ISSN1027-5495. Functional Materials, 32, No.1 (2025), p. 56-62
doi:http://dx.doi.org/10.15407/fm32.01.56 © 2025 — STC "Institute for Single Crystals"

High temperature oxidation of AlB_{12}-Al electric spark coatings on Steel 45

A.P.Umanskyi[1], V.B.Muratov[1], V.E.Sheludko[1], T.V.Khomko[1], I.S.Martsenyuk[1], M.A.Vasilkovskaya[1], V.V.Kremenitsky[2]

[1] I.N. Frantsevich Institute for Problems of Materials Science, National Academy of Sciences of Ukraine, 3 Omelyana Pritsaka (Krzhyzhanovsky) Str., 03142 Kyiv, Ukraine
[2] Technical Center, National Academy of Sciences of Ukraine, 13 Pokrovskaya Str., 04070 Kyiv, Ukraine

Received August 16, 2024

The article deals with the study of the resistance of electrospark coatings of the composition AlB_{12}-50 wt.% Al to high-temperature oxidation. The coatings are applied to Steel 45 using an ALIER-52 installation (mode 4). High-temperature oxidation of coated Steel 45 samples was carried out in a Nabertherm furnace, in the temperature range of 500, 600, 700, 800, 900 and 1000 °C, in air with exposure at each temperature for 1 hour. The structure of the coatings was studied using a JEOL JSM-6490 LV SEM equipped with an INKA Energy 350XT energy-dispersive spectrometer. The microhardness of the coatings was measured using a PMT-3 microhardness tester (P = 0.5 N). After oxidation, phases of Fe-Al intermetallic compounds, aluminum nitrides of different stoichiometric compositions, AlB_{12} and Al_2O_3 were found in the coating. The weight gain of the coated sample was found to be much less than that without the coating; this is explained by the formation of compounds that are resistant to high-temperature oxidation. The developed coatings can be used to protect parts operating under high-temperature oxidation conditions.

Keywords: AlB_{12}-Al electric spark coating, High-temperature oxidation, Microstructure, SEM, Microhardness

Високотемпературне окислення електроіскрових покриттів AlB_{12}-Al на Сталі 45. *О.П.Уманський, В.Б.Муратов, В.Є.Шелудько, Т.В.Хомко, І.С.Марценюк, М.А.Васильківська, В.В.Кременицький.*

Статтю присвячено дослідженню стійкості до високотемпературного окислення електроіскрових покриттів складу AlB_{12}-50 мас.% Al. Покриття нанесено на Сталь 45 на установці ALIER-52 (4 режим). Високотемпературне окислення зразків Сталі 45 з покриттям проводили в печі Nabertherm, в інтервалі температур 500, 600, 700, 800, 900 та 1000 °C, на повітрі, витримка за кожної температури – 1 год. Структуру покриттів вивчено за допомогою CEM JEOL JSM-6490 LV, що оснащений енергодисперсійним спектрометром INKA Energy 350XT. Мікротвердість покриттів вимірювали на мікротвердомірі ПМТ-3 (P = 0.5 Н). Після окислення у покритті виявлено фази інтерметалідів Fe-Al, нітриди алюмінію різного стехіометричного складу, AlB_{12} та Al_2O_3. Встановлено, що приріст ваги зразка з покриттям набагато менше такого без покриття, що пояснюється утворенням у покритті сполук, стійких до високотемпературного окислення. Розроблені покриття можуть бути використані для захисту деталей, що працюють за умов високотемпературного окислення.

1. Introduction

High-temperature oxidation, which often leads to corrosion, is a serious problem for equipment parts operating at high temperatures. One of the methods to protect against high-temperature oxidation is the application of various coatings, including electrospark alloying ones. The essence of electrospark alloying (ESA) [9] consists in transferring and depositing of an electrode material (anode) eroded by a spark discharge onto the surface of a part (cathode) to form (on the latter) of a hardened layer with improved physical and mechanical properties. Various refractory compounds, namely carbides, nitrides, aluminides, silicides, and borides can be used as the anode material [10-12]. Among the latter, aluminum dodecaboride AlB_{12} is of interest. The method of its synthesis from Al and BN developed at the Frantsevich Institute for Problems of Materials Science of NAS of Ukraine, turned out to be more rational and cost-effective than direct synthesis from Al and B [13]. AlB_{12} has a low density (~2.52 g/cm^3), and its crystalline structure (icosahedral boron framework) determines its high hardness (22-24 GPa) and infusibility (2070 °C) [14].

However, the low crack resistance of aluminum dodecaboride significantly limits the scope of its application [14]; therefore, it is advisable to use AlB_{12} in combination with a ductile binder metal. It is promising to use aluminum having high plasticity, low density (2.7 g/cm^3) and low melting point (660 °C). Earlier it was found that Al wets AlB_{12} well with contact angles ($\Theta \approx 20$ deg), and there are no secondary phases in the interaction zone at the Al-AlB_{12} interface [14]. In addition, aluminum with a resistivity of 2.7 μΩ·cm, acts as an additive increasing the conductivity of the AlB_{12}-Al composite (a resistivity of AlB_{12} – 10^6 Ω·cm), which is of great importance in ESA. In particular, the composite material AlB_{12}-50 wt.% Al was used in the deposition of ESA-coatings on titanium (VT1-0) and aluminum (D1) alloys, as well as on Steel 45 [15-17].

The aim of the work is to investigate the resistance of AlB_{12}-Al ESA-coatings to high-temperature oxidation.

2. Experimental

The samples were prepared from the AlB_{12} powder (d_{ave} = 120÷150 nm) synthesized at the IPMS of NASU according to the procedure described in [18]. First, a porous AlB_{12} ceramic framework was obtained. Then it was impregnated with an Al melt in vacuum ($1.33 \cdot 10^{-4}$ Pa) at a temperature of ~1100 °C. This made it possible to obtain the aluminum-matrix composite of AlB_{12}-50 wt.% Al in the form of a bar of 50×50×5 mm in size, from which the electrodes for ESA were cut by the electro-erosion method. The structure of the material consists of three phases: a metal matrix, AlB_{12} grains (the size of which varies in the range of 1-4 μm) uniformly distributed in the matrix, and Al_2O_3 particles [17].

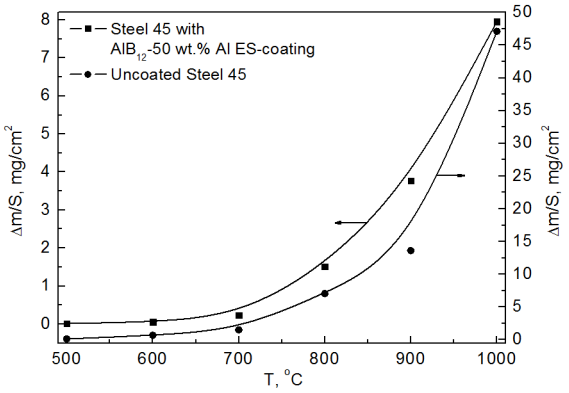

Fig. 1. Weight gain of the Steel 45 samples (coated and uncoated) at the various temperatures

ESA of the samples of Steel 45 (GOST 1050-88) of 1×1×1 cm in size was carried out on an ALIER-52 installation (SCINTI, Chisinau, RM) at the 4 mode [17].

High-temperature oxidation of the samples with AlB_{12}-50 wt.% Al ESA-coating was carried out in a Nabertherm furnace 30-3000 °C (Nabertherm GmbH, Lilienthal/Bremen, Germany), at temperatures of 500, 600, 700, 800, 900 and 1000 °C, in air. Heating rate was 10-15 °C/min, exposure time at each temperature – 1 hour. The weight gain of the samples was determined on an OHAUS Adventurer AR0640 electronic scale with an accuracy of 10^{-4} g.

The microhardness of the coatings after oxidation was measured on a PMT-3 microhardness tester at a load of P = 0.5 N.

The structure of the coatings was studied using a JEOL JSM-6490 LV scanning electron microscope equipped with INKA Energy 350XT energy-dispersive spectrometer (Oxford Instruments plc.).

3. Results and discussion

Fig. 1 shows the dependences of weight gain for Steel 45 samples (ESA-coated and uncoated) on the oxidation temperature. The weight gain of the uncoated sample is several times greater than that of the coated one (for example, in case

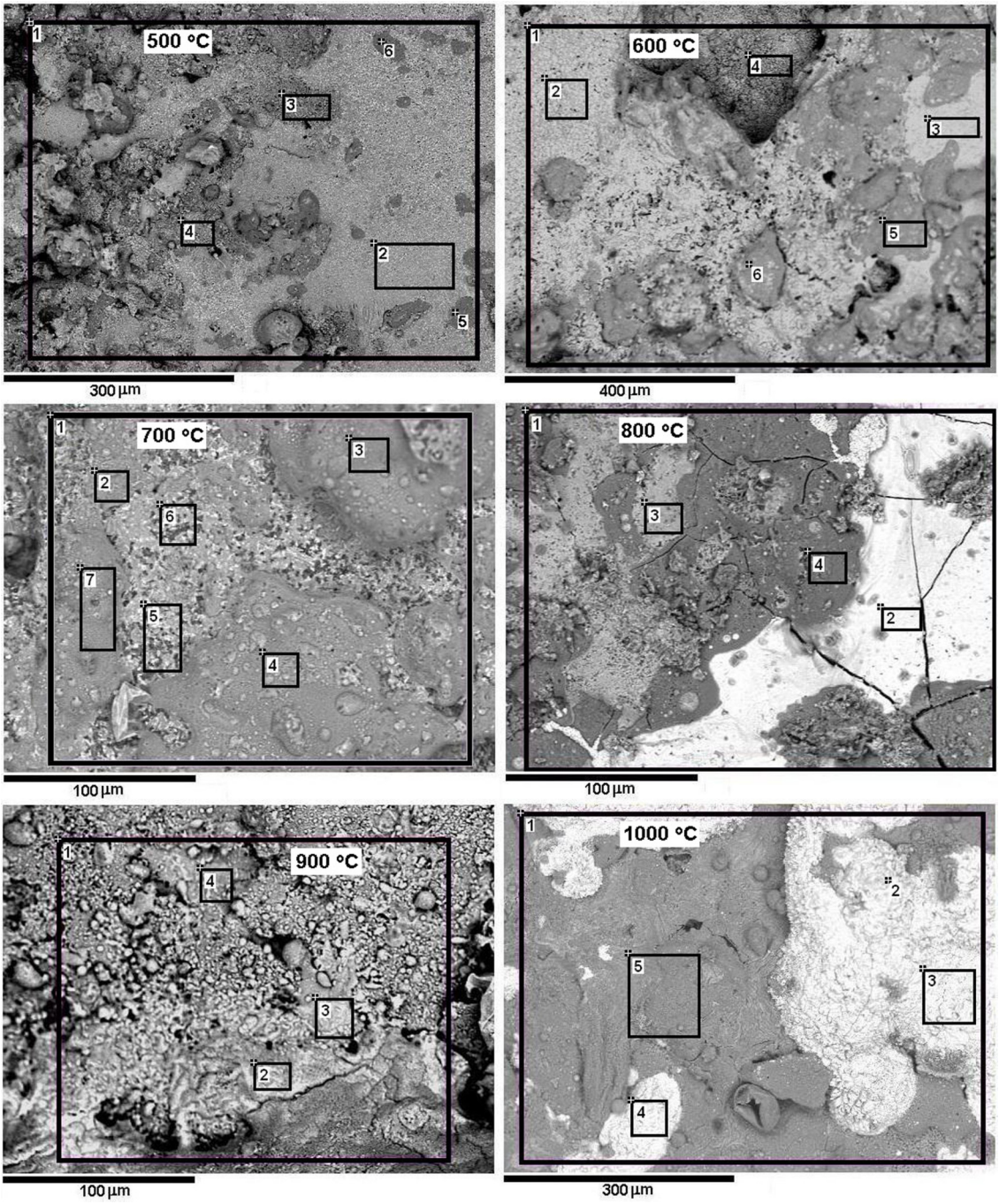

Fig. 2 – Microstructure of the surface of the ES-coating AlB_{12}-50 wt.% Al on Steel 45 after oxidation at various temperatures

of T = 1000 °C Δm/S is 47.098 and 7.955 mg/cm^2, respectively).

To explain the fact, it is necessary to pay attention to the phase composition of the ES-coating before oxidation [17]. The main phases in the coating are $Al_{13}Fe_4$, $AlFeO_3$, AlB_2 and Al_2O_3. In addition, intermetallic compounds AlFe and $AlFe_3$ (in small quantities) are also present. Iron aluminides are known to have good resistance to high-temperature oxidation and sulfidation [19, 20]. There is no doubt that Al_2O_3 has a positive effect on oxidation resistance over a wide temperature range [21-23]. The $Al_{13}Fe_4$ phase also significantly increases high-temperature oxidation resistance, for example, of carbon steels after laser alloying [24, 25]. The $AlFeO_3$ phase shows no weight change at T > 520 °C [26]. Only AlB_2, which is stable up to 750 °C, quickly oxidizes at T > 750 °C [27]. So, the ES-coating consists of

Table 1 – Chemical composition of the surface (Fig. 2) of the ES-coating of the AlB_{12} - 50 wt.% Al composite on Steel 45 at various oxidation temperatures

Oxidation temperature, °C	Spectrum (probable phase)	Element, wt.%						Total
		O	Al	Fe	N	C	Mn	
500	1	9.52	83.95	6.53				100.00
	2	2.99	91.39	5.62				100.00
	3 ($Al_{1.07}N_{0.23}$)	18.96	70.62	2.60	7.82			100.00
	4	15.76	79.50	4.74				100.00
	5 ($Al_{1.03}N_{0.44}$)	17.03	67.95		15.02			100.00
	6 ($Al_{0.9}N_{0.6}$)	15.07	64.45		20.48			100.00
600	1	13.49	72.26	7.01	7.24			100.00
	2 ($Al_{1.2}N_{0.1}$)	4.55	83.17	8.37	3.90			100.00
	3 ($Al_{1.22}N_{0.11}$)	3.90	80.35	11.76	3.99			100.00
	4 ($Al_{0.95}N_{0.18}$)	21.30	62.99	9.44	6.27			100.00
	5 ($Al_{0.9}N_{0.47}$)	19.04	61.31	3.42	16.24			100.00
	6 ($AlN_{0.28}$)	22.55	66.04	1.78	9.62			100.00
700	1	19.99	67.89	3.71	8.41			100.00
	2 ($Al_{1.07}N_{0.38}$)	13.99	70.71	2.05	13.24			100.00
	3	29.45	64.79			5.75		100.00
	4 ($Al_{0.97}N_{0.37}$)	21.45	64.28	1.43	12.85			100.00
	5 ($Al_{13}Fe_4$)	3.26	60.79	35.95				100.00
	6 ($Al_{13}Fe_4$)	3.16	59.38	37.46				100.00
	7 ($Al_{1.05}N_{0.17}$)	23.06	69.04	1.95	5.94			100.00
800	1	18.23	47.66	33.52				100.00
	2 (AlFe)	4.14	31.47	64.39				100.00
	3 ($Al_{13}Fe_4$)	1.76	61.41	36.83				100.00
	4 (Al_2O_3)	43.79	53.81	2.40				100.00
900	1	47.59	50.22	2.19				100.00
	2 (Al_2O_3)	41.80	52.73	5.47				100.00
	3 (Al_2O_3)	43.97	53.91	2.12				100.00
	4 (Al_2O_3)	40.87	56.67	2.46				100.00
1000	1	31.89	31.21	32.21		2.75	1.94	100.00
	2	0.64	0.26	95.06			4.04	100.00
	3 (Fe_2O_3)	29.56	0.67	68.26			1.51	100.00
	4 (Fe_2O_3)	28.23	0.6	70.21			0.96	100.00
	5 (Al_2O_3)	41.17	51.71	7.12				100.00

compounds resistant to high-temperature oxidation at the temperatures from 500 to 1000 °C, which explains the data in Fig.1.

The microstructure of the ES-coating after oxidation is shown in Fig. 2. It can be said that various intermetallic compounds Fe-Al (Table. 1) retain their presence in the coating in the temperature range of 500-800 °C. It is also necessary to note the presence of aluminum nitrides, Al, Al_2O_3 and Fe_2O_3.

The coatings oxidized in the temperature range 500-700 °C contain nitrogen. It can be assumed that in this temperature range, reactions occur with the formation of aluminum nitrides of different stoichiometric composition [28]. For example, at T = 500 °C, nitrides with

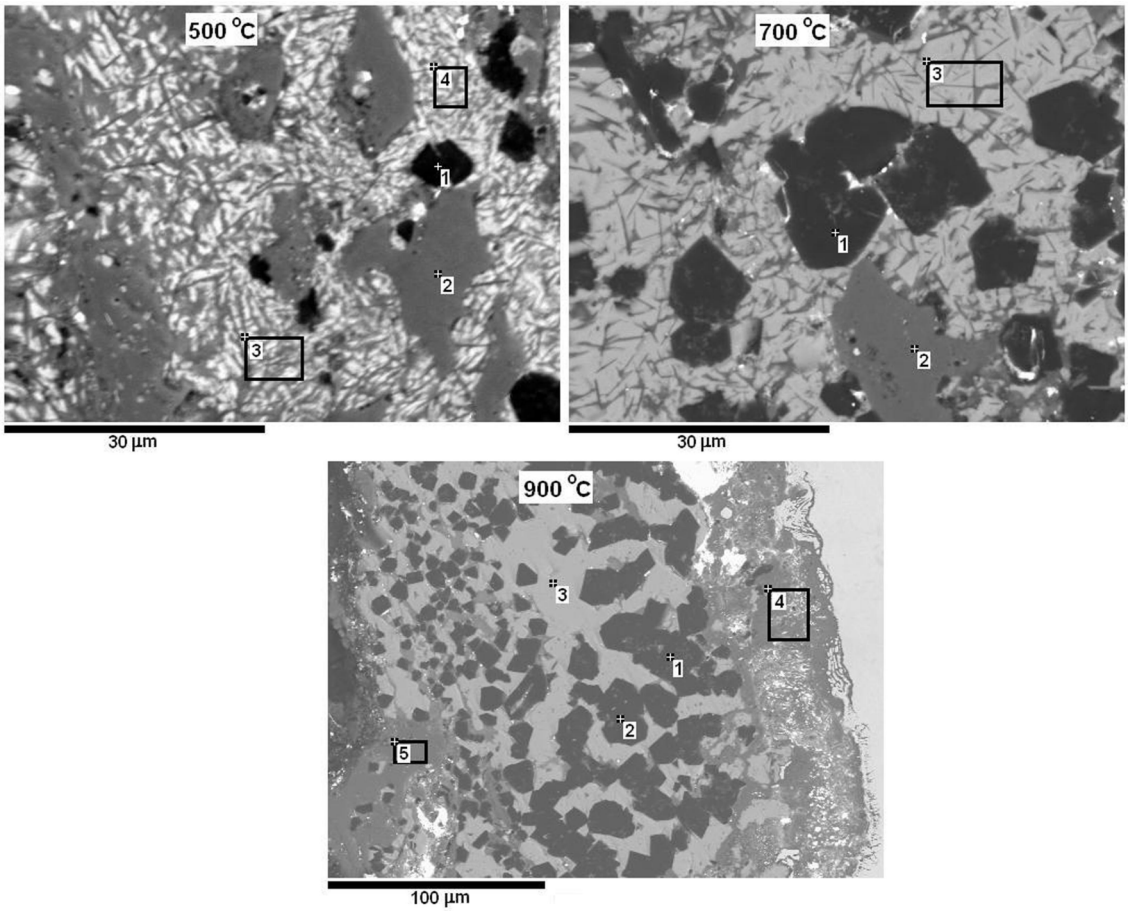

Fig. 3 – Fragments of microstructures of the cross-section of ES-coating AlB_{12}-50 wt.% Al on Steel 45 after oxidation at various temperatures

Table 2 – Chemical composition of the cross-section of the ES-coating of the AlB_{12} - 50 wt.% Al composite on Steel 45 at the oxidation temperatures of 500, 700, and 900 °C (Fig. 3)

Oxidation temperature, °C	Spectrum (probable phase)	Element, wt.%						Total
		B	O	Al	C	N	Fe	
500	1 (AlB_{12})	80.96	0.89	18.16				100.00
	2 ($Al_{0.89}N_{0.24}$)		26.94	58.68	6.15	8.23		100.00
	3 ($FeAl_6$)		2.04	74.84			23.12	100.00
	4 ($FeAl_6$)			75.06			24.94	100.00
700	1 (AlB_{12})	85.64		13.08	1.28			100.00
	2 ($Al_{0.84}N_{0.2}$)		23.30	55.63	9.00	7.07		100.00
	3 ($Al_{13}Fe_4$)			61.35			38.65	100.00
900	1 (AlB_{12})	83.37		13.82	2.81			100.00
	2 (AlB_{12})	85.50		13.13	1.37			100.00
	3 ($Al_{13}Fe_4$)			60.19	2.13		37.68	100.00
	4		44.54	31.56	11.23		12.66	100.00
	5 ($Al_{0.94}N_{0.49}$)		21.15	61.98		16.87		100.00

x = 0.2-0.6 ($Al_{1.03}N_{0.44}$, $Al_{1.07}N_{0.22}$, $Al_{0.9}N_{0.6}$, Table 1) are formed. At T = 600 °C, the stoichiometric coefficient x = 0.08-0.5 ($Al_{0.9}N_{0.47}$, $Al_{1.2}N_{0.1}$, $Al_{0.95}N_{0.8}$), and at T = 700 °C, x=0.16-0.38 ($Al_{1,07}N_{0.38}$, $Al_{0.97}N_{0.37}$, $Al_{1.05}N_{0.17}$). When oxidizing samples at T = 800, 900 and

1000 °C, no nitrogen was observed in the ES-coating composition.

After holding at T = 500, 700 and 900 °C, the following phases were revealed in the microstructure of the cross-section: AlB_{12}, nitrides of different stoichiometric composition and intermetallic compounds $FeAl_6$ and $Al_{13}Fe_4$ (Fig. 3, Table. 2).

During the ESA process at plasma temperatures ($2 \cdot 10^4$ K) in air, thermal-oxidative destruction of the anode and cathode occurs [29]. In addition, as a result of significant thermal loads, various processes (thermomechanical, hydrodynamic, diffusion) lead to intensive mass transfer of components (cathode and anode). As a result, part of the AlB_{12} phase on the surface undergoes intense oxidation with the formation of oxides and borates [30] and another part can diffuse into the depth of the coating, which is confirmed by the analysis of the cross-section of the ES-coating (Fig.3).

In [31], the appearance of the $FeAl_6$ phase in the temperature range of 400-670 °C (during a solid-state reaction between Fe and Al nanolayers) is reported. The $FeAl_6$ phase is metastable and, under certain conditions, (holding at T = 600 °C for various time periods – from 2 to 24 hours) can be transformed into a stable compound $Al_{13}Fe_4$ as, for example, shown in [32].

After oxidation at T = 500, 700 and 900 °C, the microhardness H_μ of the ES-coating was 10.6, 8.7 and 9.8 GPa, respectively (before oxidation H_μ ~ 10 GPa [17]).

4. Conclusions

1. Using the ESA method, the AlB_{12}-50 wt.% Al composite-based coatings were formed on Steel 45, followed by isothermal oxidation in the temperature range of 500-1000 °C.

2. The dependence of the weight gain of coated and uncoated samples on the oxidation temperature was studied, and it was shown that ESA significantly increases the resistance of samples to high-temperature oxidation.

3. The microhardness of samples H_μ after oxidation in the range of 500-900 °C practically does not change.

4. In practical terms, the AlB_{12}-Al system is a promising material for applying ES-coatings to parts operating under extreme temperature oxidation conditions.

References

1. Handbook of Environmental Degradation of Materials. 3d Edition. Ed. by M.Kutz, Elsevier, William Andrew, (2018). https:/doi.org/10.1016/C2016-0-02081-8.
2. High Temperature Corrosion. Ed. by Z.Ahmad, IntechOpen, London, UK (2016). https:/doi.org/10.5772/61546.
3. N.Birks, G.H.Meier, F.S.Pettit. Introduction to the High-Temperature Oxidation of Metals. 2d Edition, Cambridge University Press, Cambridge, UK (2006). https:/doi.org/10.1017/CBO9781139163903.
4. Z.Li, W.Gao, P.Kwok et al., *High Temp. Mater. Proc.*, **19**, 443 (2000). https:/doi.org/10.1515/htmp.2000.19.6.443.
5. Z.O.Dolgiy, W.Z.Shao, A.V.Kozyr et al., *Adv. Mater. Res.*, **538-541**, 175 (2012). https:/doi.org/10.4028/www.scientific.net/AMR.538-541.175.
6. S.A.Pyachin, A.A.Burkov, N.M.Vlasova et al., *Sci. pap. Komsomolsk-na-*Amure *State Univ.*, **I-1**, 49 (2017). DOI: doi.org/10.17084/2017.I-1(29).8.
7. A.V.Kozyr, L.A.Konevtsov, S.V.Konovalov et al., *Letters on Materials*, **8**, 140 (2018) [in Russian]. https:/doi.org/10.22226/2410-3535-2018-2-140-145.
8. J.Wang, M.Zhang, S.Dai et al., *Coatings*, **13**, 1473 (2023). https:/doi.org/10.3390/coatings13081473.
9. A.E.Gitlevich, V.V.Mikhailov, N.Ya.Parkansky et al. Electrospark Alloying of Metal Surfaces, Ştiinţa, Chisinau (1985).
10. A.D.Verkhoturov, I.A.Podchernyaeva, L.F.Pryadko et al., Electrode Materials for Electrospark Alloying, Nauka, Moscow (1988).
11. A.D.Verkhoturov, S.V.Nikolenko, *Strength. Technol. Coat.*, **2**, 13 (2010).
12. M.S.Storozhenko,O.P.Umanskyi, V.B.Tarelnyk et al., *Powder Metall. Met.Ceram.*, **59**, 330 (2020). https://doi.org/10.1007/s11106-020-00166-1
13. O.O.Vasiliev, V.B.Muratov, T.I.Duda, *Physics and Chemistry of Solid State*, **18**, 358 (2017). https://doi.org/10.15330/pcss.18.3.358-364
14. P.S.Kisly, V.A.Neronov, T.A.Prikhna et al, Aluminum Borides, Nauk. Dumka, Kiev (1990) .
15. A.P.Umanskyi, M.S.Storozhenko, V.E.Sheludko et al., *Functional Materials*, **28**, 694 (2021). https:/doi.org/10.15407/fm28.04.694.
16. A.P.Umanskyi, M.S.Storozhenko, V.E.Sheludko et al., *Metallophys. Adv. Technol.*, **43**, 1443 (2021). https:/doi.org/10.15407/mfint.43.11.1443.
17. A.P.Umanskyi, A.I.Dukhota, V.E.Sheludko et al., *Functional Materials*, **29**, 514 (2022). https:/doi.org/10.15407/fm29.04.514.

18. UA Patent 107193 (2016).
19. P.F.Tortorelli, K.Natesan, *Mater. Sci. & Eng. A.*, **258**, 115 (1998).
20. M.Zamanzade, A.Barnoush, and C.Motz, *Crystals*, **6**, Article Number 10 (2016). https://doi.org/10.3390/cryst6010010.
21. Y.Du, Q.Li, S.Chen et al., *Coatings*, **12**, Article Number 1641 (2022). https://doi.org/10.3390/ coatings12111641.
22. M.Kitano, H.Ishii, Y.Shirai et al, *J. Vac. Sci. Technol. A.*, **29**, Article Number 021002 (2011). https://doi.org/10.1116/1.3543709.
23. J.Małecka., *High Temp. Mater. Proc.*, **34**, 35 (2015). https://doi.org/10.1515/htmp-2013-0112.
24. S.Rajendran Pillai, P.Shankar, R.V.Subba Rao et al., *Mater. Sci. Technol.*, **17**, 1249 (2001).
25. M.Ali Abro, J.Hahn, and Dong Bok Lee., *Korean J. Met. Mater.*, **56**, 350 (2018). https:/doi.org/10.3365/KJMM.2018.56.5.350.
26. S.-F.Wang, C.Zhang, G.Sun et al., *Opt. Mater.*, **36**, 482 (2013). https://doi.org/10.1016/j.optmat.2013.10.014.
27. M.L.Whittaker, H.Y.Sohn, R.A.Cutler., *J. Solid State Chem.*, **207**, 163 (2013). http://dx.doi.org/10.1016/j.jssc.2013.09.028.
28. V.V.Vasil`ev, A.A.Luchaninov, V.E.Strel`nitsky, *VANT. Ser. Physics of radiation damage and radiation materials science (86)*, **3**, 167 (2005)
29. V.S.Kovalenko, A.D.Verkhoturov, L.F.Golovko et al., Laser and Electroerosion Hardening of Materials, Nauka, Moscow (1986).
30. S.Okada, T.Atoda, *J. of the Ceram. Soc. Jap.*, **88**, 547 (1980).
31. R.R.Altunin, E.T.Moiseenko, and S.M.Zharkov, *Phys. Solid State*, **62**, 200 (2020). https://doi.org/10.1134/S1063783420010059.
32. J.Arbeiter, M.Vončina, B.Šetina Batič, J.Medved, *Materials*, **14**, Article Number 7208 (2021). https://doi.org/10.3390/ma14237208.