Physical and chemical cleaning of the surface of power metal optics for the purpose of increase in beam firmness

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Abstract. Features of the choice of solvents for the physical and chemical cleaning of power optical elements in accordance with the parametric solubility theory were investigated. When cleaning the surface from the model contaminant with halogenated hydrocarbons, visually observed white film of alkali and alkaline earth metal salts that are not soluble by this class of solvents and iridescent bands from the interaction of hydrocarbons with the metal remain on the surface. All this greatly impairs the optical properties of the surface. It was shown that, when using solvents, it is necessary to inhibit the interaction of halogenated hydrocarbons with mirrors by stabilizing solvents or by selecting the regimes for carrying out the physicochemical purification process, or by thereof combination.

1. Introduction

In industry, in science and technology, powerful CO₂ lasers emitting at a wavelength \( \lambda = 10.6 \ \mu \text{m} \) are used [1]. In the middle infrared region, CO and HF (DF) lasers are used [2]. Reflectors are usually cooled mirrors [3–9] made of copper, aluminium, beryllium, molybdenum, silver, etc. They have high thermal conductivity and a reflection coefficient in the operating range, which makes it possible to use mirrors without additional interference coatings that reduce the radiation strength. Cooling reduces the effect of thermomechanical distortions in the shape of mirrors, which require regular cleaning to restore performance.

Optical durability of power optics is the main requirement for laser systems operating at high radiation intensities. Optical stability in the continuous mode of radiation is due to a combination of absorptivity and thermomechanical properties of the material [10]. In the pulsed mode, plasma of low-threshold optical disruption of the gas, initiated by evaporation of the ions of the material from the surface, can occur near the surface, which can sometimes be damaged with the appearance of irreversible changes [3–5].

In the framework of the theory of thermal optical breakdown of solid transparent dielectric inclusions, the reason for the appearance of luminous spots on the metal under the action of laser radiation, which are distinguished by their brightness on the general background of the irradiated zone,
is explained. Inclusions are local initiators of the development of optical breakdown of air near the surface [5, 11–14]. On these formations, the reflection of light is markedly reduced, and the temperature of their melting and evaporation considerably exceeds the corresponding values of the metal. The effect is enhanced by the interaction of the laser pulse with surface electromagnetic waves [15], since up to 100% of the radiation can be absorbed in this case.

In the process of using mirrors with a gradual increase in power, appears the effect of "laser cleaning". [15–18]. Due to the evaporation and burning out of the absorbing centres, the optical stability threshold increases. However, the selection of the regime is very complicated, since "laser cleaning" can be accompanied by oxidation of the metal.

The parameters of technological contaminations on the surface of metallic mirrors formed during optical processing and during operation and decreasing the optical stability of the mirror are revealed in this work. The efficiency of solvents for cleaning optics was also investigated.

The degree of impurities contamination of the surface of the irradiated optical element affects the occurrence of irreversible changes in the material, in particular, the absorption capacity, and, consequently, the thresholds of gas breakdown at the surface. It was noted in [11–14] that under the action of the first pulse on the unpurified surface, the threshold intensity is always several times lower than under the action of "subsequent" pulses. In [12], when the metal surface was irradiated consecutively with a series of pulses from a CO2 laser, the energy expenditures for the formation of the plasma rose with increasing in the number of pulses to a certain value, at which they remained constant, i.e. the surface was cleaned in the presence of an air-breakdown plasma by removing the defects which absorb radiation. It was shown in [13] that the initial absorbing power for copper and aluminum targets, was 10–12 % and 6 %, respectively, but after laser cleaning it was reduced to 2–3 %, which is typical for pure unpolished samples.

2. Materials and methods
In reality, metals are covered with a sorbet layer of dielectric, mostly organic, contaminants. These may be areas of the surface covered with a continuous thin film or single ("island") film formations.

Since purification is a reduction of surface contamination to a certain level (surface modification), it is interesting to investigate the plasma formation threshold caused by this contamination as a function of the contamination radius (provided that it is small in comparison with the depth of the optical absorption).

Analysis the increase of the temperature of dielectric impurities on the basis of the theory [19] makes it possible to determine the initial heating of the absorbing contaminants by formula

$$\Delta T = \left[ \frac{\omega \chi'' E_0^2}{c_s} \right] t,$$

where ω is the circular frequency of light; \(\chi''\) is the imaginary part of the susceptibility; \(c_s\) is the heat capacity; \(E_0\) is the field intensity; \(t\) is the time of exposure.

The depth of optical absorption is the reciprocal of the absorption coefficient

$$\mu = \frac{8\pi^2 \chi''}{\lambda n},$$

where \(\lambda\) is the wavelength in vacuum; \(n\) is the refractive index.

For short radiation pulses of duration \(t_p\), it is necessary to use the equation for \(\Delta T\), in which \(t = t_p\). In many cases, \(t\) is determined by the time \(t_c\) of heat transfer from the inclusions. For stationary heating

$$t = \frac{t_0 - \alpha^2}{D_t},$$

where \(D_t\) is the thermal diffusion coefficient.
The value $D_\tau$ for many solids at room temperature is of the order of $10^{-2}$ cm$^2$c$^{-1}$, as a result, $t_\tau \sim 1$ μs for the particles with a radius of $1$ μm. If the particle radius is $\leq 0.1$ μm, and $t \geq 10^{-8}$ s, the increase of the inclusion temperature can be recorded

$$\Delta T_{ss} = \left[ \frac{\omega \chi'' k_0 a^2}{D_\tau c_\tau} \right] t$$

(4)

It follows from equation (4) that the field strength required to achieve a critical temperature for inclusions of $\sim 0.01$ μm should be $\sim 2.1 \cdot 10^6$ Vcm$^{-1}$ (for $\lambda = 10.6$ μm), which is comparable with the plasma formation of a pure material (for example, of glass). Consequently, inclusions with a radius of $0.01$ μm from the point of view of lowering the threshold are less dangerous compared to larger ones. Inclusions $\geq 1$ μm can be easily detected and removed. The most dangerous from the viewpoint of reducing the threshold of plasma formation are inclusions with a radius of $\sim 0.1$–$1.0$ μm located in the surface layer and having an optical absorption depth of $10^{-3} \div 10^{-4}$ cm. The critical radius ($r_{cr}$) of the spherical inclusion, less than which its absorption cross section begins to decrease, is at the wavelength $\lambda = 10.6$ μm for dielectrics. The critical radius ($r_{cr}$) of the spherical inclusion, less than which its absorption cross section begins to decrease, is at the wavelength $\lambda = 10.6$ μm for dielectrics

$$r_{cr} = \mu^{-1},$$

(5)

where $\mu$ is the radiation absorption coefficient.

Equation (5) defines a minimum limit, indicating below what size on the treated surface after physical and chemical cleaning inclusions may be present. Thus, for $\lambda = 0.63$ μm, the maximum impurity size below which it is impractical to clean the surface is $\sim 0.1$ μm. The presented evaluations have largely a qualitative nature, since under pulse actions the index ($D_\tau$) can increase to $10^6$ times [3].

Structural defects (grain boundaries, dislocations, vacancies, etc.) contribute to a decrease in the plasma formation threshold by more than 2 orders of magnitude [14].

Surface inclusions, having a much larger (compared to bulk) absorption, along with a decrease in the plasma gas formation threshold near the metal, are also responsible for the destruction thresholds caused by their thermal explosion [11].

The choice of solvents for the physical and chemical cleaning of power cells in accordance with the parametric solubility theory was carried out as follows. An analysis of the process contaminants present on the surface of the metal showed that their bulk (up to 85 % by weight) mainly includes rosin pitch (with a rosin content of up to 70 % by weight), used to manufacture a polisher for processing optics. The pitch is a polymerization type compound whose solubility parameter ($\delta$) is not determined from the heat of evaporation or other quantities. Therefore, it is determined experimentally by the nature of solubility in solvents. For rosin, $\delta = 18$ J$^{1/2}$cm$^{-3/2}$ [20].

3. Result and discussion

At the first stage, a kinetic analysis of the physical and chemical process of dissolving the rosin pitch was carried out in solvents with an indicator ($\delta$) close to rosin. The choice of solvents was carried out from various classes of selectivity according to Snyder [21, 22]. Then we carried out a kinetic analysis of the physical and chemical process of dissolving the rosin pitch in these solvents, for which 1 g of resin was placed in a container and dissolved in solvents. The amount of resin dissolved after each cycle of contact was determined on an EF-3MA electronic fluorometer (table 1).

The data in Table 1 show that acetone and diethyl ketone have the maximum solubility with respect to rosin pitch (after 4–5 cycles of dissolution, the rosin is not detected, completely passing into solution). Somewhat worse, its dissolution occurs in diethyl carbonate, xylol, methylene dichloride, 2–butanol. The bulk of the rosin pitch dissolves after 6–7 cycles (only insignificant amount of visually observed suspension remains undissolved).

The results of the experiment (table 1): rosin pitch is most effectively dissolved in solvents belonging to the class "VI" of polar selectivity according to Snyder. Therefore, in order to obtain the optimum
solvent for this pitch, similar studies of the process of its dissolution in solvents of the class "VI" of polar selectivity (table 2) were carried out.

According to tables 1 and 2, among solvents with a class "VI" of polar selectivity, acetone and methylethyl ketone have a maximum solubility with respect to rosin pitch. It can be assumed that for rosin pitch, the index (δ) is 19.8 J^{1/2}cm^{-3/2}, which corresponds to the solubility parameter of acetone, in which it dissolves most effectively.

| Solvent          | Amount of model solvent, mg | Dissolution cycles |
|------------------|-----------------------------|--------------------|
|                  | 1 | 2 | 3 | 4 | 5 | 6 | 7 |
| 1. Acetone*, δ = 19.8 J^{1/2}cm^{-3/2} | D | 51.5 | 6.7 | 6.2 | ND |
| 2. D | 82.3 | 32.4 | 11.6 | 10.8 | 9.0 | 8.6 S |
| 3. D | 70.3 | 50.4 | 38.5 | 27.1 | 14.9 | 7.3 S |
| 4. - | - | D | 165 | 37.3 | 11.3 | 10.0 S |
| 5. - | - | D | 65.4 | 33.2 | 10.6 | 8.7 S |
| 6. - | - | D | 83.1 | 49.9 | 21.3 | 17.4 S |
| 7. D | 63.8 | 10.1 | 6.9 | 6.1 | ND |
| 8. D | 65.9 | 17.8 | 11.9 | 7.2 | 7.1 | ND |
| 9. D | 83.4 | 41.3 | 21.2 | 12.4 | 11.5 | 10.9 |
| 10. D | 70.1 | 40.3 | 25.4 | 15.2 | 12.9 | 8.8 |
| 11. D | 79.9 | 40.4 | 30.3 | 21.5 | 14.7 | 10.6 |
| 12. - | - | D | 63.2 | 31.4 | 20.3 | 14.7 S |
| 13. - | - | D | 23.2 | 10.0 | 8.6 | 6.3 S |
| 14. - | - | D | 161 | 36.1 | 10.9 | 9.8 S |
| 15. - | - | D | 75.0 | 40.7 | 22.6 | 11.2 S |
| 16. D | 69.4 | 39.2 | 22.4 | 14.8 | 9.9 | 7.8 S |
| 17. - | - | D | 153 | 40.9 | 31.1 | 23.5 S |
| 18. - | 200 | 79.9 | 51.4 | 35.9 | 23.7 | 16.9 S |
| 19. D | 62.0 | 6.7 | 4.9 | 4.3 | 3.3 | 3.4 S |

Notes. D > 200 mg. S is suspension. ND – not detected.
1. Acetone*, the solubility parameter (δ) = 19.8 J^{1/2}cm^{-3/2}; class of polar selectivity is "VI". 2. 1-Butanol*, δ = 23.2; class of polar selectivity is "II". 3. 2-Butanol*, δ = 22.1; class of polar selectivity is "II". 4. Petrol **; class of polar selectivity is "0". 5. Freon-114B2 ****, δ = 15.09; class of polar selectivity is "V". 6. Freon-12 ***, δ = 12.5; class of polar selectivity is "V". 7. Diethyl ketone*, δ = 18.0; class of polar selectivity is "VI".
8. Diethyl carbonate*, δ = 18; class of polar selectivity is "VI". 9. m-Cresol *, δ = 22.7; class of polar selectivity is "VII". 10. Xylene*, δ = 18.0; class of polar selectivity is "VII". 11. Methylene chloride***, δ = 17.0; class of polar selectivity is "V". 12. Nitromethane***, δ = 25.2; class of polar selectivity is "VII". 13. 2-Propanol***, δ = 23.6; class of polar selectivity is "II". 14. Petroleum ether**; class of polar selectivity is "0". 15. Freon-113***, δ = 14.8; class of polar selectivity is "V". 16. Furane*, δ = 18.7; class of polar selectivity is "I". 17. Cyclohexane*, δ = 16.8; class of polar selectivity is "0". 18. CCl4*, δ = 17.8; class of polar selectivity is "V". 19. Ethanol***, δ = 26.6; class of polar selectivity is "II". Solvents: *with an index (δ) close to rosin; **are used for cleaning widely. Their value (δ) is difficult to determine due to a large range of boiling point (≤ 40 °C) and because of a large range of densities; ***are used for cleaning in the optical and microelectronic industries; ****does not contain chlorine, which destroys ozone, has a low boiling point – 47.35 °C, refers to halogen-substituted aliphatic hydrocarbons considered to be the most effective in cleaning of optics, has a smaller specific gravity – 2.3 g/cm³ and volatility, as well as has greater resistance to thermal heating and UV radiation in the presence of water and air.
Table 2. Amount of resin in the solvent.

| Solvent | Amount of resin in the solvent, mg |
|---------|----------------------------------|
|         | Dissolution cycles               |
|         | 1  | 2  | 3  | 4  | 5  | 6  | 7  |
| 1       | >200 | 58.4 | 9.1 | 7.0 | 1.1 |
| 2       | >200 | 55.3 | 8.9 | 6.8 | 3.2 | CD |
| 3       | >200 | 72.6 | 12.4 | 9.3 | 6.5 | CD |
| 4       | >200 | 62.0 | 11.9 | 9.8 | 6.1 | CD |
| 5       | >200 | 83.5 | 15.4 | 10.0 | 9.1 | 4.3 | CD |

Note. 1. Methyl ethyl ketone (δ = 19.0). Cyclohexanone (δ = 19.7). 3. Diethyl phthalate (δ = 20.5). 4. Ethyl formate (δ = 19.7). 5. 1,4-Dioxane (δ = 19.7). CD is complete dissolution.

In addition to it, there are other contaminants on the surface of the metal optics. The main mass of contaminants (up to 10% by weight) are various kinds of oils, greases and fats of mineral and animal origin. Such impurities are most effectively removed by chlorine-substituted hydrocarbons [22]. When choosing the optimum solvent for such impurities, we mainly used solvents with a class "V" of polar selectivity.

As a model contamination, we used spindle and diffusion (VM-5) oils and grease from human hands. These impurities (total amount of 100 mg, taken in equal proportions) were applied to copper mirrors (Mob grade copper), previously purified by acetone. Data on the amount of pollutant that passed into the solvent after each cycle of their contact were determined on the EF-3MA fluorometer (table 3).

Table 3. Number of model pollutant.

| Solvent | Number of model pollutant, mg |
|---------|--------------------------------|
|         | Dissolution cycles |
|         | 1  | 2  | 3  | 4  | 5  | 6  | 7  |
| 1       | 12.8 | 10.4 | 9.3 | 8.2 | 7.5 |
| 2       | 24.1 | 18.1 | 11.3 | 9.2 | 8.0 | 6.5 | 3.2 |
| 3       | 25.0 | 18.9 | 12.2 | 9.6 | 8.1 | 6.9 | 4.0 |
| 4       | 41.0 | 25.1 | 14.9 | 10.9 | 8.1 | CD |
| 5       | 80.0 | 20.0 | CD |
| 6       | 45.0 | 29.4 | 16.2 | 8.5 | CD |
| 7       | 51.0 | 25.1 | 16.9 | 7.0 | CD |
| 8       | 23.2 | 14.1 | 10.6 | 7.8 | 6.9 | 4.9 | 2.0E |
| 9       | 21.1 | 15.8 | 13.9 | 10.9 | 7.9 | 5.1 | 1.5E |
| 10      | 38.5 | 22.1 | 17.2 | 13.9 | 8.5 | CD |
| 11      | 76.1 | 23.9 | CD |
| 12      | 65.9 | 30.9 | 3.2 | CD |
| 13      | 20.0 | 15.1 | 13.1 | 10.5 | 7.9 | 5.3 | 1.0E |

Note. 1. Acetone*. 2. 1-Butanol*. 3. 2-Butanol*. 4. Gasoline*. 5. Freon-114B2*. 6. Freon-12. 7. Methylene chloride. 8. Nitromethane*. 9. 2-Propanol*. 10. Petroleum ether*. 11. Freon-113 12. CCl₄. 13. Ethanol*.
E is an emulsion.
CD is complete dissolution.
As it was shown in our experiments, the most effective model pollutant is dissolved by halogenated hydrocarbons: after 2–3 cycles it dissolves completely. However, the cleaning of optics by halogen-substituted hydrocarbon solvents was accompanied by a number of negative aspects: on the surface to be cleaned, a white coating was visually observed, and also appeared iridescent stains, that worsened the optical characteristics of the metal.

From the practice of optical processing of nonferrous metals we know that this coating consists of salts of alkaline and alkaline earth metals, relatively poorly soluble in organic solvents, especially in hydrocarbons and their halogenated derivatives, somewhat better – in alcohols, amides, sulfoxides, ketones, nitro derivatives and water [23]. This assumption was tested on solvents of these classes with different solubility parameters after removal of rosin pitch and oil contaminants from the surface. The dissolution cycle time was 5 minutes; the presence of impurities (white coating) on the surface was evaluated visually after each cycle of processing of the optical element. The data on the presence of inorganic salts on the surface of the metal after each contact with the solvent are shown in table 4.

Table 4. The presence of inorganic salts on the surface.

| Solvent          | Dissolution cycles | Note  |
|------------------|--------------------|-------|
|                 | 1  | 2  | 3  | 4  | 5  |      |
| 1.               | NWC |    |    |    | IS |       |
| 2.               | NWC |    |    |    |    |       |
| 3.               | NWC |    |    |    |    |       |
| 4.               | NWC |    |    |    | IS |       |
| 5.               |    |    | WC |    | IS |       |
| 6.               |    |    | WC |    |    |       |
| 7.               | NWC |    |    |    | IS |       |
| 8.               | NWC |    |    |    |    |       |

Note. NWC – no white coating. WC – white coating. IS – iridescent stains. 1. Acetone. 2. 1-Butanol. 3. 2-Butanol. 4. Water (δ = 47.2). 5. Dimethylformamide (δ = 24.4). 6. Nitromethane. 7. 2-Propanol. 8. Ethanol.

4. Conclusions
Water and aliphatic alcohols most effectively dissolve inorganic salts that are present on the surface. After 1–2 cycles, the white coating from the surface disappears.

Along with the effective removal of the model contaminant, halogenated hydrocarbons interact with the metal of the mirror, causing a degradation of the optical characteristics. In connection with this, when using these solvents, it is necessary to inhibit the process of interaction of halogenated hydrocarbons with the surface of mirrors by stabilizing the solvents or by selecting the regimes for carrying out the physicochemical purification process, or by thereof combination.

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