Intensification of the modes of physicochemical cleaning of metal optics

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^aPlekhanov Russian Economical University, Moscow, 117997 Russia ^bInstitute of Electrophysics and Electric Power, Russian Academy of Sciences, St. Petersburg, 191186 Russia ^cTver State University, Tver, 170100 Russia At present, in industry, science and technology, powerful CO2-lasers, emitting at a wavelength of $\lambda = 10.6 \,\mu\text{m}$ are widely used. In the mid-infrared region, CO ($\lambda = 3-8 \,\mu\text{m}$) and HF ($\lambda = 2.7 \,\mu\text{m}$) (DF ($\lambda = 3.8 \,\mu\text{m}$)) lasers are used. Their laser resonators usually use cooled mirrors made of copper, aluminum, molybdenum, etc. These metals have high values of thermal conductivity and reflection coefficient in the operating range, which makes it possible to use such mirrors without additional interference coatings, which usually reduce the radiation strength. Cooling allows to stabilize the working temperature of the mirror and reduce the effect of thermal deformations on their shapes. Since any absorbing particles on the mirror surface will significantly reduce its performance, this necessitates regular cleaning of the mirrors to restore operating parameters.

During the manufacturing process, a surface layer is formed on the mirrors, saturated with abrasive particles and other technological impurities. This layer differs markedly in structure and properties from the bulk of the material. Studies have shown a direct dependence of the most important performance characteristics on the optical properties of the surface layer, the presence of impurities in it.

The objects of research were flat mirrors made of: 1) oxygen-free copper of the MOb brand and bronze Cu-Zr with a diameter of 40 and 50 mm with the following optical characteristics: surface shape N = 2; form error $\Delta N = 0.2$; optical purity class P = V; 2) aluminum-magnesium alloy (Mg content - 5.8-6.8%) of the AMG-6 brand with a diameter of 50 mm (N = 2; $\Delta N = 0.5$; P = V); 3) aluminum casting alloy based on the Al-Si system with a Si content of 6-8% of the AL-9 brand with a diameter of 50 mm (N = 2; $\Delta N = 0.3$; P = V); 4) aluminum casting alloy based on the Al-Zn-Mg system with a Zn content of 3.5-4.5%, Mg - 1.5-2% of the AL-24 brand with a diameter of 100 mm (N = 2; $\Delta N = 0.3$; P = V); 5) molybdenum with a diameter of 50 mm (N = 2; $\Delta N = 0.5$; P = V); 6) titanium-containing stainless steel, belonging to the austenitic class, of the 12X18H10T brand with a diameter of 100 mm (N = 1; $\Delta N = 0.5$; P = V). Optical elements of the same materials are taken from the same batch and manufactured by the free abrasive method according to the standard technology.

To elucidate the influence of the role of optical parameters (plasma formation threshold, adhesion of optical surface, geometric shape, reflection coefficient, etc.), the relationship of these characteristics with the energy characteristic of detergent medium in the process of physicochemical cleaning was investigated. In this case, the choice of detergent medium for cleaning of metal optics should be determined taking into account the behavior of their characteristics during their cleaning and operation.

The dissolution process always involves several stages: 1) transfer of solvent to the cleaning surface, at which the reaction occurs; 2) dissolution; 3) removal of reaction products from the surface.

The main provision of the parametric theory of solubility is the decisive role of the solubility parameter (δ) in the classification and selection of solvents used in [13]. It is believed that the dissolution of the components will occur at any of their ratios if the molar enthalpy of mixing (ΔH) is close to "0" in the equation:

$$\Delta H = \left(\delta_1 - \delta_2\right)^2 V_1 \phi_1 \phi_2, \qquad (1)$$

где δ_1 , δ_2 - параметры растворимости компонентов; ϕ_1 , ϕ_2 - объемные доли компонентов; V₁

– мольный объем растворителя. From equation (1) it follows that the closer the values of the solubility parameters of the solvent and the solute, the better mixing of components occurs. Of course, the compatibility of the components to be mixed in a certain way depends on the proximity of their solubility parameters.

To analyze the speed of the processes of physicochemical cleaning of mirrors, we used solvents, that are widely used in the optical and electronic industries. These are ethanol, gasoline, acetone, petroleum ether, carbon tetrachloride, methylene chloride, freon-112, freon-113, 113, isopropyl alcohol. We also used solvents, which were close in their solubility) parameter to the solubility parameter of the technological contamination, present on the mirror. These are, first of all, freon-114B2, nitromethane, tert-butanol, 2-butanol, butanol, acetonitrile, benzyl alcohol, diethyl ester of malonic acid.

These solvents had the energetics of intermolecular bonds ("specific density of cohesion energy", close to the energetics of intermolecular bonds of the surface layer of the mirror (in particular, to technological contaminations)). This made it possible to change the surface energy of the optics and determine the changes in the energy characteristics of the mirror, first of all, the ionization energy and the adhesion energy.

1,2,3-benzotriazole, N-methylmaleimide, N-methylphthalimide, N-octadecylnaphthalimide were used as emulsifying additives with protective properties. The listed solvents were used in experiments to obtain versatile information on key issues of the problem of physicochemical cleaning of optical elements.

In practice, the cleaning rate has to be determined experimentally under certain conditions of the cleaning process [17]. During the entire process of removing contaminations, it continuously decreases as the surface contamination decreases: on average, 90-95% of contaminations are removed in the first half of the cleaning time, and the remaining 5-10% - in the second.

Contaminations on the surface of mirrors, as a rule, consist of a liquid phase (oil, grease) and a solid phase pitch and rosin resin, bitumen, asphaltenes, polymerized particles, abrasive and dust particles, etc.). In particular, a mixture of pine pitch and rosin (the so-called pitch and rosin resin) is used in gluing and polishing resins for polishing the optical surface and can be from 15 to 75% by weight. from all technological contaminations. Therefore, it was on her example that experiments were carried out to determine the cleaning speed (table 1).

Table 1 - The amount of pitch and rosin resin, that has passed into the solvent used for cleaning in the optical and microelectronic industries, depending on the ordinal number of the dissolution cycle*

Количество пекканифольной смолы							ы	Приме-
Растворитель	в растворителе, мг							чание
	Циклы растворения							
	1	2	3	4	5	6	7	
1. Дибромтетрафторэтан (фреон-114В2, δ = 14,7Дж ^{1/2} см ⁻ ^{3/2})	-	-	>200	65,4	33,2	10,6	8,7	Взвесь
2. Дихлордифторметан (фреон- 12, $\delta = 12,5 \mbox{Д} \mbox{$ {\rm m}$}^{1/2} \mbox{cm}$^{-3/2}$)$	-	-	>200	83,1	49,9	21,3	17,4	Взвесь
3. Метиленхлорид ($\delta = 17.0 \text{Д} \text{ж}^{1/2} \text{см}^{-3/2}$)	>200	79,9	40,4	30,3	21,5	14,7	10,6	
4. Нитрометан ($\delta = 25,2$ Дж ^{1/2} см ⁻ ^{3/2})	-	-	>200	63,2	31,4	20,3	14,7	Взвесь
5. 2-Пропанол*** (δ = 23,6Дж ^{1/2} см ^{-3/2})	-	-	>200	23,2	10,0	8,6	6,3	Взвесь
6. 1,1,2-Трихлортрифторэтан (фреон-113, δ = 14,8Дж ^{1/2} см ^{-3/2})	-	-	>200	75,0	40,7	22,6	11,2	Взвесь

Примечание. *Циклы растворения имеют одинаковые временные периоды.

Contaminations from the surface of the mirrors are removed, along with dissolution, also due to emulsification of the liquid phase (formation of an emulsion) and dispersion of the solid phase (formation of dispersions).

When using for cleaning mirrors a solvent-emulsifying agent (based on solvents and surface-active polar organic substances (surfactants), which lower the surface tension of the solution and thereby provide wetting of the contaminated surface, helping to remove contaminations. At the same time, in addition to dissolving of contamintions, the process of their emulsification is underway. This allows to significantly increase the detergent action and, as a result, work (A_{admc}), that determine the affinity of the detergent medium for contamination. Surface wetting depends on the composition of the detergent medium, surface tension, and the material to be cleaned.

The detergenting action consists in the removal of liquid and solid contaminftions from the surface and translation them into the detergent medium in the form of a solution or dispersion. The main phenomena, that determine the detergenting effect, are the processes of physicochemical adsorption (A_a), wetting (A_w), emulsification (A_e), dispersion (A_d), foaming (A_f), micelle formation (A_{mf}) and stabilization (A_s).

To intensify the cleaning process, it is advisable to use the immersion of the mirror in the detergent medium with its activation by submerged jets or the displacement of the object in the detergent medium, or bringing the detergent medium to the surface of the element. That is, when cleaning of metal optics, it is necessary to rationally use all of the factors, influencing the cleaning work (A_c) - work (A_{admc}) , depending on the composition of the detergenting and cleaning medium, and work (A_{midm}) associated with the mechanical effect of the detergent medium, with the predominant use (A_{admc}) . In this case, the properties of the mirrors must be taken into account.

The study of the proposed model of the physicochemical process of cleaning mirrors was carried out simultaneously with the study of optical elements made from materials of high-energy laser systems.

Conclusion

Analysis of the main cleaning and detergenting processes shows their high energy intensity. Direct energy costs for cleaning are $\geq 2.5\%$ of the consumed energy, and the time consumption for a number of industries are up to 10% of the total time required for the manufacture of a mirror, which indicates great opportunities for improving cleaning processes and reducing their labor and energy consumption.

The verification of the model of the physicochemical process of removing contaminations from the surface of the mirrors, proposed by the authors, was implemented on an installation, operating in a semi-automatic mode in a closed technological cycle (at present, it has exhausted its resource), and on its laboratory version, as well as from the assessment of the optical characteristics of the mirrors and its durability during operation.

Thank you for your attention!



