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EFFECT OF GLASS-FABRICS AND HIGH-MELTING POWDER FILLERS ON THERMAL PROTECTIVE PROPERTIES OF THERMOSETTING LAMINATES

ABSTRACT

The present work investigates the ablative and thermal properties of phenol formaldehyde glass-fabrics laminates filled with mixtures of corundum Al_2O_3 and carbon C powders. The laminates specimens of dimensions 10x25x35 mm were treated with hot combustion gases having a temperature of more than 2800ºC. The carbonization of the thermosetting matrix was observed. Statistical methods for planning experiments were used, and the effect of components on the average rate of ablation, the maximum back side temperature of specimen and the average mass waste under intensive heat flow after 30 s of treatment with hot combustion gases was established. The best thermal protective properties were exhibited by the laminate containing 30% matrix, 25% fibre glass-fabric reinforcement, 9% corundum, and 36% carbon powder.

Keywords: *ablative shields and coats, thermosetting glass laminates, high-melting fillers*

INTRODUCTION

The use of modified plastics as ablative materials protecting against excessive temperature increase was connected with the middle of XX century, directly with arms industry as well as aeronautical, rocket and space techniques [1, 2]. These materials can also be used in the design of passive fire-proof protections for large cubature supporting elements in building structures [3], communication tunnels [4, 5] and for the protection of data stored in electronic, optical and magnetic carriers [6].

The development of compositions, manufacturing technologies and research into the characteristics of ablative materials has become of great importance due to the threat of terrorists attacks. It is in the USA that the analysis of the causes and consequences of such disastrous events as Oklahoma City or World Trade Centre attacks [3] or explosions of inflammable materials (fires in the Alps tunnels: St. Gotthard, St. Bernard, the tunnel under the Mont Blanc between 1999 and 2001 [4, 5]) has brought about a thorough scientific investigation into the behavior of such materials [7–10].

ITA (International Tunneling Association) recommends that the fire-resistant covers of fire-safety systems in tunnels should limit temperature growth of concrete to 350°C [4, 5] (higher temperatures reduce concrete rigidity even below 50% of its nominal values [11]) and protect it against flaking and peeling. The steel structural elements must not exceed 300°C [4], as tensile strength and rigidity of steel diminish rapidly at higher temperatures. Carbon steel may exhibit as much as 6 to 8 times lower durability and nearly twice lower rigidity [6] at above 800°C (temperature of a typical office block fire [3]).

Good protective (fire- and thermal-buffer) properties can be attained using composite polymer coatings with typical ablative composite matrices (phenol resins [12-14], epoxy resins [15–19]) including fillers increasing thermal stability of a composite [12–20]. Once the ablation temperature of ~ 200°C is exceeded by polymer resins, endothermic reactions are initiated that raise their effective specific heat considerably. Pure resins are good ablative materials. They require reinforcement, however, due to their low decomposition temperature, porosity and fragility of the ablative layer produced. Powders [12, 15, 17, 21–23] or fibre fillers [13, 14, 16, 24, 25] or reinforcing plates [25, 26] of high melting temperatures build a composite structure that substantially improves thermal protective and thermal mechanical properties of a polymer ablative composite.

The ablation process is the process of exchanging of heat and mass which, due to physical changes and chemical reactions, results in chemical and structural changes of the material with simultaneous heat absorption, which reduces heating up of the material below the front of ablation. The heat influx causes relocation of the ablation front deeper into the material and thickening of the porous ablative surface. [6, 27]

In the paper [27] Yu. I. Dimitrienko proposed a classification of ablation processes in composites treated with heat fluxes. The process of mass loss $m = \rho \cdot V$ (where ρ is density and V is volume) due to the heat and thermo-mechanical impact of gas fluxes may result in a change in either density or volume as well as in a simultaneous change of both values.

The process of density loss where the volume remains unchanged is a pyrolysis which occurs in temperatures 500 - 1000°C and is characteristic for polymer composites. Such a process is called volumetric ablation. The process in which there occurs a volume loss with unchanged density is called surface ablation. It is typical for oxidization o graphite, metals and their alloys, glass as well as some types of fusible ceramic materials. A simultaneous occurrence of both processes of thermal degradation is referred to as combined ablation. Combined ablation usually takes place in high temperatures (1000 - 1500°C) and results from thermal and erosive gas impact. In all of the above-mentioned cases there occur ablative wear (which is sometimes purely erosive) of the basic material. [27]

To be able to take the full advantage of ablative materials we need to be aware of their ablative wear characteristics, which have to be taken into consideration at the early stage of the technological design. This includes a loss in active volume of the material that is not subject to ablation. The effect is characterized by linear ablation rate v_a [μm/s] defined as the average rate of dislocation of the ablation front i.e. the average rate of formation of ablative surface and so-called vitreous slag. If we determine the rate of ablation it is possible to determine the temporary location of the ablation front and, in consequence, to determine the thickness of active insulating layer [9, 28].

Despite many years of experience with ablative materials, the relationship between the phases type and composition with ablative properties, within the context of others operational properties of the composites used as thermal protection shields, remains still not evaluated qualitatively and quantitatively [1, 4, 7].

EXPERIMENTAL METHODS

The following materials (input variables x_i) have been used to prepare the specimens of thermosetting glass laminates with powder fillers: two kinds of phenol formaldehyde resins (liquid resin Modofen 54S and adhesive resin Nowolak MR in mass proportions 1 : 1) for matrix; glass-fabric (250 g/m^2) as fibre reinforcement; as well as powder fillers, corundum Al_2O_3 with grains of 2 to 5µm with the minimal contents of aluminium oxide of 99.5% (95% α Al_2O_3) and fine grain carbon powder C of 5 µm and purity of 98%.

The number of sample phase compositions, equal to the number of scheduled experiments (N = 8), was determined on the basis of the adopted design of experimentation, i.e. an orthogonal 1st order full-factorial matrix of the type $2^3 = 8$ including single replications, where two state levels (lower level -1 and upper level +1) and three independent input variables (x_i) (i = 1, 2, 3) occur, determined by means of the mathematical dependence (1) [29]:

$$x_i = \frac{x - \bar{x}_i}{\Delta x_i} = \pm 1 \quad (1)$$

with

x_1 – mass contents of the matrix: 24% (level -1) and 30% (level +1), $\Delta x_1 = 3\%$;
x_2 – number of glass-fabrics layers: 8 layers (level -1) i 12 layers (level +1) ; $\Delta x_2 = 2$;
x_3 – mass proportion of Al_2O_3 corundum to the total mass of both fillers $Al_2O_3/(Al_2O_3 + C)$: 20% (level -1) and 80% (level +1), $\Delta x_3 = 30\%$.

The components of the response variable $y_i(x_i)$ (the output parameters) are: the average rate of ablation v_a, (µm), the average maximal temperature of the rear surface of specimen t_{s_max}, (°C) and an average relative ablative (erosive) mass loss U_a, (%) after 30 s of treatment with hot combustion gases.

The so-called "ablative gun" [30] of our own construction stand [6] has been used for the classical ablative properties tests (Fig. 1). The specimens (10x25x35 mm cubes) were treated of oxy-acetylene mixture of hot combustion gases having a temperature of more than 2800ºC during 30 seconds.

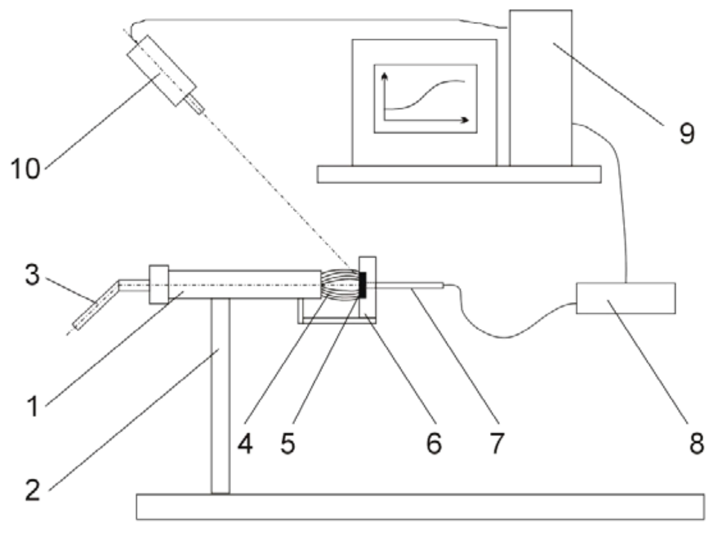

Fig. 1. Measurement stand: 1 – the ablative gun with flammable gases stabilization, 2 – a tripod, 3 – a torch, 4 – a flame, 5 – the testing sample, 6 – a sample casing, 7 – the thermocouple, 8 – the temperature measurer of $t_s(\tau)$, 9 – a computer, 10 – the pyrometer and the thermovision camera to $t_{pa}(\tau)$ measurement

RESULTS AND DISCUSSION

The registration of the back side temperature (t_s) of specimen have been performed (Fig. 2). Furthermore, the average rate of ablation (v_a) and the average ablation mass waste of laminates (U_a) has been also evaluated. There are three output variables, components of the response function (Table 1).

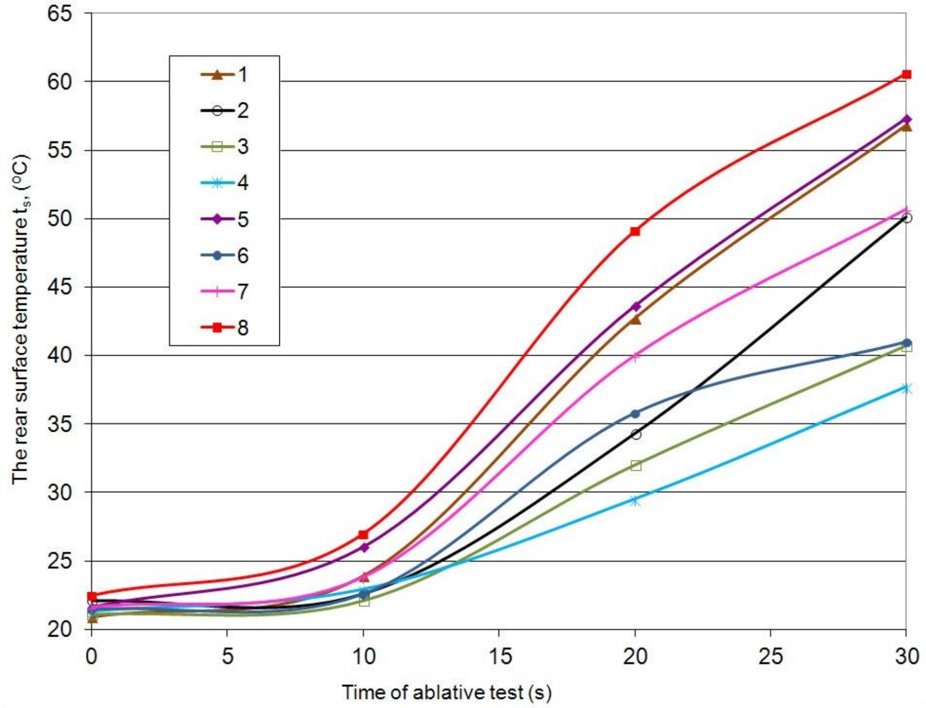

Fig. 2. Changing of the rear surface temperature ts during 30 s of the heat flux exposition

The greatest temperature growth, t_s, was recorded for composite 8 and the lowest for specimen 4 in the entire duration of the 30-second-long ablative test. The final greatest temperatures, t_{s_max}, of the same specimens are maximum and minimum, respectively. The variable x_3 – relation of Al_2O_3 mass to the sum total of masses of both the fillers (Al_2O_3 + C) – is the composition parameter than clearly differentiates both the specimens. Specimen 4 contains more than 3.5 times more carbon powder and more than 4.5 times less of corundum than specimen No. 8.

***Table 1.** The results of ablation (thermal protective) tests*

Parameter		Number of test							
		1	**2**	**3**	**4**	**5**	**6**	**7**	**8**
Matrix (x_1) [%]		24	30	24	30	24	30	24	30
Fibreglass fabric (x_2) [%]		18	18	25	25	13	13	19	19
Powder fillers (x_3) [%]	Al_2O_3	11.6	10.4	10.2	9.0	50.4	45.6	45.6	40.8
	C	46.4	41.6	40.8	36.0	12.6	11.4	11.4	10.2
v_a [μm/s]		121	158	125	128	130	166	157	172
t_{s_max} [°C]		56.8	50.1	40.7	37.7	57.3	41.0	50.7	60.6
U_a [%]		10.8	11.0	9.6	8.3	6.9	5.9	6.7	7.3

The aim of the experiment was to find such a composite whose values of the average ablation rate v_a, the maximum back side temperature t_{s_max} and the average mass waste U_a are the lowest. These conditions have been fairly met by specimen 4 whose phase composition consists of 30% matrix, 25% fibre glass fabric reinforcement, 9% corundum Al_2O_3, and 36% carbon powder C (Fig 3).

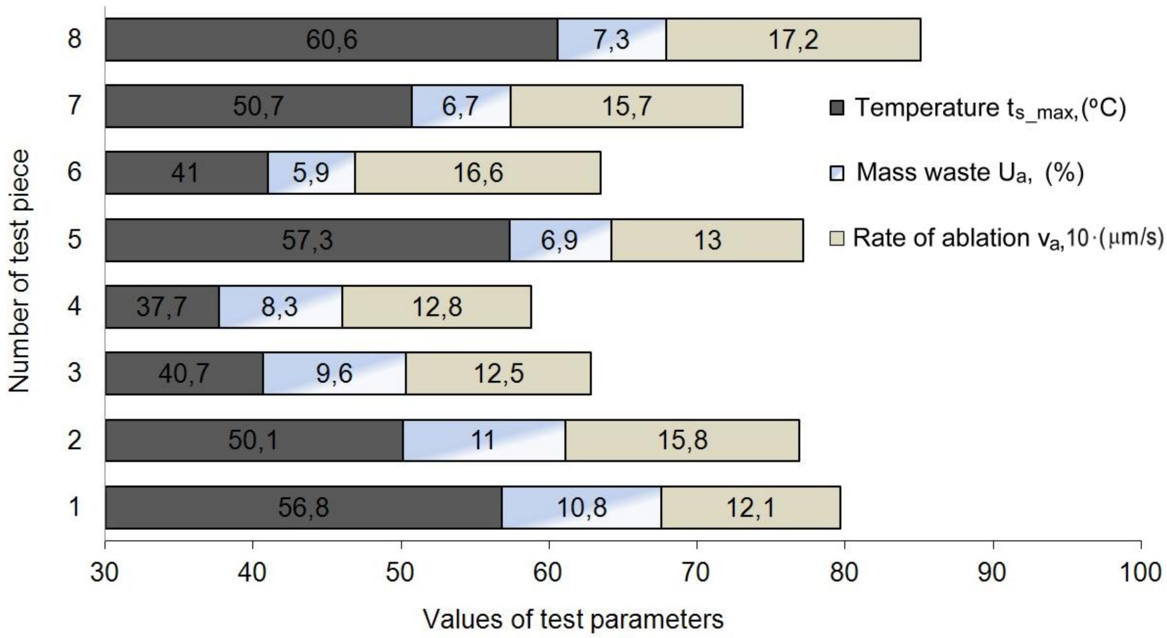

Fig. 3. Results of ablative research: the max. temperature t_{s_max}, the mass waste U_a and the rate of ablation v_a

The evaluation of ablative thermal protection properties of thermosetting glass laminates were carried out on the basis on a first order 2^3 statistical experimental research program. The regression coefficients of all function components have been calculated. The statistical analysis of the tests results allowed the determination of the threshold relevance of the regression coefficients b_i and estimation of their effect on the thermal protection properties.

Moreover, the variance $s^2(y)$, error in determination regression and interaction coefficients $s(b_i)$ and their level of statistical significance ($b_{sign} \geq b_i$) have been determined on the basis of t-Student test at confidence level $\alpha_p = 0.05$ (Table 2) [29].

Table 2. *Statistics of coefficients the equations of the response variable*

Function y_i	b_0	b_1	b_2	b_3	b_{12}	b_{13}	b_{23}	b_{123}	$s^2(y)$	$s(b_i)$	b_{sign}
v_a [μm/s]	144.5	11.4	-	11.5	-6.9	-	7.5	-	47.61	2.4	5.6
t_{s_max} [°C]	49.3	-2.02	-1.93	3.06	3.74	-	5.19	2.82	5.81	0.85	1.96
U_a [%]	8.29	-0.17	-0.34	-1.61	-	0.09	0.63	0.39	0.04	0.07	0.16
Equations	$y_i(x_i) = (b_0 + b_1x_1 + b_2x_2 + b_3 x_3 + b_{12} x_1x_2 + b_{13} x_1x_3 + b_{23} x_2x_3 + b_{123} x_1x_2x_3) \pm s(\overline{y})$										

Analysis of the interaction and regression coefficients indicates:

- The type of loose filler used (b_3) has the greatest effect on ablative thermal protective properties – a higher share of carbon at the expense of corundum reduces both the rate of ablation v_a and temperature t_{s_max}.

- The proportion of composite matrix (b_1) is of equal importance – a reduction of resin content does increase v_a yet lowers t_{s_max}.
- Simultaneously increasing the resin content and number of fabric layers, and the consequent lower share of powder fillers (b_{12}), slows v_a and raises the temperature of the specimen back side, t_{s_max}, without clearly affecting the ablative mass waste U_a;
- Raising the number of fabric layers and Al_2O_3 content (a lower content of C) impairs the thermal protective properties (b_{23}) – all the three parameters rise.

Figure 4 is an example of a graphical interpretation of the dependence of v_a on phase compositions of the tested composites. Changing value of the independent variable x_i alters, to a greater or lesser extent, the rate of ablation in accordance with the component function equation expressed for the test object, $v_a(x_i)$.

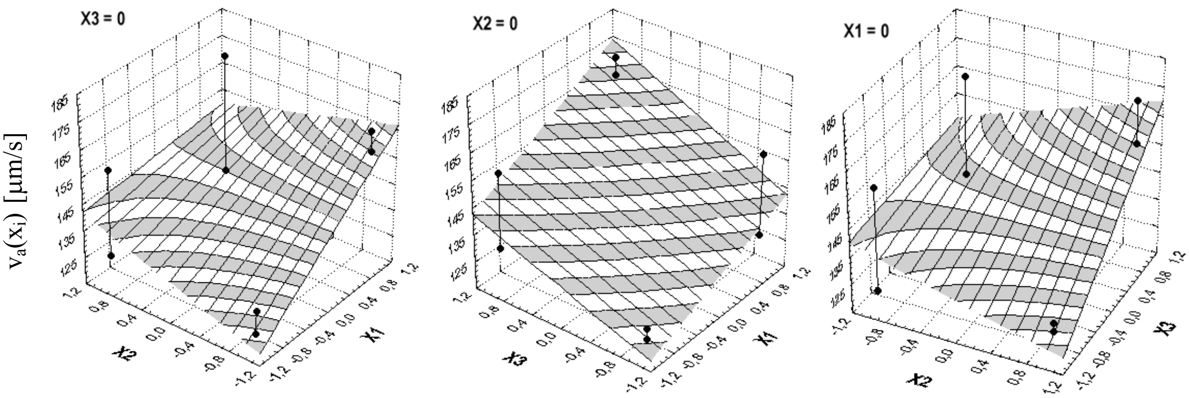

Fig. 4. Diagrams of the dependences $v_a(x_i) = (144.5 + 11.4x_1 + 11.5x_3 – 6.9 x_1x_2 + 7.5x_2x_3 \pm 6.9)$ μm/s, in a set of code variables x_i

STRUCTURES OF ABLATIVE SAMPLES

Experimental samples after the ablation process were covered with chemically crosslinked resin in cylindrical moulds (plastic tubes). After hardening the resin, it was cut along the heat flux direction in the symmetry axis of the ablative surface. Samples were cut mechanically at slow speed and with cooling to avoid temperature increase in the cross-section, which could affect the structure and thermal stability of the polymer. Next, samples were wet polished using sandpaper with decreasing grain size and then wet polished using felt with polishing paste (corundum). No corrosives were used. Then pictures of the ablative layer structures and the basic material were taken using an optical microscope.

Photo 1 shows an ablative surface where secondary ablation processes have taken place, including melting of complex ceramic structures produced by impact of heat from silica compounds (contained in a glass-fabric) and the powder fillers: aluminium oxide Al_2O_3 and carbon dust C as well as carbon arising from the process of matrix pyrolysis. Solidified layers of ceramic ‘fans’ (light, irregular bands in the upper parts of the specimens) can be seen. An area of the so-called vitreous slag – a porous substance of low thermal conductivity, solid product of pyrolysis and secondary ablation – is apparent in the ablative layer’s structure below.

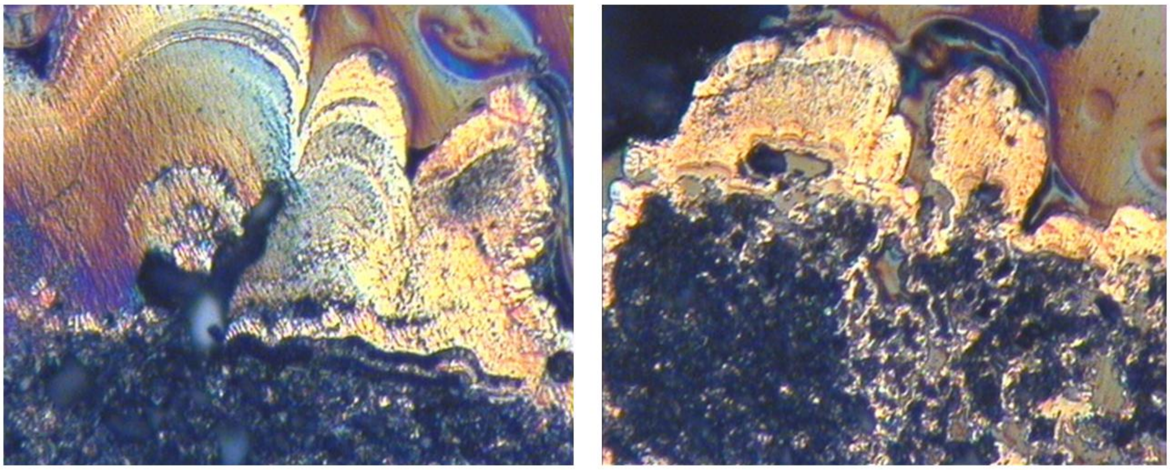

Fig. 5. Structure of specimen 6's ablative surface after an ablation time of 30s with apparent 'fans' of solidified ceramic layers, amplified. Magn. x250

The boundary between primary and secondary ablation in the ablative layer can be noted in Fig. 5a and 5b. In Fig. 6a, the front of secondary ablation has come to a halt between layers of the fabric, i.e. against loose particles. The vitreous slag (the dark area of primary ablation) is situated below the solidified ceramic compounds (the light area of secondary ablation). Figure 6b shows ablation to have stopped at the fabric layer – only fibres along the surface of the specimen microsection are melted. A solidified, fine-grained ceramic structure, a zone of transformations and secondary reactions, nearly free from solid products of pyrolysis, can be seen above the fabric. It can be surmised only the resin matrix of the composite has decomposed beneath the fabric's longitudinal fibres, while the temperature there has not risen locally above 700°C (the fibres do not display softening).

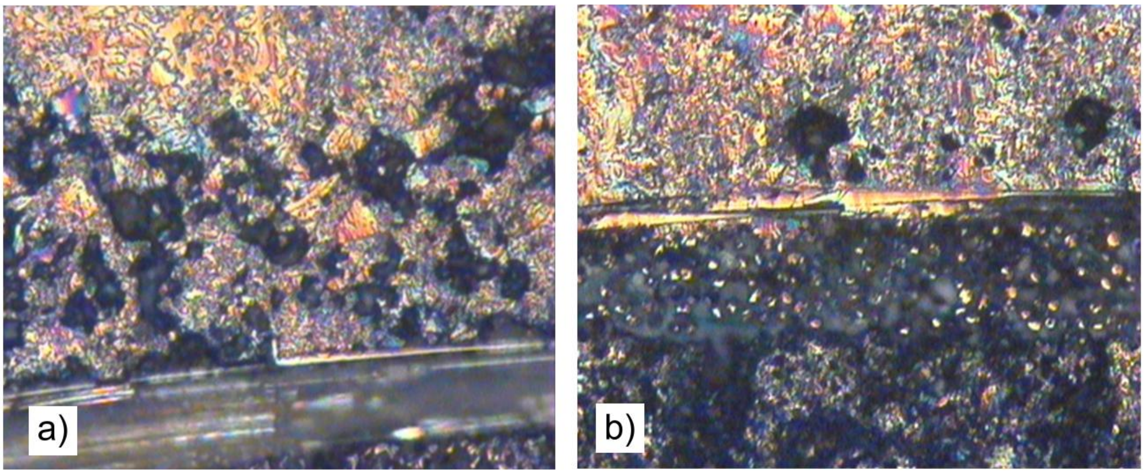

Fig. 6. Ablation front: a) between the glass-fabric layers, specimen 2, b) on the glass-fabric boundary, specimen 3. Magn. x250

Native material of the composite which has not undergone the process of ablation is illustrated in Photo 3a - large, light, angular grains of the corundum Al_2O_3 powder filler can be seen against the background of black carbon dust C and structural defects – bubbles generated in the production process. Transverse reinforcing fibres (the circular structures in the right upper part of the photo) can also be seen.

The fine-grain structure of the solidified ceramics (secondary ablation) with typically dendritic grains (the light areas) is apparent in Fig.7 against the background of the dark, porous vitreous slag (the material residue of the primary ablation process). The ceramic grains have not sharp but obtuse edges, evidence they are produced by chemical reactions of the secondary ablation substrates (based on carbon, corundum and silica compounds), followed by solidification when the effect of the heat flux can no longer be felt.

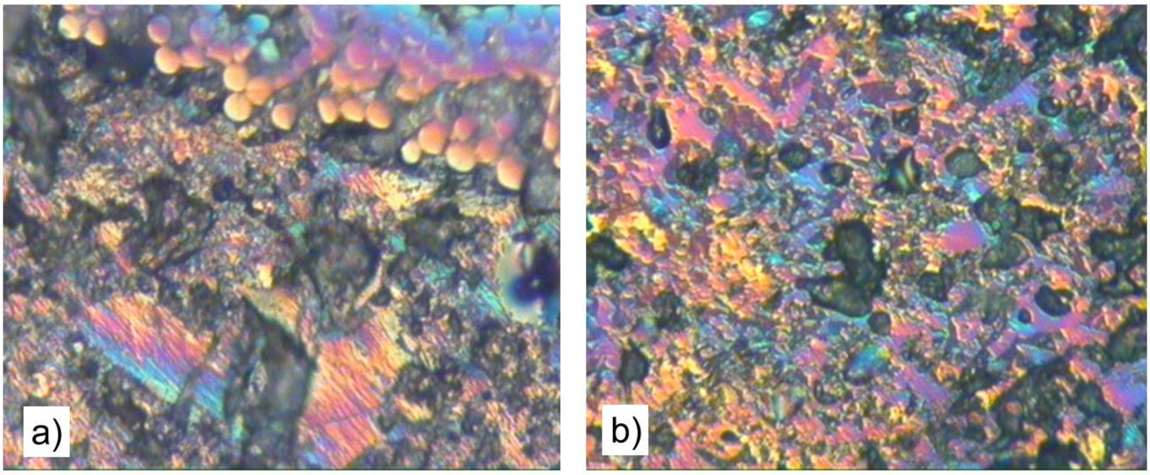

Fig. 7. Ablative specimen: a) native material, b) ablative layer, specimen 1. Magn. x250

CONCLUSIONS

1. The best thermal protective properties, i.e. the average ablation rate and simultaneously the lowest temperature of the rear surface area, how also the lowest ablative weight loss (the highest thermal stability) were exhibited by the thermosetting hybrid laminate containing 30% matrix, 25% fibre glass-fabric reinforcement, 9% corundum Al_2O_3, and 36% carbon powder C.
2. The type of loose filler applied shows the greatest impact on boosting thermal protective properties of the tested composites. Increasing the share of phase carbon at the expense of corundum is recommended, while preserving the average proportion of the glass-fabric layers.
3. Preserving the average number of glass-fabric layers (variable x_2) is statistically reasonable, however, application of the same number of glass-fabric layers though with a lower area density would be indicated for further experimentation – this would allow for increasing the shares of both the matrix and loose fillers.
4. For technological reasons and due to values of the coefficient (b_1), the resin content should not be modified though it is acceptable and even recommended (especially if a fabric with a lower area density is used) given the higher share of carbon dust.
5. There is no straightforward mutual impact of the independent variables x_i on thermal destruction of the material, although characteristics of thermal protective material ablation are apparent (Fig. 5-7), with the thermal energy flux expended on: thermal degradation and pyrolysis of the composite matrix; melting of the glass-fabric and decomposition of silica compounds; thermal-chemical generation of new ceramic structures based on silica, carbon

and corundum; phase transitions of the chemical products and other material components which have not been decomposed; creation of a passive thermal protective layer with a low thermal conductivity (vitreous slag).

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