https://doi.org/10.21122/2227-1031-2025-24-1-12-23

UDC 621.9.048.7: 621.375.826: 621.373.8: 546

# On Energy Efficiency Characteristics of Laser Erosion on Oxidic Surfaces of Carbon Steels, Cast Iron and Low-alloy Non-ferrous Alloys During Deoxidizing Cleaning

**Part 1**

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**Abstract.** A comparison of operating characteristics has been carried out for laser erosion cleaning (LC) processes studied in recent years and prospective for metalworking manufacturing of products/pieces from a number of carbon steels, cast iron and low-alloy non-ferrous metal alloys from oxidized layers formed as products of gas or other corrosion, often having inhomogeneous structure and porosity. To analyze the efficiency of various (in terms of layer composition) laser processes, it is advisable to use a group of parameters that affect the energy efficiency of LC-processing during the deoxidizing of surfaces. This group includes: a) the time-integrated energy criterion ($K_{en1s}$) of heating up to the melting point and/or evaporation temperatures of the layer and, sometimes, a metal substrate located underneath it (or the thermochemical efficiency of the heating, which is derived from the $K_{en1s}$), determined from energy consumption; b) irradiation power per surface unit ($N_0$), or the ratio of $N_0$ to the thermal conductivity of the layer; c) the pressure amplitude of the shock wave (SW) front in the laser plasma near the surface ($P_{sw-p}$) or the dimensionless parameter that includes it, equal to the ratio of $P_{sw-p}$ to the shear stress for the oxidized layer/metal substrate interface. The dimensionless $K_{en1s}$ criterion (or similar ones) will be more convenient in some cases for modeling and scaling of LC-processes than dimensional complexes, including thermal criteria such as DMF ("difficulty of melting factor"), which were tested in calculation of plasma spraying of ceramic materials. In this group of efficiency parameters, such a characteristic as the normalized (for example, with $K_{en1s}$) Peclet number, which characterizes the rate of propagation of the melting (or evaporation) boundary along the surface when scanning the beam, is also applicable. The considered characteristics, based on preliminary data, make it possible to evaluate the contribution of the mechanisms of the layer removal during pulsed LC, i.e.: 1) thermal effect ("ablation") with "slow" heating to the melting point of the oxide (or to its evaporation temperature) in thermodynamically quasi-equilibrium regimes; 2) initiation of thermoelastic stresses in the crystal lattice of oxide phases under the impact of high power pulse, resulting in the formation of a network of cracks in the oxide film and its exfoliation from the metal substrate ("spallation", it is approximately characterized by the maximum stress achieved during LC at the film/substrate interface); 3) plasmadynamic mechanism of the action of pressure on the surface due to the generation of near-surface plasma with a shock wave in it (with a pressure amplitude of up to $\geq$10 MPa). When assessing LC-processes taking into account efficiency characteristics, it is advisable to use a special set of verified data selected according to the thermophysical properties of layers of an analyzed type.

**Keywords**: laser erosion, cleaning of metal pieces, oxidized surface, steels, non-ferrous metal alloys, energy efficiency characteristics, mechanisms of layer removal, oxides, surface deoxidizing, energy/power consumption

**For citation:** Devoino O. G., Gorbunov A. V., Shpackevitch D. A., Lapkovsky A. S., Gorbunova V. A., Koval V. A., Kovaleva S. A. (2025) On Energy Efficiency Characteristics of Laser Erosion on Oxidic Surfaces of Carbon Steels, Cast Iron and Low-alloy Non-ferrous Alloys During Deoxidizing Cleaning. Part I. *Science and Technique*. 24 (1), 12–23. https://doi.org/10.21122/2227-1031-2025-24-1-12-23 (in Russian)

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# О характеристиках энергоэффективности лазерной эрозии при очистке от оксидов поверхностей углеродистых сталей, чугуна и низколегированных сплавов металлов

**Часть 1**

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**Реферат.** Проведено сравнение технологических характеристик изучаемых в последние годы и актуальных для металлообрабатывающего производства процессов лазерной эрозионной очистки (ЛО) изделий из ряда углеродистых сталей, чугуна и низколегированных сплавов цветных металлов от оксидных слоев из продуктов газовой или иной коррозии (часто имеющих негомогенную структуру и пористость). Для анализа эффективности различных (по составу слоев) лазерных процессов целесообразно использовать группу параметров, влияющих на энергоэффективность ЛО при деоксидировании поверхности. К этой группе отнесены: а) интегральный по времени энергетический критерий ($K_{en1s}$) нагрева до температур плавления и/или испарения слоя или (иногда) расположенной под ним металлической основы (или производный от $K_{en1s}$ термохимический КПД нагрева), определяемый по энергозатратам; б) мощность (амплитудная или иная) излучения на единицу поверхности ($N_0$) или отношение $N_0$ к теплопроводности слоя, а также в) амплитуда давления фронта ударной волны (УВ) в лазерной плазме вблизи поверхности ($P_{sw\text{-}p}$) или включающий ее безразмерный параметр, равный отношению $P_{sw\text{-}p}$ к напряжению сдвига для границы оксидный слой / металлическая основа. Безразмерный критерий $K_{en1s}$ (или аналогичные ему) в ряде случаев будет удобнее для моделирования и масштабирования процессов ЛО, чем размерные комплексы, например тепловые критерии типа DMF (“difficulty of melting factor”), апробированные ранее в расчетах плазменного напыления керамических материалов. В данной группе параметров эффективности применима и такая характеристика, как нормированное (например, по $K_{en1s}$) число Пекле, характеризующее скорость движения границы плавления (или испарения) вдоль поверхности при сканировании луча. Рассматриваемые характеристики по предварительным данным позволяют оценить вклад основных механизмов удаления слоев в ходе импульсной ЛО: 1) теплового воздействия (“ablation”) с «медленным» нагреванием до точки плавления оксида (или до его испарения) в термодинамически квазиравновесных режимах; 2) инициирование термоупругих напряжений в кристаллической решетке фаз оксидов при воздействии импульса с высокой удельной мощностью, с образованием за счет этого сетки трещин в оксидной пленке и ее отслаиванием от металлической основы (“spallation”, приближенно характеризуемое достигаемым максимальным напряжением на границе пленка/основа); 3) плазмодинамический механизм действия фронта УВ на поверхность за счет генерации околоповерхностной плазмы с локальной УВ (с амплитудой давления до ≥10 МПа). При оценке процессов ЛО с учетом характеристик эффективности целесообразно использовать массив верифицированных данных, подобранных по теплофизическим свойствам слоев данного типа.

**Ключевые слова:** лазерная эрозия, очистка металлоизделий, окисленная поверхность, стали, сплавы цветных металлов, характеристики энергоэффективности, механизмы удаления слоя, оксиды, деоксидирование поверхности, энергозатраты

**Для цитирования:** О характеристиках энергоэффективности лазерной эрозии при очистке от оксидов поверхностей углеродистых сталей, чугуна и низколегированных сплавов металлов. Часть 1 / О. Г. Девойно [и др.] // *Наука и техника.* 2025. Т. 24, № 1. С. 12–23. https://doi.org/10.21122/2227-1031-2025-24-1-12-23

## Introduction and research task

A significant task for machine building and metalworking industries is the replacement of mechanical and thermal methods for cleaning the surfaces of metal parts from unwanted oxidized layers, i.e. rust and scale composed of mixture of oxidic compounds of Fe(II) and Fe(III) on steels and similar layers on some non-ferrous metal alloys [1–21]. Removal of layers of these types using modern high energy processing techniques, in particular, laser methods, as efficient and environmentally acceptable ones, has been actively developed in recent years with the aim of commercialization. At the same time, work is underway to automatize laser cleaning (LC) from oxide layers of types mentioned to ensure optimal cleaning duration and energy consumption [1, 4, 6]. In this case, it is important to measure and analyze the levels of parameters that determine the LC efficiency in order to select power-efficient variants for removing these corrosion-induced surface layers from metal products. The overview of current data [1–9, 11–21] on LC-processes for oxides removal from important grades of steels and some alloys shows the presence of published results on the regimes of removing at least ten types of layers (up to 1–2 mm thickness) that form oxidized compounds on the surface of a number of steels and alloys: mixed $FeO_x$ in the form of scale or rust on carbon steels, similar ones on the cast irons (gray one, etc. [5, 15]), the films based on $Al_2O_3$ on aluminum alloys, the films of CuO and $Cu_2O$ on copper and its alloys, the film based on titania on titanium alloys, the film based on ZnO on zinc alloy, the film based on MgO on magnesium alloy, the films of $WO_3$–type on tungsten parts, the films based on PbO (with impurities, e.g. $PbCO_3$ salt) on lead alloys, film based on $Ag_2O$ + AgO (with impurities) on silver alloy.

At the same time, the characteristics of power efficiency of laser erosion during surface deoxidizing of carbon steels and metal alloys can be of considerable importance for the optimization of efficiency of laser processes (and the corresponding technologies) that differ in the regimes and oxidic layer composition, and in this regard, the selection and testing of these characteristics are of significant interest and can be taken as the task of our investigation as applied to the processes of LC from oxidized heterogeneous layers on steels and alloys of the specified group. It is also important that, according to data overviewed, there are still few studies aimed at solving this problem, including those related to the comparison of the power efficiency parameters of LC-processes for different oxidic layers on the metals.

## Possible parameters for evaluation of the power efficiency of processing in the technology of laser removal (LR) of oxidic layers

For a comparative analysis of the efficiency of various (by the composition of removed layers) laser processes, it is possible, based on the data of our preliminary analysis, to use a group of parameters that characterize to a certain extent the power efficiency (energy productivity level) of processing, including: a) the time-integrated dimensionless energy criterion ($K_{en1s}$) for heating to the melting or evaporation temperatures of the layer (or such derived value as thermochemical efficiency of the heating), which can be measured as the value based on the specific energy input; b) the specific power (amplitude value or time-averaged one) of irradiation per unit of the surface ($N_0$ = power density); c) the amplitude of the pressure of shock wave (SW) front in partially ionized gas/laser plasma near the surface ($P_{sw\text{-}p}$).

Let us approximately express the energy consumption of laser irradiation (LI) in J per kg of oxidic material, absorbed in solid removed layer due to thermal conductivity [10] at the stage of heating of the oxide being removed (at LC) from the initial temperature to its melting point $T_m$ in the form:

$$Q_{1w} = \frac{\kappa_1 \Delta T_1 \, t_1}{\rho_1 S}, \tag{1}$$

and the cleaning rate (in m$^2$ of material per second) for steady regime of the processing can be specified:

$$G_w = \frac{d_s^2}{t} = v \, d_s, \tag{2}$$

where $t_1$ – the time for surface heating from the initial temperature (~298 K) to the $T_m$ of the layer; $d_s$ – the diameter of laser spot on the heated surface; $S$ – the spot area; $v$ – the linear scanning speed of the beam along the surface; $\Delta T_1 = T_m - T_0$ (where $T_m$ and $T_0$ are the temperatures of the layer at the melting point and at standard conditions (298 K), respectively), $\kappa_1$ and $\rho_1$ are, respectively, the characteristic values of thermal conductivity and density of the layer for $\Delta T_1$. It should be noted that in the considered group of parameters of power efficiency of the LC-process, the energy criterion according to A.L. Suris can be also used, which, apparently, is applicable for the considered process, by analogy with high-temperature technologies for plasma reactor production of some ceramic materials [22]. In incomplete version, i.e. considering only conductive heat transfer to condensed phase in the axial direction within the LI spot (given by equation (1), in the system for the LC process of oxidic layers) it can be written as a dimensionless ratio:

$$K_{en1} = \frac{Q_{1w}}{Q_{1w-ox}}. \tag{3}$$

The value of $Q_{1w-ox}$ can be found as the thermal effect of heating the layer $\Delta H$ (in units of J per kg of the initial layer), calculated on the equilibrium approach, determined by the value of the parameter $EC$ (at $T = T_m$). A more complete variant of this $K_{en1s}$ (which takes into account not only the conductive heat flux into heating spot zone in the axial direction, but also other mechanisms of heat transfer which occur in all directions in the system for the LC) can be specified, by analogy with the efficiency parameter (the energy efficiency) of plasma-chemical systems [23, 24], with a different ratio:

$$K_{en1s} = \frac{E_{1w}}{Q_{1w-ox}}. \quad (4)$$

Here $E_{1w}$ – total value of energy consumption of the LC-processing (for such case of the process as laser heating to melting point of the surface layer) in units of J/(kg of removed oxidic layer). The energy consumption for the LC process of the analyzed type at a processing steady regime can be found as:

$$EC_{1w} = \frac{Aq_0 t_s}{\rho_{sl}\delta_{sl}}, \quad (5)$$

where $A$ – absorptance for LI on the surface; $q_0$ – power density of incident irradiation on the surface (in W/m$^2$ units); $t_s$ – averaged time (duration) of heating of each surface point (i. e. full exposure time at LC per surface unit); $\rho_{sl}$ and $\delta_{sl}$ – density and thickness of heated (up to required temperature) layer, respectively.

The above-mentioned parameters $EC_{1w}$ and $EC_{0w}$ (defined in $W$ per 1 kg of heated oxidic layer, and the value of $EC_{0w}$ differs from expression (5) only by the absence of the absorptance $A$ in the ratio) are expressed as some functions from the value of energy consumption $EC_0$ and similar value $EC_1$ per unit (i.e. in units of W/(m$^2$ of heated (visible, i. e. neglecting the porosity) surface area of the layer)).

Also, taking into account the approach using the methods of similarity theory and previously used for modeling of heat transfer and energy balances in laser cutting of steels [25], such dimensionless similarity criteria can be adopted to calculate the energy parameters of the LC-processes of the oxides (Table 1): a) the Peclet number Pe (which can be considered as the normalized (with thermal diffusivity) rate of laser processing of the material) and b) the dimensionless power of absorbed LI by the surface material $W_{lp}$. The thermal diffusivity (used in the Pe) is expressed as $a = \kappa/(\rho \cdot c_p)$, where $\rho$ and $c_p$ are the density and specific heat capacity (in J/(kg·K)) for oxidic layer, averaged for the full temperature range under consideration. The value of the enthalpy difference for the material $\Delta H$ can be calculated using different variants, depending on the required maximal temperature of the LC-process (e. g. $T_b$ or $T_m$), selected for technological reasons, and on the accuracy of calculations required:

$$\Delta H_1 = \int_{T_0}^{T_m} c_{p,s}\,\mathrm{d}T + \Delta H_m + \int_{T_m}^{T_b} c_{p,l}\,\mathrm{d}T + \Delta H_v \quad (6)$$

(it is the variant for heating with layer melting and vaporization ($\Delta H_v$ – heat of vaporization; $\Delta H_m$ – heat of melting). For the case of heating only to melt, the $\Delta H_2$ value (i.e. form (7)) includes the first two terms of (6).

The dimensionless $K_{en1s}$ criterion (or similar thermal parameters), according to our preliminary estimation (by analogy with the previously used variant of this criterion in high-temperature technologies of plasma processing of ceramic and other materials, as, for example, in [22]), in some cases will be more suitable for simulation and scaling of the LC-processes with oxide melting than dimensional complexes based on such thermal engineering criteria as DMF (“difficulty of melting factor”) and similar ones, tested earlier (in [26–29], etc.) in calculation of some plasma spraying technologies with ceramic powders. As an analogue of this $K_{en}$ criterion, such dimensionless “REC coefficient” (i.e. the degree of conservation of thermal energy in heated material during ablation process), proposed in [30] for energy balance calculations of surface laser heating processes with metal ablation, can be also considered.

**Estimation of thermal characteristics of the operating process, including the mechanism with a shock wave and power efficiency parameters during laser removal of oxidic layers**

The group of parameters that was selected to characterize the physical mechanisms of removing oxidic layers during LC of the steels and alloys is given in Table 1. For the realization of calculations to evaluate these mechanisms our prepared data set (Table 2), based on [31–81] properties, can be also used.

It is important, that as shown in [82], under LC conditions with pulsed lasers, the “shock wave ejection mechanism” prevails at intensive laser plasma (in terms of dynamic effect on surfaces) rather than the mechanism of photon pressure from the LI-beam. It is possible to use also some dependencies when using the approach described in Table 1 (taking into account the data [83]) for estimation of such parameters of SW, as the temperature of its front (according to equations (3 and 5) in [84]), and its density [85].

*Table 1*

**Set of proposed parameters for characterizing the main mechanisms of removing oxidic layers during LC-processing of the carbon steels and some alloys**

| Layer removal mechanism | Key parameters for this mechanism, their dimensions | Formula for the parameter |
|---|---|---|
| 1) thermal quasi-equilibrium heating (with melting or/and evaporation of the layer on metal substrate), i. e. thermal ablation | Energy criterion $K_{en1s}$ and thermochemical efficiency for the heating $\eta_{TC}$ (dimensionless); energy consumption for LC-processing of the removed layer $E$' (in J/kg) | $K_{en1s}$ – on the equation (4),<br>$\eta_{TC} = \alpha_{TC}/K_{en1s}$,<br>where $\alpha_{TC}$ – conversion degree of the initial solid oxidic material to final product form (liquid or other) |
| 2) dynamic (generation of thermoelastic stress to destruct solid layer and/or its exfoliation from the metal), i. e. "spallation" | Specific absorbed power $N_0$ (in W/m$^2$) and the parameter $N_0/\kappa$ (in K/m), i. e. the ratio of $N_0$ and the value of thermal conductivity of the removed layer | $N_0 = P_0/S$,<br>where $P_0$ – initial (excluding partial reflection of the laser irradiation by oxidic surface) power of the laser beam (in W) and $S$ is the area of LI-spot on the surface (when the beam is directed normal to the surface $S = \pi d^2/4$) |
| 3) plasma effect (gas dynamic action of the shock wave (SW) from the laser plasma on the solid surface of removed layer), i. e. the "shock wave-mechanism" | The pressure amplitude of the shock wave front $P_{sw\text{-}p}$ (in Pa) or the dimensionless parameter $P_{sw\text{-}p}/\tau_A$ (where $\tau_A$ is the shear stress (in Pa) for the (oxidic layer/metal substrate)–interface | $P_{sw\text{-}p}$ can be calculated by several methods (in particular, with use of three proven variants for laser plasma [83–88]):<br>$P \approx \Delta P = \frac{8}{25}\left(\frac{1}{\gamma+1}\right)\left(\frac{E_p}{R_s^3}\right)Y^4$ (variant I on [83] (*));<br>$P = 32.2\left(\frac{\alpha}{2\alpha+3}\right)^{2/3}\rho_0^{1/3} I_0^{2/3}$ (variant II [88] (**));<br>$P = \left(\frac{P_1}{\gamma+1}\right)\left(\frac{2\gamma-(\gamma-1)M_s^{-2}}{M_s^{-2}}\right)$;<br>$t = \left(\frac{2}{5c}\right)^{5/3}\left(\frac{E_p}{\alpha_1\rho_0}\right)^{1/3} M_s^{-5/3}\left(1+\beta M_s^{-2}\right)$, and<br>$\beta = \omega(k+1)(k+2)/\left[k(2+3k)\right]$<br>(last three equations can be used to calculate SW front pressure (for the moment $t$ (≈ LI-pulse duration)) on variant III [84, 86, 87] (†)) |
| Additional key parameter (dimensionless): Peclet number Pe for the process of heating of the removed oxidic layer during the LC-process | | $\mathrm{Pe} = \frac{vd}{a} = \frac{G_{1w}}{a}$<br>(optionally can be also possible to use one more variant with normalization of Pe number (e.g. with $K_{en1s}$ value for LC-process) |

*Symbols*: $G$ – layer removal rate; $a$ – thermal diffusivity of the layer; $v$ – scanning speed of the laser beam along the surface; $d$ – diameter of the spot on the surface (with the beam directed normal to this).

*Notes*: * – in this variant I: $\gamma$ – heat capacity ratio (the ratio of specific heats) for gas in SW zone (most typically for air, $\gamma = c_p/c_v$ = 1.40 (at 293 K, 0.101 MPa)); $R_s$ – radius of SW, $Y = f(\gamma) = 1.03$ [83]);

** – this equation (for the variant II) uses the value of pressure $P$ (in kbar, i.e. $10^8$ Pa), the values of density $\rho_0$ (in g/cm$^3$) and specific power of LI pulse $I_0$ (in GW/cm$^2$); here the values of the coefficient of interaction efficiency in SW $\alpha$ were recommend as 0.25 (at $\lambda \approx 1064$ nm [88]) and as 0.40 (at such $\lambda$ values as 532 and 355 nm) [89];

† – in this variant III: $M_s$ – Mach number (amplitudic), $c \approx 346$ m/s – sound velocity in air (at 298 K and at pressure $P_1$ = = 0.101 MPa [84]); $E_p$ – energy (maximal) of pulse of LI that is incident on surface (in J), $\alpha_1 \approx 0.8$ is gas dynamic constant for air [84], $\beta \approx 1.21$ is the special aerodynamic parameter [84, 87], $\omega = 2.0$ is the gas dynamic coefficient [84], $k = 3$ is a dimension (for 3D geometry of the SW) for the analyzed spherical SW).

*Table 2*

**Physical and chemical properties (including standard enthalpy of formation $\Delta_f H^0$, thermal effects of phase transitions ($\Delta H_m$, $\Delta H_v$), total enthalpies of heating of phases to their melting and boiling temperatures ($T_m$, $T_b$), specific heat capacity $c_p$), absorptance $A$, thermal conductivity κ and thermal diffusivity $a$ for oxides that are components of oxidized layers on some steels and structural materials subjected to laser cleaning (basically for conditions at the pressure $P \approx 0.1$ MPa)**

| Composition | $\Delta_f H^0$, MJ/kg | $\Delta H_m$, MJ/kg; $\Delta H_v$, MJ/kg | $c_p$ (at 298 K and at $T \to T_m$), J/(kg·K) | $T_m$, K | $T_b$, K | $\Delta H_1$ on the equation (6), MJ/kg | $\Delta H_2$ on the expression (7), MJ/kg | Thermal conductivity (at 298 K and at $T \to T_m$) κ (*), W/(m·K) | Density (at 298 K and at $T \to T_m$) ρ (*), kg/m$^3$ | Thermal diffusivity $a$ (at 298 K and at $T \to T_m$) $a$ (*), m$^2$/s (·10$^6$) | Absorptance of LI $A$ (at wavelength λ ≈ 1.064 μm) at $T \approx 300$ K (if not specified otherwise) for smooth samples |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 |
| Hematite $Fe_2O_3$ | –5.169 [31]) | 0.5448 ([32]); no reliable data (n.d.) | 652.52; 913.03 (at 1800 K) [31] | 1812 (†) [32] – 1838 [8] | 2973 [8] | – | ~1.87 (on the combination of data [31, 32]) | 0.58 [34, 35], ~1.0–2.0 (†) (at 300 K); ~3.3 (at $T_m$ [75]) | 4900 [39], 5240 [32], 5260 [35], ~5050 (†) (at 300 K); 4950 (at $T_m$ [75]) | ~0.70 (♦) (at 293 K) [38, 39]; ~0.73 (at $T \approx T_m$ [75]) | 0.60 (◊) [8]; 0.69 (†) [40, 41] |
| Magnetite $Fe_3O_4$ | –4.841 [31]) | 0.5960 ([32]) – 0.5967 ([33]); 1.287 [33] | 637.92; 867.26 (at 1800 K) [31] | 1870 [32] | 2896 [32], 3273 [8] | ~4.06 (on the combination of data [31–33]) | ~1.88 [31] | 3.50 (at 300 K [42]); ~3.0 (at $T_m$ [75]) | 5100 (†) (at 298 K); 4850 (at $T_m$) [75] | 1.06 (at 300 K) and ~0.713 (at $T \approx T_m$) [75] | 0.815 (†) (averaged value); 0.53 (◊) [8]; 0.80–0.83 [40, 43] |
| Wüstite $Fe_{1-x}O$ (at $x \leq 0.06$) | –3.787 [31] for FeO); –3.868 [44] for $Fe_{0.947}O$) | 0.3354 (for FeO) [32], 0.4547 (for $Fe_{0.95}O$) [33]; 3.34 (at $T_b$ = = 2785 K for ~FeO) and ~6.28 (for $Fe_{0.95}O$) [33] | 695.53; 891.24 (at 1600 K) [31] | 1642–1644 (at FeO) [75] | 3687 [45, 46], 2785 (for FeO) [33], (3200-3400 – on calculation [75]), 3000 (†) | ~6.05 (for FeO) on the combination of data [31–33], [45, 46, 75] | ~1.42 (for FeO) on the combination of data [32] and [31] | 1.80 (at 300 K [47]); ~4.3 (at $T_m$ [75]) | 6000 [32], 5870 [33], ~5950 [47], 7750 [39], ~6000 (†) (at 300 K); ~5450 (at $T_m$) [75] for FeO | 0.42 (at 300 K); ~0.873 (at $T \approx T_m$ [75]) | 0.81 (†) (averaged value); 0.81 [40, 48]; for FeO-melt – 0.70 (***) (at λ = = 600–1064 nm at $T > 2000$ K) [74, 75] |
| $Al_2O_3$ | –16.435 ±0.013 (corundum, i. e. α-$Al_2O_3$ phase) [32, 33] | 1.090 [32], 1.109 [31], 1.093 [51], 1.068 [52], 1.149 [53], 1.162 (†) [17, 50], 1.093±0.029 [54]; 4.763 (†) [33] – 4.760 [53] | 772.56; 1361.32 (at 2300 K) [31] | 2327 [32] – 2288 [52] | 3253 [33, 52] – ≥3273 [51] | ~9.92 (on the combination of data [31] for α-$Al_2O_3$ and [32], [33], [17, 50]) | ~3.41 (on the combination of data [31] for α-$Al_2O_3$, [32] and [28, 50]) | 35.0 (at 273 K) and 8.0 (at 973 K) [32], 35.0 (at ~300 K) [36] (sintered ceramics); 30.0 (at 373 K) and 7.4 (†) (at 2073 K) for ceramics (with ρ = 3800 kg/m$^3$) [32]; from 28.9÷30.3 (at 373 K) to 5.78÷6.07 (at 1873 K) and 9.0 (at 2273 K) [33]; for $T$ = 300÷2070 K on the equation (‡) from [81]; 27.0 (~at 300 K) [55]; ~7.0 (at 2300 K) [57]; ~34.0 (at 300 K) (†) | For α-$Al_2O_3$ – 3970 [32, 33] ÷ 3986 [32] (α-$Al_2O_3$ at 300 K), 3987 (†) [28, 50]; 3750 (†) (at $T \to T_m$ [57]) | 11.04 (†) (§ – at 298 K); from 0.96 (at 473 K) to 0.48 (at 1473 K) for sprayed coatings with δ ≈ ≈ 320 μm ($p$ ≈ 2.2 %) [59] and close level in [68]; ~1.15 (for ~2200 K) [58], ~1.39 (†) (§ – for 2300 K on the properties from [32, 31, 33, 57]) | Decrease from 0.74÷0.79 (†) (at 273–400 K) to 0.39÷0.43 (at 1773–1800 K) [33] (***); from 0.22 (at 1073 K) to 0.56 (at 1873 K) for λ = 0.665 μm and 0.12 (at 1273 K) for λ = 1.0–3.0 μm) for powders of $Al_2O_3$ [33] (⁝), ~0.75 (for λ ≈ 10.6 μm, at ~300 K) [56, 36] |

*Continuation of Table 2*

| 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 |
|---|---|---|---|---|---|---|---|---|---|---|---|
| MgO | –14.927 ±0.007 [31, 32] | 1.922 ± 0.104 [33], 1.910 [32], 1.920 [53], 1.918 ± 0.144 [54]; 13.504 [33] 11.772 **(†)** [53] | 918.27; 1391.18 (at 2100 K) and 1475.78 (at 3100 K) [31] | 3098 [32, 53] | 3873 [32], 3873 [53] | ~18.45 (on the combination of data [31], [32] and [53]) | ~5.39 (on the combination of data [31] and [32]) | From 36.0 (at 373 K) to 5.8 (at 1473 K) and 9.2 (at 1973 K) [32]; from 34.5÷40.0 (at 373-400 K) to 9.0÷14.0 (at 2073-2273 K) [33] ]; ~36.0 (at 300 K) **(†)** | 3650 [33], 3579 – 3600 **(†)** [32] (at 300 K); ~3500 (at $T \rightarrow T_m$ ) | 10.92 **(†)** (at 298 K); ~2.05 **(†)** (§ – for (1973÷2273 K) on the properties from [32, 31, 33]) | Decrease from 0.72÷0.73 **(†)** (at 273–400 K) to 0.29÷0.31 (at 1773–1800 K) and 0.58 (at 2300 K) [33] (***); from 0.17 (at 1073 K) to 0.44 (at 1873 K) for λ = 0.665 μm and 0.28 (at 293 K) for λ = 1.0 μm) [33] (⁝) |
| $TiO_2$ | –11.820 (rutile) [32, 31] and –11.754 (anatase) [31] | 0.851 (rutile) [32], 0.839 (rutile) [33], 0.838 (anatase) [53], 0.577 (rutile) **(†)** [28, 50]; 7.496 [33] | 690.91 (at 298 K) and 972.00 (at 2000 K) (rutile); 691.16 (at 298 K) and 971.88 (at 2000 K) (anatase) [31] | 2116÷ 2185 (rutile) and 1833 (anatase) **(†)** [32], 2143 (rutile, in $O_2$-medium) [33, 53]; ~2150 (rutile, at 300 K) **(†)** | 3200 (with decomposition) **(†)** [33], ~3273 [32] | ~11.12 (rutile) – ~11.21 (anatase) (on the combination of data [31], [32] and [33]) | ~2.30 (rutile) – ~2.00 (anatase) (on the combination of data [31] and [32]) | 9.0÷13.0 (rutile at 273 K) [32], 6.5 (at 373 K) [32], from 6.53 (at 373 K) to 3.31 (at 1273-1473 K) [33], from 5.2÷5.9 (at ~300 K) to 3.9 (at 773 K [61]) and up to 2.85 (at 1073 K [60]) for high density polycrystalline ceramics; ~11.0 (rutile) and ~6.5 (anatase) (at ~300 K) **(†)** | 3900÷4230 (anatase) **(†)**, 4170 and 4230÷4260 (rutile) **(†)**, 4170 (brookite) [32] (при ~300 K); 4245 [28, 50]; 4235 (rutile), 4120 (anatase), 4050 (brookite) [53] (at ~300 K); 4066 (at 1873 K [62]) | ~3.75 for rutile **(†)** and ~2.32 **(†)** for anatase (§ – at ~300 K); ~0.838 for rutile (§ – at ~(1473÷ 2000 K)) | Increase from 0.82 **(†)** (at 400 K) to 0.90 (at 1300 K) [33] (***), in vacuum; 0.27 (at 1223 K) for λ = 1.0 μm) for powder of $TiO_x$ [33] (⁝) |
| Film of $TiO_2$ (mixture of rutile and anatase) with impurity of $Ti_2O_3$, at δ ≈ 20 μm [63] (~50 μm [7]) on the TA15 alloy [7, 49] | ~(–11.8) (our estimation with taking into account the data for rutile and anatase on [32, 31]) | Approximately 0.577 (as for rutile on the data [28, 50]); 7.496 [33] | 1264 [7, 49] | 2123 [49] – 2184 [7] | 3673 [7] | ~11.12 – 11.21 (by analogy with the data for individual $TiO_2$) | ~2.00 – 2.30 (estimation, – by analogy with the data for individual $TiO_2$) | 0.62 [49] ÷ ÷ 10.4 **(†)** [7] | 4320 [49] | ~1.905 (§ – at ~300 K based on the data [7]) | 0.30 [7], 0.45 [49], 0.58 (***) **(†)** [49] (~at $T \geq 298$ K) |
| Tenorite CuO | –1.962 [31], –1.977 [32] | 0.468 **(†)** [33], 0.616 [32], 0.700 [53]; n.d. | 531.02; 746.75 (at 1500 K) [31] | 1500 **(†)** [32], 1609 [33], 1720 [53] (‴) | n. d. | – | 1.276 (on the combination of data [33], [31] and [32]) | 1.01 (at 318.8 K) [33]; ~33.0 [64] | 6310 **(†)** [32], 6400÷6450 [33] | ~0.301 **(†)** (§ – at ~318.8 K) | 0.798 **(†)** (our calculation from the data [2, 65]); ~0.80 (at 1100 K) [67] (***) in air |
| Cuprite $Cu_2O$ | –1.193 [31]), –1.192 [44]) | 0.458 **(†)** [32], 0.449 [53]; n.d. | 437.06; 670.83 (at 1500 K) [31] | 1517 **(†)** [32], 1515[33], 1513 [53] | 2073 (with decomposition) [33] | – | 1.139 (on the combination of data [31] and [32]) | 5.58 **(†)** (at 299 K) and 4.86 (at 360 K) [32] | 6000 [32] at ~300 K | ~2.13 **(†)** (§ – at ~299 K) | ~0.79 [69], 0.804 **(†)** (our calculation from the data [2, 65]) |

*End of Table*

| 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 |
|---|---|---|---|---|---|---|---|---|---|---|---|
| ZnO | –4.306 ± ± 0.003 [32, 31] | 0.8599 [32]; ~8.582 (heat of decomposition of ZnO [33]); n.d. | 495.0 ± 2.6 [33]; 494.0 [32] | 2247 [32, 33] | ≥ 2073 (with decomposition) [33] | – | 1.824 (on the combination of data [33] and [32]) | 23.4 (at 300 K), 17.0 (at 473 K) and 5.3 (at 1073 K) [32]; 0.595 (at 323 K for porous compacted powder sample) and from 17.05 (at 473 K) to 5.0 (at 1073 K) for dense polycrystalline sample [33]; ~17.0 (at ~300 K) **(†)** | 5600-5676 [32], 5660 **(†)** [33] (at 300 K) | 8.37 ÷ ÷ (6.08 **(†)**) (§ – at ~300 K) | 0.91–0.82 (at 1140–1330 K for single crystal sample) and increase from 0.24 to 0.63 (from 1160 K to 1500 K for powder of ZnO) [33] (***); ~0.90 **(†)** (at 298 K for single crystal sample at λ = 1.0 μm) [33] |
| Structural low carbon steel (SCS) | ~0 | ~0.2473 (SCS) **(†)** [32] – 0.270 (◊) [70] (in MJ/kg of steel); approximately 6.34–6.367 MJ/kg of steel | 440÷760 (for the range of 293÷ 873 K) and 650 at 1473 K [71]; ~920 (at ~1800 K for SCS Q345 [8] (♯)) | 1808 [8] (for Q345-type SCS (♯)) | 3023 [8] (for Q345 (♯)) | ~8.51 (estimated value, as for the Fe, with taking into account the data in [75]) | ~1.152 (estimated value, as for the Fe, with taking into account the data in [75]) | ~52.0 [8] (SCS Q345 (♯)) **(†)**, 49.8 [72, 73] (AISI 1095 steel); 30.24 (for SCS at 1623 K) [66]; 27.3 (for the range of 1073–1473 K) and 37.5 (at $T \leq 1073$ K [71]; 36.5 (for melt of SCS) [70, 75] | 7860 (at 300 K) [8] (for SCS Q345 (♯)) and [39] (for SCS with 0.08÷0.17 % fraction of carbon) | 14.9–15.1 **(†)** [39] and 19.0 (at 300 K) [76]; ~7.19 **(†)** (our recalculation for ~1800 K for SCS Q345 (♯)) [75] | 0.35 (◊) [8], 0.46 **(†)** [72–73] (SCS AISI 1095 †), 0.52 [40] (R4 ‡) and 0.30 [77] (AISI 1006 ††); 0.30–0.36 ($T \approx 300$ K) and 0.31–0.32 ($T \approx 1270$ K) for 35NCD16 ( ⁑ ) [79]; 0.35–0.38 (at 1809–3000 K) for SCS [78] |
| Aluminum alloy 6061 (95.8÷ ÷98.6 % Al, impurities of Mg, Si, Fe, Cu, Zn, Cr) [80, 55] | ~0 | 0.389 [80]; 10.50 [80] | 1050.0 [80]; 921.0 (for the melt) [80] | 933 [80] | 2703 [80] | ~13.18 (based on the data in [80]) | ~1.054 (based on the data in [80]) | 223 [80]; 106 (for melt of the alloy) [80] | 2549 [80]; 2224 (for the melt) [80] | 83.32 (при ~298 K); 51.75 (for the melt at $T > 933$ K) | 0.08 [80]; 0.20 (for the alloy melt) [80] |

**Nomenclature**: † – preferable parameter values for the practical use (for complicated cases at different published values of the parameter) – on our analysis recommendations; ◊ – for SCS of S235JR G2 grade (EU standard, composition in wt.% – 0.063% C, 0.41% Mn, 0.13% Si, 0.34% Ni, 0.10% Mo, 98.68% Fe) [70]; ♯ – Q345 SCS (PRC standard, its composition is 0.21 wt. % C, 0.96% Mn, 0.12% Si and up to 98.5% Fe) – Russian analogues - 09G2, 09G2S, 10G2B steel grades; * – parameter values were determined for material porosity $p = 0$; ♦ – parameter values were determined for porosity of sintered material $p = 20\%$; (‡) - for thermal conductivity of crystalline $Al_2O_3$ (in W/(m·K)) in the temperature range $T = 373$–2073 K, the approximation equation is: $\lambda_{Al2O3} = 93.81362 - 0.26631 \cdot T + 3.19292 \cdot 10^{-4} \cdot T^2 - 1.75732 \cdot 10^{-7} \cdot T^3 + 3.67188 \cdot 10^{-11} \cdot T^4$ [81]; *** – the values of $\varepsilon_{in}$ (normal integral emissivity) are given; ⁝ – the values $\varepsilon_{\lambda n}$ (normal monochromatic emissivity) are given; ‴ – for CuO (monoclinic) [53]; § – our calculation based on the given (in publications) values of properties (including κ, $c_p$, ρ) for a shown substance (at the specified $T$).

## Methodology for experimental investigation of laser cleaning of the oxide layers

A comparative description of the experimental data, including energy consumption parameters, for a number of typical variants of laser removal of oxidic corrosion products from steels is briefly presented in [10], including using the results of a series of our experiments on LC from mill scale layers (30–50 μm of thickness (δ)) on carbon steel samples. In this case, the LC-processing was carried out on experimental setup using the laser with high-frequency nanosecond pulses (HFNPs) with pulse energy ≤ 1.0 mJ and its duration $t_p$ = = 120–150 ns [10]. The rate of LC-removal of the layer (containing mainly the magnetite $Fe_3O_4$ phase on our data of XRD analysis) in the optimal regime is at a level of ≥ 0.005 $dm^2$ of scale surface per second (at operating time-averaged thermal power of the beam $P_0 \approx 28$ W, emitting in near-infrared region) and at one pass of the beam the layer decreasing was such as $\Delta\delta \approx 6.5$ μm. St3 grade steel was used as the plate sample material (δ = 4 mm) in our experiments. The detailed data will be presented in the Part II of our article. A comparison and analysis of the results for laser surface deoxidizing [10] and other published data were carried out using systematized data on physical properties of a number of oxides, presented in Table 2.

It should be noted that the set of data on the properties of oxides and important for engineering metallic materials (typical grade of low carbon steel and one of the commercial aluminum alloys) presented in Table 2 allows us to propose comparative conclusions for at least three properties of these materials: 1) for the energy capacity of heating (in the equilibrium approximation) up to phase transition temperatures, 2) for thermal conductivity, 3) for optical absorptance. Comparison of the energy consumption levels for isobaric (at $P \approx \approx 0.1$ MPa) heating (according to the $\Delta H_1$ and $\Delta H_2$ values in Table 2) for the analyzed oxides and for the unoxidized metals shows that the level of the $\Delta H_2$ parameter for the considered types of metals (for them $\Delta H_2 \approx 1.05–1.15$ MJ/kg) is quite lower than for the oxides (except the copper oxides), i.e. approximately in 1.7 times or even more. This indicates higher energy consumption needed to heat the oxides of iron, aluminum, and titanium in the region up to their melting points. At the same time, the values of the $\Delta H_1$ (i. e. for conditions with heating up to boiling point) parameter for metals and oxides are at a quite comparable level. Comparison of the thermal conductivities of these groups of materials shows that for the metals this parameter (≥36 W/(m·K)) is significantly (several times) higher than for most of the oxides (except for $Al_2O_3$ at low temperatures (~34 W/(m·K)). Concerning the specified optical characteristics of the compared materials, it is evidently that for the metals under consideration (in solid and liquid phases) the level of values of integral emissivity (ε) and absorptance of radiation ($A$) (for the conditions with monochromatic irradiation) is noticeably poorer (≤0.46) than for the case of main considered oxides ($Fe_3O_4$, FeO, $Al_2O_3$, $TiO_2$, $CuO_x$), for which these characteristics values, as it was found, are not lower than 0.70.

**CONCLUSIONS**

1. A comparison was carried out for a number of characteristics that determine the level of efficiency and energy consumption for laser removal of surface corrosion products for the group of published data with the processing regimes of oxidized layers (up to 2 mm in thickness) on commercial grades of steels and alloys based on nine types of metals, including FeOx layers (in a form of scale or rust on steels or cast iron), as well as the films, which based on $Al_2O_3$, based on $TiO_x$ phases, based on CuO and $Cu_2O$ phases, based on ZnO (on a zinc alloy surface), based on MgO, based on $WO_x$, based on PbO (with impurities of lead carbonate and others substances), and based on $Ag_2O$ and AgO (with sulfide impurities).

2. The considered efficiency characteristics ($K_{en1s}$, energy consumption and others), based on our preliminary data, make it possible to estimate the realization of main mechanisms for removing oxide layers during the pulsed LC. Analysis of the LC-processes taking into account the characteristics was based on the parameters of typical (in the field of LC of oxides) regimes of processing of oxidized carbon steels (including the data from our experiments) with the use of pulsed lasers, as well as some samples of aluminum, copper and titanium alloys and cast iron with surface oxidic phases – $Fe_3O_4$, $Al_2O_3$, CuO, $TiO_2$ and others. The set of values obtained for the efficiency characteristics will be presented in Part II of our article and these data are suitable to estimate the effect of possible mechanisms of $MeO_x$-layer removal during the LC-processes.

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Received: 27.06.2024
Accepted: 27.08.2024
Published online: 31.01.2025