 0.8 to 6% as we increase h from 1 to 50μ . For crucible and crucible-free Ni films ($h \approx 16\mu$, $\sigma_u \approx 100$ – 120 kg/mm²), the values of ϵ_p amount to about 0.7 and 1.4%, respectively.

f) They were not able to demonstrate necking in most of the studies on mechanical properties of films performed on compliant machines. Only the tests in^[28] on a rigid machine made it possible to reveal necking in the deformation of monocrystalline Au films several microns thick. We have observed similar effects in polycrystalline Cu and Ni films. We performed the tests on the machine described in Sec. 1.5. As we see (Fig. 16), necking is manifested more clearly with increasing h . Here it was possible to estimate for the first time the true ultimate strength S_u . For Cu and Ni condensates, it amounts to 110–140 and 170–200 kg/mm², respectively. These S_u values are close to the ultimate strength realized in very thin Cu^[30] and Ni^[29] films.

3.2. Features of Deformation and Failure of Films

Information on the features of plastic deformation of films is of interest because these problems have been studied only for $h > 100\mu$, even for massive foils.^[64]

We have conducted a series of experiments to study these problems. A grid of lines was ruled on the surface of the films at intervals from 50 to 500μ . This made it

*We note that the parameter h appreciably affects ϵ_p for massive foils.^[97–99]

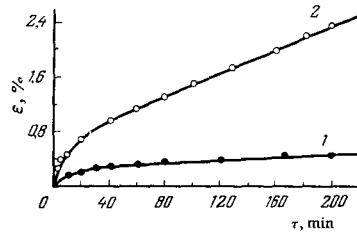


FIG. 17. Creep curves of Cu films ($T_s = 120^\circ$, $h = 30\mu$). $\sigma = 25$ (1) and 42 kg/mm^2 (2).

possible to study the distribution of uniform (ϵ_{un}) and concentrated (ϵ_{con}) deformation along the specimen. As it turned out, $\epsilon_{\text{un}} = 8\text{--}12\%$, and $\epsilon_{\text{con}} = 70\text{--}90\%$ for annealed Cu films 50μ thick. These are smaller by a factor of two than the corresponding values for cylindrical specimens.^[64] In contrast to cylindrical specimens, the concentrated deformation of films is localized in a very narrow region along the failure crack. Here the dimensions of the localization zone are very near the size of h . Thus, the overall plasticity of films is fundamentally determined by ϵ_{un} , and the thinner the film is, the narrower the localization zone, and the greater the role played by uniform deformation.

When one studies the mechanical properties of films, one usually notes their very low plasticity. However, we must take into account the fact that a considerable part of ϵ is made up of the component ϵ_{un} , which differs little from ϵ_{un} for high-strength massive materials. For example, for high-strength Cu films ($\sigma_u = 70 \text{ kg/mm}^2$, 20μ thick, ϵ_{un} is as low as 2.5%. On the other hand, cold worked steel having a similar σ_u shows $\epsilon = 11\%$, while $\epsilon_{\text{un}} = 3\%$.^[65] Steel subjected to thermomechanical treatment shows the same ϵ_{un} values.

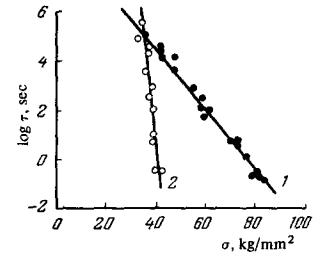
As is the case with foils, the specific features of deformation of films make possible failure that is plastic in nature, but brittle in external appearance.^[64] Indeed, when the reserve of ϵ_{un} has been exhausted, further elongation is practically impossible, owing to the sharp localization of the deformation. Furthermore, the specimen may contain a high potential energy of elastic deformation. Consequently, failure occurs at a very high velocity. Here, the thinner the film is, the smaller the zone of localized deformation, and hence, the greater the simulation of brittle failure, which is characterized by absence of localization along the crack.

Analogous conclusions have been drawn in studying the dislocation mechanism of failure of monocrystalline films in the transmission electron microscope.^[15, 58, 59] When the elastic deformation rises to $\sim 1\%$, the film breaks at very high velocity. The failure amounts to an instantaneous plastic deformation caused by very marked thinning of the specimen and by the high stresses just before the moment of occurrence of plastic flow. The latter involves passage of dislocations through the film by a transverse slip mechanism, and also creation of new dislocation sources. The described mechanism also holds for monocrystalline electroplated films.^[15]

3.3. Creep and Endurance of Films

As we mentioned above, one observes an appreciable creep in films if one maintains them under a stress

FIG. 18. Time-dependence of the strength of Cu films. 1—freshly condensed ($T_s \cong 120^\circ$) and 2—annealed (250°C) films.



$\sigma < \sigma_{0,2}$ at room temperature. We present below our results obtained in the course of the studies^[24, 62] on Cu films tested on a micromachine having a special apparatus for maintaining constant stress and recording the strain (see, e.g.^[106]).

Figure 17 shows typical creep curves of high-strength Cu condensates. The rate of creep continually declines with time (stage of unestablished creep), and then the stage of steady-state creep sets in with a constant velocity v . Here v increases sharply with increasing applied stress. Cu films obey well a linear relation of $\log v$ to the stress as v varies by four orders of magnitude (see also^[62]). According to the studies of S. N. Zhurkov and his associates,^[101, 102]

$$v = v_0 \exp\left(-\frac{Q_0 - \gamma\sigma}{RT}\right), \quad (1a)$$

$$\tau = \tau_0 \exp\left(\frac{U_0 - \gamma\sigma}{RT}\right), \quad (1b)$$

where τ is the time until failure, v_0 , τ_0 , Q_0 , and U_0 are constants, and γ is a structurally-sensitive strength criterion. They preferentially used the relation (1b) in^[101, 102] in order to increase the accuracy of measurements by using a wide range of τ values.

Figure 18 shows the results of the study of endurance of films. As we see, a linear relation of $\log \tau$ to the applied stress holds as τ varies from 10^{-1} to 10^5 sec. If we assume that relation (1b) is applicable to vacuum condensates, it turns out that $\gamma = 0.18 \text{ kcal}\cdot\text{mm}^2/\text{mole}\cdot\text{kg}$. This is an order of magnitude smaller than γ for massive copper.^[102] On the other hand, $\gamma \sim 1/\alpha$, where α is the mean disorientation angle of the blocks in the polycrystal. Thus, the value of α in films can exceed α for massive metals by an order of magnitude. This is confirmed by the results of direct measurements using the electron-diffraction microbeam method.^[76]

Equation (1b) implies that $U = U_0 - \gamma\sigma = RT \ln(\tau/\tau_0)$. If we assume that $\tau_0 \cong 10^{-13}$ sec, we can determine the relation $U(\sigma)$, and estimate by extrapolation U_0 , which is the activation energy of the failure process at zero stress.^[101]

Calculations for high-strength copper films give $U_0 \cong 30 \text{ kcal/mole}$ (the parameters U_0 and Q_0 are similar in size). Annealing the films at 250°C does not change the linear nature of the relation (Fig. 18), but considerably increases U_0 , to 60 kcal/mole .

According to the kinetic conception of failure,^[101] the values of the parameter U_0 should be close to the energy of sublimation of the metal, i.e., the binding energy of the atoms in the crystal structure, which is 82 kcal/mole for copper. According to the most recent information,^[107] the anomalous values of U_0 observed in massive metals in a non-equilibrium state are illusory. The given deviations are due merely to instability of the

structure, i.e., inconstancy of the parameter γ . Instability is ascertained by special treatment of the results of measurements at different testing temperatures.^[107] Such a method is inapplicable to objects in an extreme non-equilibrium state, i.e., condensed films (see Fig. 18). We can only note that prolonged annealing at 100°C (three hours) does not affect the obtained relation nor the value of U_0 . Furthermore, prolonged loading of the films (six days under 32 kg/mm²) does not affect their strength appreciably.

Structural studies of the objects during testing^[107] are required for a correct explanation of the observed anomalies. We note in conclusion that one can make the following hypothetical explanation of the cited deviations, owing to the considerable substructural differences between films and massive non-equilibrium metals. Since they occur in large numbers in films, crystal lattice defects, in particular vacancies, micropores, etc., can lower the initial activation barrier U_0 (or Q_0). In other words, these defects should facilitate the process of breaking interatomic bonds in the specimen being tested. Annealing decreases the number of defects, and hence increases the parameter U_0 (or Q_0).

Thus, study of creep and of endurance of strength of condensed films may prove promising for the further development and generalization of the kinetic theory of failure, besides being important in practice.

3.4. Effect of Rolling of Vacuum Condensates

Information is to be found in^[70,71] on the fact that plastic deformation (10–30%) decreases the number of excess point defects in tempered massive metals. Since condensed films contain a large number of point defects (see Chap. 4), we considered it interesting to study the effect of deformation on the strength of these objects.

The first experiments on rolling Cu films^[24] showed that 15–35% deformation lowers their strength characteristics. This is especially marked in the highest-strength condensates. High-strength Cu and Ag films ($h = 30\text{--}50\ \mu$) have recently been studied, the extent of rolling being increased in stages to 80%. The microhardness H and ultimate strength σ_u were measured for each of 10–15% of deformation. The results are given in Fig. 19 and in Table VI.

Table VI

Extent of rolling, %	0	25	35	50
Ultimate strength, kg/mm ²	73–82	64–72	68–78	68–73

The graph shows the mean values of H ; the scatter did not exceed $\pm 3\%$. As we see, the curves of variation of H for Cu and Ag are not monotonic. The films lose considerable strength as the extent of rolling is increased to 20–30%. Here the values of σ_u decrease by as much as $\sim 15\%$. When the films are deformed by about 40%, one observes an increase in H and σ_u , but the original values are not reached. Further rolling weakens the films, and the values of H and σ_u approach the characteristics of massive rolled metals.

Remarkably, the excess vacancies are found to be eliminated^[70,71] (according to the variation in electric

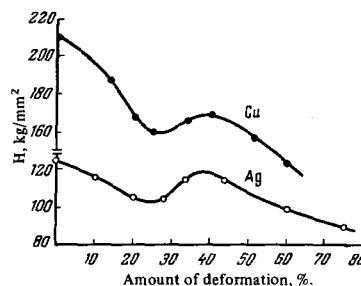


FIG. 19. Effect of rolling on the microhardness of Ag and Cu films having $h = 20\text{--}50\ \mu$.

resistivity) precisely at deformations of 10–30%. Furthermore, according to the data of^[72], the electric resistivity of tempered Pt specimens as a function of the extent of deformation is characterized by a curve having a minimum (cf. Fig. 19).

The weakening mechanism, which involves liquidation of the excess point defects, can be described only in general features at present.^[70] As they move, the dislocations “absorb” the point defects. Thus, as the applied stress is increased, the path is cleared for new dislocations. Hence their progress is facilitated, and this must lead to weakening. The reverse change in the strength of films at deformations above 20–30% apparently involves changes in the substructure, owing to pile-up of a large number of new dislocations in the rolling process. Approach of the mechanical characteristics of films to those of massive deformed metal with further rolling (above 40%) may be due to an entire set of factors: decrease in the disorientation angles of blocks, breakdown of the ideal structure of the crystallite-blocks (see^[60]), etc.

Further studies are needed for a final explanation of this effect of rolling.

4. STRUCTURE (SUBSTRUCTURE) OF HIGH-STRENGTH CONDENSED FILMS

The structure and substructure of films, which are formed under conditions of extreme supercooling and supersaturation as compared with the crystallization conditions of massive bodies, is an independent topic meriting a detailed review. We shall merely briefly discuss this problem to the extent necessary to explain the experimental results given above and to elucidate the nature of the high strength of films.

a) Under certain conditions of preparation, condensed films contain all the known crystal lattice defects: point, surface, and bulk defects. The fundamental information on these defects has been obtained by studying monocrystalline films in the transmission electron microscope at high resolution (see, e.g., the review^[73]).

Since formation of films involves extremely rapid quenching of the condensed layers of metal, these objects can contain a large number of vacancies. For example, dislocation loops were found^[73] in studying Au films, arising from condensation of accumulations of vacancies.* Another variety of point defects has also

*An approximate estimate of the highest concentration of vacancies in films, as made indirectly from the variation in the crystal-lattice parameter,^[89] gives extremely high values: about 0.1–0.2%. This is more than an order of magnitude higher than the concentration of vacancies in massive metals quenched by the usual methods.

been observed: accumulation of atoms of the residual gases impinging on the condensate while it was growing. Films contain large numbers of dislocations, whose density is as high as 10^{10} – 10^{11} per cm^2 , even in monocrystalline objects.^[73] Studies of films of metals and alloys have also made it possible to detect large numbers of packing defects of the deformation and twinning types.^[73] It has been shown here^[74] that the density of these defects increases with decreasing T_S and with increasing ω_C . An example of bulk defects in films is micropores, whose formation has been ascribed to coalescence of vacancies.^[75]

b) Development of diffraction methods of investigation (electron and x-ray diffraction) has recently made it possible to obtain valuable information on the substructure of vacuum condensates.

First, the mosaic structure of thin films is distinguished by high dispersity: the minimum dimensions of the crystallite blocks amount to only about 0.003 – 0.01μ .^[24, 77–79, 82] The dispersity increases with decreasing T_S ,^[21, 34, 79, 81, 82] with increasing ω_C ,^[34, 79] and with decreasing h in the range below 0.1μ .^[77, 79]

Second, there are very large microstresses,^[21, 34, 77–82] which indicate the high elastic limit for deformation of the blocks. This agrees with the data of direct strain measurements under external loading of films.^[60, 62]

Third, the disorientation angles α between the mosaic blocks in films are as much as tens of degrees,^[76] which exceeds the α for massive metals by an order of magnitude.

The presence of a highly developed substructure and the multitude of crystal-lattice defects give films a considerable non-equilibrium character.^[53] This leads to large changes in the substructure during condensation and even during subsequent aging at room temperature. For example, massive films show considerable structural inhomogeneity through their thickness.^[34, 83]

As we know, structural stability of metals depends considerably on the impurity content. Here even thousandths of percents shift the recrystallization temperature by tens of degrees.^[84] Indicative in this regard are data on the effect of the degree of vacuum^[34, 85] and the method of evaporation^[49, 55] on the structure of vacuum condensates. For example, as the vacuum is improved from 10^{-2} to 10^{-9} Torr, the dimensions of the crystallites in thin Au films increase from 0.01 to 3μ .^[85]

c) The features of the substructure of condensates presented above make it possible to explain a number of the experimental results (see Chaps. 2 and 3), and to express some ideas on the nature of the high strength of films. We note that the possibilities of detailed analysis are limited by the small number of studies made jointly on the substructure and the mechanical properties. They have been performed only on films having $h \geq 0.5 \mu$.^[21, 24, 34] According to current ideas, high strength can be attained in the presence of a large number of effectively blocked dislocations. As we noted above, films contain a multitude of crystal-lattice defects, which must restrain considerably the motion of dislocations. This is confirmed by the nature of the deformation curves, which involve considerable hardening (see Sec. 3.1).

The fundamental reasons for blocking of dislocations in films also include the small dimensions of the crystallites, together with their considerable disorientation.

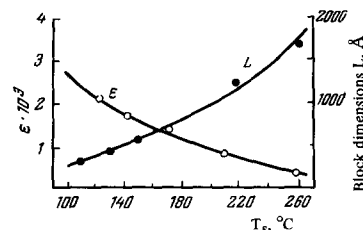


FIG. 20. Effect of T_S on the block dimensions L and the amount of microstrain ϵ in Cu films.^[34]

Recent experiments indicate that alloying by the residual gases and impurities arising from the evaporator plays a considerable role.

The cited substructural features permit us to draw a certain analogy between films and massive metals deformed at low temperatures.^[15, 18, 39] The latter are also characterized by extreme crystal-lattice distortion. Let us give some recent results^[86] in favor of such a comparison. According to these, rolling copper by 90% at 20°K makes it possible to obtain a foil having a strength of 65 – 67 kg/mm^2 (cf. the strength of Cu films; Table II).

Let us discuss the effect of the conditions of preparation on the substructure and mechanical properties. Here we shall use the data for Cu films having $h \geq 0.5 \mu$, for which a joint study of the cited problems has been conducted.^[21, 24, 34]

With increasing T_S , one observes a monotonic decline in the diffraction broadening, a growth in the block dimensions, and a decrease in the microstrain (or the microstresses) (Fig. 20). The minimum block dimensions amount to only 250 Å . The level of microstresses in films is considerably above the yield point of massive copper, being as much as 60 kg/mm^2 . The cited variations in the substructure are accompanied by decrease in the values of H and σ_U .

As we noted above, the non-equilibrium nature of films gives rise to a considerable inhomogeneity through their thickness. This is manifested by measuring H ^[33] or by structural study.^[34, 83] While condensates are being formed, relaxation and recrystallization processes occur in the previously condensed layers, while a dispersed surface layer is being formed on the side facing the evaporator. Hence the degree of structural inhomogeneity is determined by the thickness of the condensate and the time taken by the preparation process. Weakening of films during the formation process gives rise to the observed relation between the strength and the thickness (see Fig. 5). Here the extent of weakening depends on the refractoriness of the metal. This is confirmed by the data on films of Ag (see Fig. 6) and Ni (see Sec. 2.1). The parameter ω_C also exerts an appreciable effect. Thus, with decreasing ω_C one finds a more marked decline in strength with increasing h , in line with the longer time that the films remain at T_S . Conversely, the greater ω_C is, the less the strength depends on h .^[34]

Above we noted the considerable effect of the degree of vacuum and the method of evaporation on the structure, and hence, on the strength of condensates. Decreasing the amount of alloying impurities in films accelerates the processes of transformation to a state closer to equilibrium, and this alters the dependence of the structure and strength on h and on the conditions

of preparation, T_S and ω_C . For example, crucible-free Ni condensates show a dependence of the strength on h , in addition to the weakening (see Fig. 9); cf. data of Secs. 2.1 and 2.3 for crucible films). The weakening processes take place to an even greater extent in less refractory metals. According to our data, the strength of crucible-free Cu films condensed at $T_S = 80-100^\circ\text{C}$ over the range $h = 1-15\ \mu$ is practically independent of h , and amounts to $40-50\ \text{kg/mm}^2$ (cf. Fig. 5).

The examples given above indicate that the presence of uncontrolled impurities in films (residual gases, material from the evaporator, etc.) is one of the fundamental reasons for the deviation in the experimental results of different authors (see Chap. 2).

Study of the substructure and mechanical properties of condensates^[34] has shown that they manifest no thickness effect for $h \geq 0.5\ \mu$, since the strength is determined by the kinetics of weakening of the films, rather than the parameter h . This conclusion is also confirmed by the lack of a relation between σ_U and h (for $h \geq 0.5\ \mu$) for annealed films of different metals: Cu (see Sec. 2.2), and Ni.^[29]

We can expect the ultimate strength to be raised by decreasing h only in the range $h \leq 0.1-0.2\ \mu$, where the substructural "thickness effect" still has an influence.^[34] That is, the parameter h directly affects the substructure of the condensates, and in particular, the size of the mosaic blocks (for details see below).

Mechanical tests on annealed films having $h \geq 0.5\ \mu$ have shown considerable deviations in the stress-strain diagram (Fig. 21), in spite of the similar values of σ_U . As we see, the thicker the film is, the lower the stress at which appreciable plastic deformation begins, and the lower the yield point $\sigma_{0,2}$. Indeed, as h increases from 15 to $60\ \mu$, $\sigma_{0,2}$ declines from 28 to $18\ \text{kg/mm}^2$. To explain this phenomenon, we have studied the structure of annealed films^[38]: we determined the dimensions of the crystallites giving rise to the spots on the x-ray diffraction patterns (cf. the data from studying the substructure of films from the diffuseness of the diffraction lines^[34]). As it turned out, the processes of grain growth L are very sensitive to the parameter h . Indeed, measurements by the microbeam method showed that $L = 3\ \mu$ in annealed films having $h = 40\ \mu$, while L amounts to only about $0.1\ \mu$ when $h = 0.5\ \mu$ ^[38]. Thus, the thickness exerts a structural effect, (in distinction from a substructural one^[34]). Such an effect is apparently due to interaction of the boundaries of the growing crystallites with the surface of the film, since the dimension L in the direction normal to the plane of the film cannot exceed h . Possibly also the probability of forming recrystallization centers declines with decreasing h . Movement of dislocations is hindered at small L , and this leads to the observed increase in $\sigma_{0,2}$.

The surface of the film^[91] can also exert a certain influence on the movement of dislocations, with a role increasing with decreasing h . The following results are indicative: Very thin layers of Cr ($\sim 0.2\ \mu$) were condensed on both sides of annealed polycrystalline Cu films having h about 15 and $50\ \mu$. As it turned out, the coating increases the $\sigma_{0,2}$ of the thinner films by $\sim 30\%$. The values of σ_U were not altered thereby. Similar effects had previously been observed only in massive single crystals.^[91] The so-called scale factor^[8] can

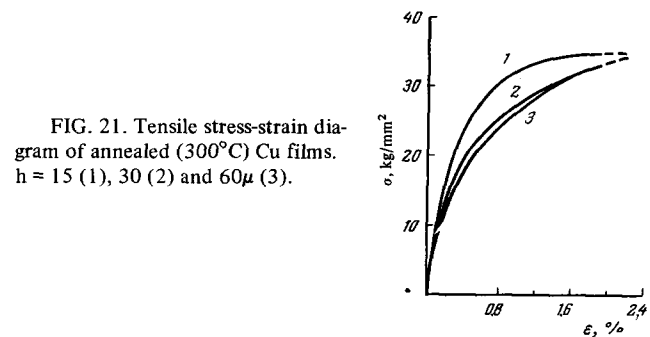


FIG. 21. Tensile stress-strain diagram of annealed (300°C) Cu films. $h = 15$ (1), 30 (2) and $60\ \mu$ (3).

also exert a certain influence on the increase in $\sigma_{0,2}$ with decreasing h .

Besides the reasons for the high strength of vacuum condensates discussed above, a reserve of further increase in σ_U lies in diminishing h . Here the thickness effect begins to be manifested at $h \leq 0.1-0.2\ \mu$.^[13,29,30] The reasons for this phenomenon can be discussed only in general outline, since the studies of the substructure of these objects^[76-82] were performed without regard to their strength characteristics.

The following factors have been discussed^[30] in explaining the increase in strength with decreasing h :

- 1) the existence of a large number of crystal-lattice defects;
- 2) surface tension, which produces a compressive stress in the film;
- 3) increased strength of the very thin surface layer, e.g., due to oxidation;
- 4) immobilization of dislocations by the surface of the film;
- 5) decreased pile-up distance of dislocations.

We have analyzed above the effect of factor 1) on the strength for $h \leq 0.5\ \mu$. As for thinner films, in contrast to^[13-15,29], the conclusion was drawn in^[38] from a study of annealed and freshly-condensed films that this factor can play no substantial role in the range $h = 0.01-0.07\ \mu$. On the other hand, according to the data of^[29], annealing Ni films having $h \geq 0.07\ \mu$ weakens them considerably.

One might partially explain the results of^[38] by a possible oxidation of very thin films during annealing. Thus we can assume that factor 1) is one of the necessary conditions for realizing high strength in thin films. According to the calculations of^[30], the amount of compression involved in surface tension corresponds to an overall increase in strength of $20-40\ \text{kg/mm}^2$ for the thinnest films studied which have $h \cong 0.01\ \mu$.

If we assume, in accord with factors 3) and 4), that the dislocations are fixed at the external surfaces of the film, then the stresses causing failure must exceed Gb/h , where G is the shear modulus and b is the Burgers vector. We can naturally assume that this relation can be fulfilled for monocrystalline films.^[15,73]

While noting the role of the surface in increasing the strength of films, we must mention the varied forms taken by this influence,^[91] which increases sharply with decreasing h .

The experimental data for polycrystalline films^[29,30] are well described by the relation

$$\sigma_n = \sigma_0 + Kh^{-1/2}, \quad (2)$$

which corresponds formally to the well-known formula

of Petch for polycrystals,^[92] if we replace the grain dimensions (the pile-up distance of dislocations) with the film thickness. To favor this replacement, we can adduce some data on the existence of a relation between the dimensions of the crystallites and the parameter h ^[29,79] (see also Chap. 5). Owing to the great scatter in the experimental points, there are no grounds for stating that the last mechanism 5) for increasing the strength is the decisive one. The other cited factors can also make a certain contribution.

In this regard, we can cite some data^[15] indicating that very thin Au films "thinned" out of massive metal manifest no enhanced strength. This example emphasizes the importance of the substructural factor. In fact, we should treat such results with caution, since fracture tests of very thin films involve considerable experimental difficulties, not to mention the reduction of σ_u due to inhomogeneous thickness of the electropolished specimens.

In our opinion,^[60] the high strength of very thin condensed films ($h \leq 0.05 \mu$) may arise from the presence of highly disperse and greatly disoriented structurally-perfect blocks. The strength of dislocation-free blocks that have grown from separate nuclei is close to the theoretical value. However, in the deformation of films it is limited by the strength of the defect boundaries.

Let us briefly analyze the studies^[15,18,36] in which, in contrast to^[13,19,28,29,30], they could not detect an increase in σ_u when $h \leq 0.1-0.2 \mu$ (see Sec. 2.1). Apparently the fundamental reason is the method of preparing and testing the specimens, and especially the "edge effects", which could be avoided in^[26,29] by testing the films in the form of scrolls. The relief of the substrate can also exert a considerable effect, which increases with decreasing h . This is illustrated by the above-discussed results of studying Ni films condensed on a sublayer of collodion (see Fig. 3a) and NaCl (see Fig. 3b).

When $h > 0.2 \mu$, the relation of σ_u to h is determined by the kinetics of weakening of the films during condensation. Here the parameter h indirectly affects the strength of the films by determining fundamentally only the length of time that they are maintained at T_S . This is confirmed by substructural studies,^[34] and also by mechanical tests of both annealed metallic films^[29] and alloy films (see Sec. 2.4), for which the strength is practically independent of h .

We note in conclusion that the vacuum-condensation method can be used also to attain another limiting state: preparing films having a perfect, defect-free structure. According to a recent communication,^[47] monocrystalline Cd films 0.15μ thick having a highly perfect structure were deformed within the electron microscope, and withstood an elastic deformation of about 2.5-3.5%. The limited nature of the information in the literature on this topic is due to experimental difficulties involved in obtaining such condensates (crucible-free evaporation, ultrahigh vacuum, etc.)

5. MULTILAYER VACUUM CONDENSATES

The method of layer composites^[87] is one of the effective methods of stabilizing high-strength condensed films at high temperatures. Here a very important advantage of layer composites, or in other words, multi-

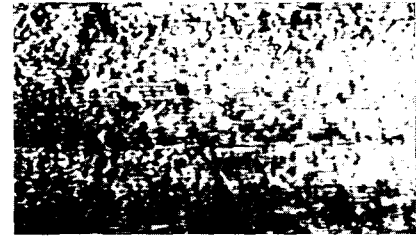


FIG. 22. Cross-section of a multilayer condensate ($\times 1800$).

$$h_{sp}^{Fe} \approx 0.3 \mu, \quad h_{sp}^{Cu} \approx 0.5 \mu.$$

layer condensates (MLC), or combinations of many alternating layers of components (Fig. 22), is that the high-strength state is stabilized for practically any h (the largest h values are limited only by the potentialities of the experimental technique, and have attained 0.1 mm in our experiments). The mechanical properties of MLC can be varied over a wide range by varying the thickness and strength of the constituent films. It is important to add that, according to^[93,96], the formation of heterogeneous ("skeletal") structures is the most promising method of producing materials having unique physico-mechanical properties.

Analysis of the recent data^[29,30] indicates that one of the reserves for considerably increasing the strength of films, besides varying their substructure, is to decrease their thickness. Hence alluring perspectives appear of creating materials by the MLC method of macroscopic dimensions having a strength close to the theoretical, consisting of a multitude of very thin films.

The results of the first experiments are described in^[90]. The MLC components were films of Cu and Fe satisfying requirements imposed on MLC components.^[87] The MLC were prepared with a special automatic apparatus. The layer composition was determined by calculation, and verified by the x-ray phase analysis method on the URS-5 OIM diffractometer. The results of^[90] and also the most recent data are given below.

The experiments showed that one gets a very substantial increase in the strength of MLC (for fixed T_S and layer composition) by decreasing the spacing of the MLC. Figure 23 shows the results of studying a MLC containing 50-60% Fe. The total thickness was 15-25 μ . The overall spacing of the components, i.e., the MLC spacing $h_{sp} = h_{sp}^{Cu} + h_{sp}^{Fe}$, was varied from 2 to 0.03 μ .

As we see, we observe a considerable increase in H for

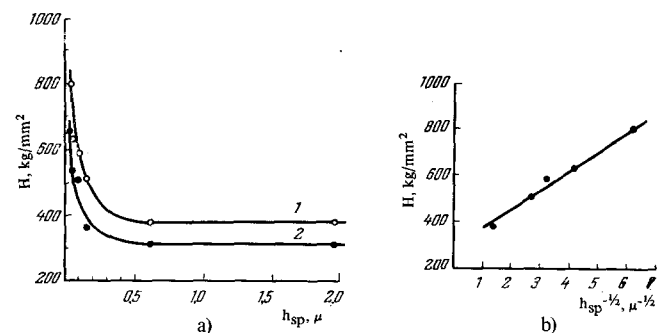


FIG. 23. Microhardness of multilayer condensates of constant composition as a function of the spacing h_{sp} . $T_S = 240^\circ$ (1) and 300° (2).

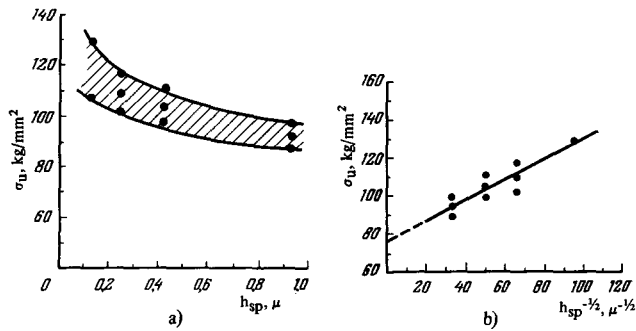


FIG. 24. Ultimate strength of multilayer condensates of constant composition as a function of the spacing h_{sp} .

$h \leq 0.2-0.3 \mu$, attaining about 800 kg/mm^2 . This is five times the hardness of massive alloys. Thus, one observes a more than twofold increase in the hardness of MLC at fixed layer composition. Brittleness of the films impedes one from determining the analogous relation for σ_u . One of the possible methods of reducing the brittleness of MLC is to lower the Fe content. In this regard, a series of MLC specimens was studied having constant composition, containing 20–30% Fe. As with the MLC having higher Fe content, one can get a considerable increase in strength by decreasing h_{sp} (Fig. 24). Here one observes a considerable increase in σ_u up to values of about 130 kg/mm^2 , together with the increase in hardness. This is 2.5 times greater than the strength of the massive aged alloys,^[67] and is close to the highest strength of whiskers of alloys of corresponding composition.^[94] Reduction of the experimental data gives a linear relation of H and σ_u to $h_{sp}^{-1/2}$ (see Figs. 23b and 24b). This agrees with the known relations for the hardness^[95] and the ultimate strength,^[92] provided we replace the dimensions of the crystallites (distance of dislocation pile-up) in the latter with the MLC spacing. Thus, the regularities established in studying the relation of the strength to h in films in the range $0.02-0.4 \mu$ are confirmed.^[28,30]

Figure 25 illustrates the effect of the spacing on the stress-strain diagram of MLC. The elastic properties and strength increase appreciably with decreasing h_{sp} . Thus, the values of ϵ_{el} increase from 0.3 to 0.6% (cf. the values of ϵ_{el} for films of metals and alloys, Sec. 3.1).

The strength of MLC also increases with increasing Fe content. Figure 26 shows the results obtained for $h_{sp} \geq 0.5 \mu$, for which the strength does not depend on h_{sp} . As we see, when $T_s \approx 250^\circ\text{C}$, the experimental points fit a straight line well. That is, an additivity law is obeyed, indicating the lack of any appreciable mutual diffusion of the MLC components, as is also confirmed by the x-ray diffraction data. One observes a deviation from a straight line at higher T_s . It is apparently due to onset of diffusion processes. The hardness of the MLC exceeds severalfold that of the massive alloys over the entire concentration range.^[67]

We have also observed the fundamental laws established for Cu-Fe MLC in studying another system, Ni-Ag, in which the components are practically mutually insoluble in the solid state. We obtained the most important results in studying the effect of the h of the film components on the substructure. We performed the

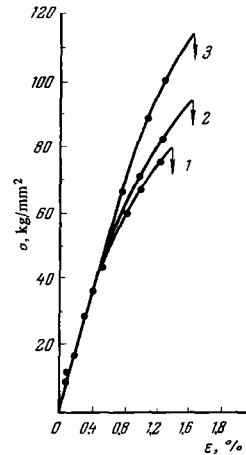


FIG. 25

studies on the URS-50 IM diffractometer, and analyzed the (111), (220), and (222) lines of Ag, with account taken of anisotropy of the elastic modulus. Ag films were chosen for reasons of convenience of calculation. We used the graphic method of Hall with approximation by Gaussian and Cauchy functions to estimate the mean dimension L of the mosaic blocks and the amount $\Delta d/d$ of microstresses. As is known, this gives limiting values of the quantities to be measured.

Table VII gives the values of the true diffraction broadening as a function of h_{sp} of the Ag films.

As we see, decrease in the spacing makes the lines considerably more diffuse.

The corresponding data on the size of the mosaic blocks and microstresses are given in Table VIII and Fig. 27.

Decreasing the spacing entails much greater disperseness of the blocks and increase in microstresses. Here L and the hardness H are well correlated with one another. Thus, the size of the mosaic blocks in MLC is determined by the thickness of the constituent films, and varies in the same direction as h_{sp} . This conclusion confirms the propriety of replacing the size of the crystallites by the MLC spacing in the relations given above (see also Chap. 4).

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Table VII

Ag thickness, μ	(hkl)	β , degrees
0.03	(111)	9
	(220)	12
	(222)	12.35
0.09	(111)	6.45
	(220)	9.14
	(222)	9.67
0.22	(111)	3.2
	(222)	5.25

Table VIII

Thickness of Ag films, μ	Calculated by Gauchy function		Calculated by Gaussian function	
	L , Å	$\Delta d/d \cdot 10^3$	L , Å	$\Delta d/d \cdot 10^3$
0.03	220	0.9	190	1.8
0.09	320	0.9	260	1.6
0.22	830	0.8	630	1.2

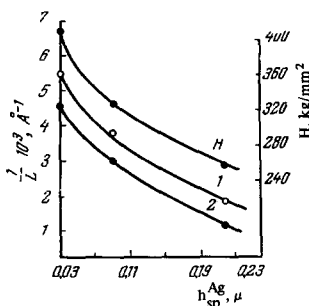


FIG. 27. The mosaic block dimensions and microhardness as functions of the Ag film spacings. (As calculated by the Gaussian function (1) and the Cauchy function (2).)

sources is hindered and the paths of free motion of dislocations are shortened with decreasing h . This is also illustrated by the stress-strain diagrams of MLC (see Fig. 25).

The performed experiments indicate the possibilities of using the MLC method to create materials of macroscopic dimensions having very high strength. Extensive potentialities of varying the mechanical properties of MLC arise upon varying the relations of h and the σ_{II} values of the constituent films. In particular, it might prove very promising to use refractory oxides, carbides, nitrides, etc., as film components.

Adopting multilayer structures, which involves a sharp increase in the role of interphase surfaces, opens up perspectives of generating new properties that can't be attained in the component materials.

6. CONCLUSION

In conclusion, let us take up the possible aspects of practical use of high-strength condensed films. Naturally, we shall discuss here only the fields of application involving the good mechanical properties of condensates, since the wide application of films in modern microelectronics, computing and semiconductor technology, etc., is generally known.

As we know, electroplating is widely used now in technology. However, application of coatings from many electrolytes is accompanied by hydriding and embrittlement, and it is limited to a certain list of metals and alloys, since many metals or combinations of alloys cannot be deposited by electroplating.

The initial experiments have shown^[104] that high-strength vacuum condensates can be used successfully as protective wear-resistant coatings (Table IX).

Table IX

Type of coating	Micro-hardness kg/mm ²	Linear wear, μ
Nickel phosphide electroplate	750—950	38
Case-hardened steel	650—750	10—13
Electroplated chromium	950—1200	7—14
Vacuum-condensed chromium	550—750	4—8

Indeed, as Table IX indicates with data of comparative tests of different types of coatings (for sliding friction with a lubricant), vacuum condensates of chromium are 5–6 times better in wear-resistance than nickel-phosphorus coatings, and 1.5–2 times better than electroplated chromium and case-hardened steel.

According to our data, vacuum coatings also show very high abrasive wear resistance, comparable with

the wear resistance of the best electroplating. In this regard, whereas the wear resistance of chrome plate declines by a half even when annealed at 300°C, the wear resistance of vacuum coatings is practically unaltered upon heating up to 300–400°C.

The initial experiments also indicate considerable promise in using films as protective fatigue coatings.

As we noted above, a reserve for further increase in strength of films is to decrease the thickness. It seems highly promising in this regard to use multilayer condensates. They make possible very high strengths (and other valuable physical properties: electric, magnetic, etc.) in objects of considerable thickness. Extensive possibilities of varying the cited properties appear here, involving use of different components of MLC components.

Much interest has been excited recently by the so-called fibrous composites, which are among the materials of the future: metals reinforced by high-strength filamentous crystals (whiskers), very thin fibers, etc. There are grounds for assuming that one can successfully use thin films as reinforcing materials, and especially films of oxides, nitrides, carbides, etc.

Finally, films can be used successfully in various devices and instruments whose elements must possess high strength along with small dimensions and weight.

This is far from a complete list of the possible practical applications of high-strength vacuum condensates.

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