ENGINEERING TRANSACTIONS • *Engng. Trans.* • **64**, 4, 473–484, 2016
Polish Academy of Sciences • Institute of Fundamental Technological Research (IPPT PAN)
National Engineering School of Metz (ENIM) • Poznan University of Technology

A Novel Hybrid Spraying Method for Obtaining High Quality Coatings

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The aim of this study is to present the development of the hybrid method, and its possible applications, advantages and limitations. The new elaborated method of spraying can be applied for the production of coatings working in an aggressive environment. In the paper, the corrosion-erosion resistance of coatings obtained by the hybrid method is presented. The structure and chemical composition of coatings are obtained by the scanning electron microscopy (SEM). The made samples were subject to cyclic corrosion test in air and at high temperature of 650°C. The changes in mass of samples in time were measured and the curve of the course of corrosion processes was specified. In this paper, the results of abrasion test on T07 stand and erosion tests under a load of 200 g in ambient and elevated temperature are presented. The presented results confirm the correctness of chosen parameters of a new, elaborated and innovative hybrid method.

Key words: hybrid method, spraying system, coatings.

1. Introduction

The classical, ultrasonic thermal spraying of coatings is widely used to coat the critical wear parts, such as: chassis, bearing, valves and turbines and their components. The process is characterized by very high deposition rate, of about [1–4]:

- 70% at a flow rate of powder of 7.2 kg/h_{armat},
- 12 kg/h of fuel gas with a liquid fuel gun.

The porosity of the obtained coating by the high velocity oxygen fuel (HVOF) system is a few percent. The coating is characterized by a very good adhesion to the substrate –approximately 60 to 80 MPa and low oxygen content – between 0.5 to a few percent [4].

Currently, the ultrasonic spraying methods are being developed in two basic directions (Tables 1 and 2):

1. The first direction is the reduction the spraying process time. The diameter modification of gun ensures the acceleration of particles in the gas stream and increases the efficiency of the process, for example, the HVAF method. This problem is well described in the literature [1–5].
2. The second direction is the reduction of the thermal stress generated in a coating during the spraying process (Table 2).
   In this regard, the following technologies can be identified [6–11]:
   a) cold spraying methods, for example: cold gas dynamic spray method (CGDM) in which the kinetic energy, i.e., the speed of the particles

Table 1. Modification of ultrasonic gun and the selected obtained structure of coatings [4–9].

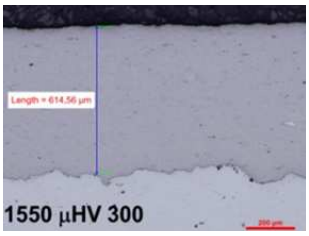
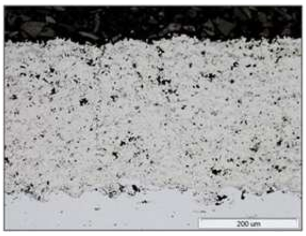
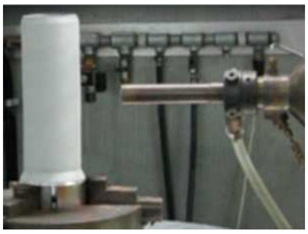
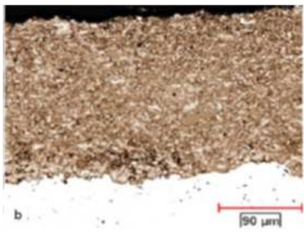
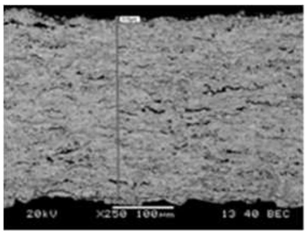
Process type	View on the gun	Selected structure	Literature
High Velocity – E-Gun Spraying			[4, 5]
High Velocity Air Fuel (HVAF)			[6, 7]
High Velocity Oxygen Fuel (HVOF)			[8, 9]

Table 2. Modifications of the ultrasonic methods to decrease the temperature of coating [4–7].

Process type	View on the gun	Selected structure	Literature
Cold spray			[4, 5]
Cryogenic spray			[6, 7]

is increased while the thermal energy is reduced. Thus, it becomes possible to obtain nearly oxygen-free coatings,

b) the thermal spray technology with cryogenic cooling presented and patented in the United States of America, which uses a cryogenic liquid as the medium of the cooling system in the thermal spray process,

c) the hybrid method – using equipment in the form of newly constructed cooling nozzles of a micro-jet type. The nozzles enable the precise and selective cooling of coating with stream of selected gases immediately after spraying. The micro-jet nozzles are patented in Poland.

The hybrid spraying technology is one of the innovative methods of thermal spraying. The advantage of this method is the ability to control the spraying structure of coating with a precise and selective cooling of the surface immediately after spraying. The construction of micro-injector gives the possibility of a modification of the classical spraying or welding methods, because it is compatible with these systems. The developed hybrid method with the forced selective cooling is characterized by high intensity of heat transfer produced by obtaining a very high coefficient of heat exchange between the applied coating and micro-streams of cooling fluid. So far, this method has not been completely described in the literature [12].

Therefore, the main aim of this article is to present the development of the hybrid method, and its possible applications, advantages and limitations. In the article, the selected results of tested coatings obtained by the innovative hybrid method are presented. For the preliminary findings of the process, the compressed air is used as the cooling medium with the micro-injector. It is most comparable to the classical HVOF process. The other gases, like nitrogen (N_2) and helium (He_2), are used in the hybrid spraying process.

2. Hybrid method – development

During the thermal spraying of coating, the molten metal, composite or ceramic particles are sprayed with a gun on the part of the construction materials or equipment. Thermal kinetic energy required to melt the powder and acceleration of molten material in the gas in order to deposit the particles on the surface landing require considerable heat input (Fig. 1).

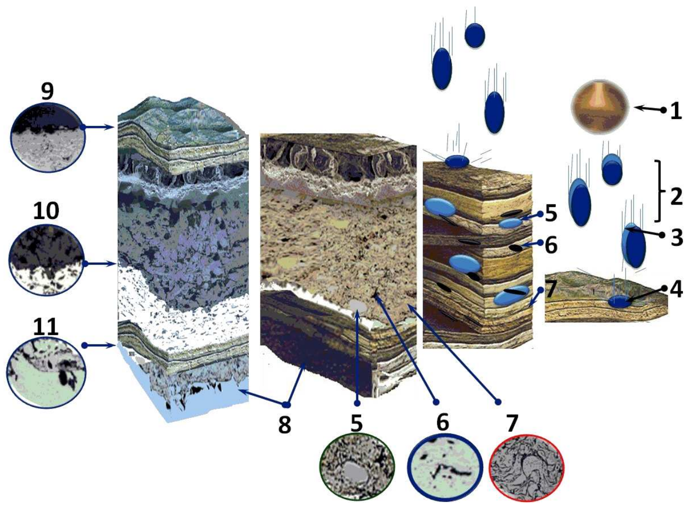


Fig. 1. Building a full coating of a desired thickness: 1 – heat source (arc, flame), 2 – speeding up particles, 3 – oxide coating, 4 – blowing particles into the ground, 5 – non- molten particles, 6 – pores, 7 – oxide layers, 8 – base material, 9 – surface roughness, 10 – transition zone in the coating layered, 11 – transition zone between the coating.

Building a full coating of a desired thickness requires repeating the spraying process (Fig. 2). This means that the thermal energy is supplied during the spraying process. This is the critical point of the process. This energy can lead to an overheating of both the coating and the substrate, and to the formation of thermal stresses in the coating. The latter is the cause of cracks and delamination of coatings during their exploitation. Therefore, the specific heat removal,

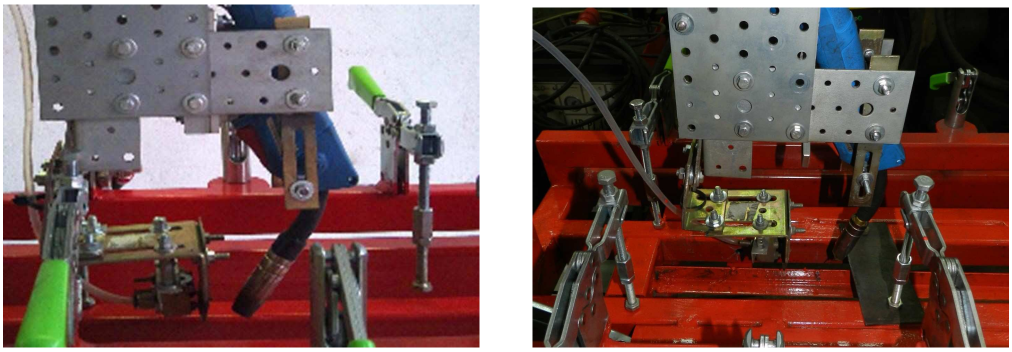


FIG. 2. Injector of cooling system in welding process [14].

immediately after the spray coating, should protect against an excessive accumulation of thermal stress. The literature data and the results of experimental studies of the material structure obtained by a micro-injector cooling process showed the positive impact of a new nozzle design for the heat removal immediately after the welding process. The nozzle (Fig. 2) was developed and patented in 2011. Until now, the micro-injector has been used only in welding processes. This solution is widely described in the literature, e.g., the national and international research publications of a Polish team from the Bialystok University of Technology, and the Silesian University of Technology in collaboration with industry [14–16].

The proposed solution is novel, and the presented results clearly indicate the advisability of the use of such equipment on a production scale. Therefore, the team undertook the investigations on the adaptation of the new solution for the thermal spraying methods.

The concept of hybrid spraying process is presented in Fig. 3.

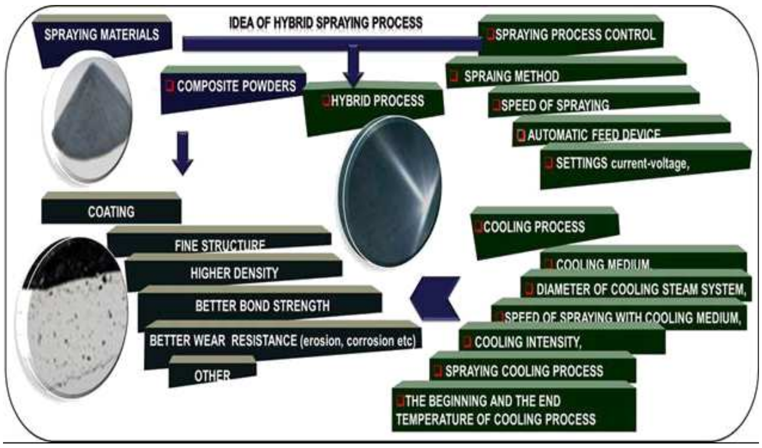


FIG. 3. Idea of hybrid spraying process.

This scheme is based on the assumption that the use of the selective and very precise method of cooling after spraying prevents an overheating of the coating and significantly reduces the transition times between stitches.

In this process, the use of suitable cooling medium will achieve the desired coating structure in a shorter time. It is also expected that it will reduce time and energy during the process.

In addition, it is assumed that

- properly designed nozzle must have compatibility with conventional methods of thermal spray coatings,
- the construction of a nozzle and cooling medium will efficiently reduce the heat energy supplied to the surface of the coating during the spray process – HVOF type,
- the nozzle allows for the preparation of supersonic finely dispersed, compact structure with a relatively low porosity, good adhesion to the substrate and a suitable density.

It was considered that the most important parameters in the cooling process are: the diameter of the stream, the distance and angle of the injector with respect to the surface being sprayed and spray gun, feed rate and the type and pressure of the cooling medium.

Initial studies showed difficulties in adjusting micro-streams of the cooling gas to the bundle of ∼4–5 cm, required for the process of spraying. Furthermore, it was found that the use of several injectors, one after another, complicated the process. Too intense cooling initiates longitudinal cracks of coatings [12].

Currently, the newly developed types of nozzles with appropriately designed membrane allow the generation of stream and adapting it to the type of spraying material. The developed new design of cooling-injectors will be the subject of a patent.

3. The concept of material and technology

The material – technology concept takes into account that during the spraying of powder materials or wire by the hybrid method, the parameters of the process can be chosen and changed. The parameters combination gives the practical possibility to control the obtained coating structure and thus determines the properties of material.

It was assumed that the cooling stream sprayed immediately on the surface of coating can lower the thermal stress in the coat, and the obtained structure will be characterized by: fine-dispersive, high density, low porosity, and very good utility properties such as: corrosion and erosion resistance. The properties should be better than the properties of comparable coatings obtained by standard thermal spraying methods.

The gases like air and nitrogen were chosen as a cooling medium in the hybrid process. The oxygen, as a cooling gas, is the most comparable to the classical process of ultrasonic spraying method – HVOF. The nitrogen was the main cooling medium in the process of thermal spraying and welding with cryogenic cooling process. According to the literature data, it was found that nitrogen gas should protect the coating against excessive oxidation during the process [2, 10]. This is characterized by absence of the oxidation potential. Therefore, to produce coatings with a high resistance to wear, nitrogen was selected as the cooling medium. The cooling streams are formed inside the injector. The construction of the injector is modeled on the design of micro-injector to welding process, but the new design allows forming the beam with a diameter of a few centimeters. This new design is connected with a gun to thermal spraying.

The materials used in the research were thermally sprayed nickel-chromium coatings obtained by the HVOF method and the hybrid method. The coatings were sprayed on the corrosion resistant steel. The distance between the surface and the gun was about 25 cm. The samples of the corrosion test had the design of rollers, so that the entire surface was protected by the obtained coating. The second part of samples was sprayed on the sheets and this part was used in the erosion and abrasion tests.

4. Methods, results and discussion

The presented results of selected studies are aimed to demonstrate the possibilities of the new hybrid method in the area of the control structure of the deposited coatings. The obtained structure of coatings is analyzed by optics (LM) and scanning electron microscope (SEM). The obtained results allow to conclude that the coatings are characterized by a high structure quality (appropriate density, compactness, very low (1–2%) porosity, uniformity and homogeneity throughout the volume) (Table 3). The chemical composition is comparable for all the studied materials.

The micro-hardness and the thickness of the coatings are measured on the TH170 micro-hardness tester and thickness gauge (Table 4). A higher micro-hardness characterized the coatings after the hybrid process. It can be assumed that small amounts of hard nitrides appeared in the structure of the obtained coating.

This hypothesis is not confirmed by the research results obtained with a scanning microscopy (Table 3). The chemical composition was comparable for all the studied materials and the nitrides were not detected.

Table 3. Microstructure and chemical composition of obtained coating in HVOF and hybrid process.

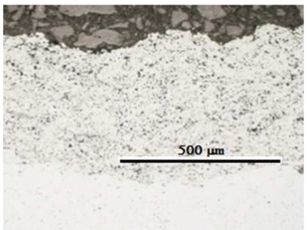
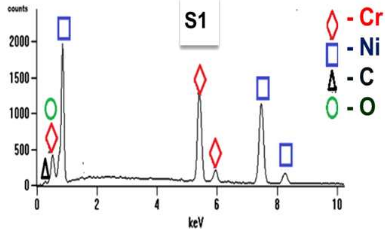
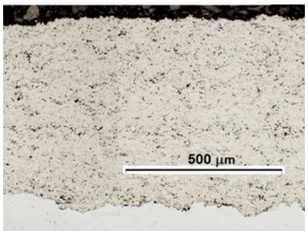
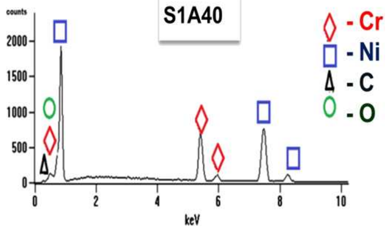
Process type	Selected structure	Chemical composition
High velocity oxygen fuel		
Hybrid method		

Table 4. Micro-hardness and thickness of coatings.

Process type	Thickness of coating	Micro hardness of coating
High velocity oxygen fuel	460 µm	1330 mHV_{300}
Hybrid method	550 mm	1450 mHV_{300}

The prepared samples are subjected to cyclic oxidation test at 650°C on the research stand presented in Fig. 4. Kinetics of corrosion process, presented in

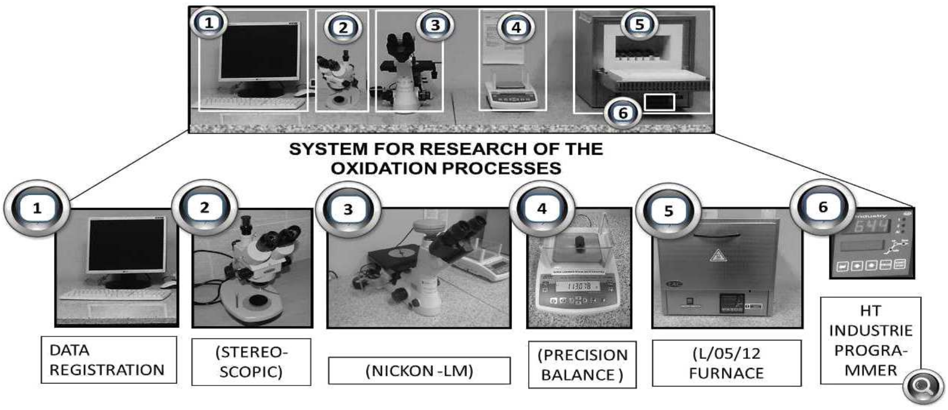
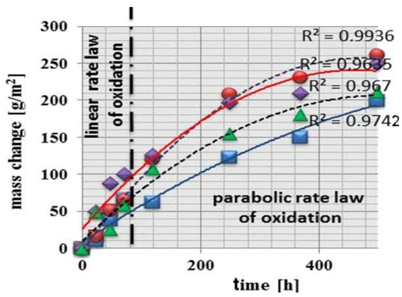


Fig. 4. Research corrosion stand.

Table 5, were analyzed through an analysis of the weight of growing scale after 24, 48, 72, . . . , 500 hours of exposition time.

Table 5. Results of oxidation test in elevated temperature.

Corrosion resistance in test conditions: air, temperature 650°C, 500 hours, mass change as a function of heating time [g/m^2]				
Description	Linear rate law M_I	Parabolic rate law $(M_F - M_I)$	M_F – mass finish [g/m^2]	Curves of mass change as a function of heating time
S1 ▲	25.8554	159.87	185.7256	
S2 ●	50.8979	159.939	210.8369	
S1A$_{40}$ ■	38.2761	122.895	161.1710	
S2A$_{40}$ ◆	87.7575	74.8761	162.6336	

The analysis of curves leads to the conclusion that for each tested coating, after an initial period of rapid weight growth, the stabilization period of oxidation is registered. This period is compatible with the parabolic rate law of oxidation.

Therefore, the reaction rate constant (k_p), was calculated from the parabolic law [13]:

$$\left(\frac{\Delta m}{A}\right)^n = k_p \cdot t + C, \tag{4.1}$$

where $n = 2$, Δm –the mass increment after exposure time, C – free parameter (correlated with the initial, non-parabolic rate law), and A – surface area for the cylinder samples calculated from:

$$A = 2\pi \frac{d^2}{4} + \pi dh, \tag{4.2}$$

where d – diameter of sample and h – height of sample.

The reaction rate constants were calculated only for the stability period of the oxidation process. The average value of the k_p parameter for the HVOF is about $1.42 \cdot 10^{-10}$ and for hybrid sprayed coatings is about $5.75 \cdot 10^{-11}$ (Table 6). The results confirm the high heat resistance of all the studied materials.

Table 6. Calculated value of the k_p reaction rate constants.

Process type	k_p for the stability period	Average value of k_p
High velocity oxygen fuel	$1.41992 \cdot 10^{-10}$ $1.4214 \cdot 10^{-10}$	$1.42053 \cdot 10^{-10}$
Hybrid method	$8.38064 \cdot 10^{-11}$ $3.1146 \cdot 10^{-11}$	$5.75266 \cdot 10^{-11}$

Next, the selected tribological properties of the obtained coatings are determined. The results of abrasion test on T07 stand (Fig. 2) and erosion tests under load 200 g in ambient and elevated temperature are presented in Tables 7 and 8.

Table 7. Results of erosion test in ambient temperature.

	Erosion wear in ambient temperature [g]					
	Temperature 20°C, rotation 600			Temperature 20°C, rotation 900		
Sample	m_1 [g] (before test)	m_2 [g] (after 1st test)	m_I [g] $(m_1 - m_2)$	m_3 [g] (after 2nd test)	m_{II} [g] $(m_2 - m_3)$	Δm [g] $(m_I + m_{II})$
S1	30.78016	30.76778	0.01238	30.69803	0.06975	0,08213
S2	27.86069	27.84689	0.0138	27.7625	0.08439	0.09819
$S1A_{40}$	28.40018	28.38848	0.0117	28.34621	0.04227	0.05397
$S2A_{40}$	30.6617	30.6498	0.0119	30.62525	0.02455	0.03645

Table 8. Results of abrasion and erosion test in elevated temperature.

	Abrasion wear [g]			Erosion wear [g]		
	Temperature 20°C, rotation 600			Temperature 650°C, rotation 900		
Sample	m_1 [g] (before test)	m_2 [g] (after 1st test)	m_I [g] $(m_1 - m_2)$	m_1 [g]	m_2 [g]	Δm [g] $(m_2 - m_1)$
S1	34.5273	34.47385	0.05345	51.5231	51.5741	0.0510
S2	34.5499	34.49969	0.05021	51.5879	51.6404	0.0525
$S1A_{40}$	34.8360	34.0265	0.04905	50.3966	50.4426	0.0460
$S2A_{40}$	34.4633	34.41743	0.04587	50.3745	50.4191	0.0446

5. Conclusion

This study confirms that the presented technology allows to obtain the desired structures of coating, which indicates the correct implementation of the spraying process. The structure of coating obtained by the hybrid method is comparable to the HVOF structure obtained with the same powder materials.

The obtained structure is finely dispersive, and with low porosity, good density and good adhesion to the substrate. The results confirm correctly selected parameters of the hybrid spraying process. The samples sprayed by the hybrid method were obtained in a shorter time than the samples coated by a conventional ultrasonic process. The consumptions of powder materials and energy were also lower by about 25%. The results must be confirmed in the future research. The presented results of the oxidation test show that the hybrid sprayed samples had better properties of corrosion resistance in elevated temperature in comparison to the samples sprayed using the HVOV method. The registered curves follow the parabolic rate law in the test conditions (650°C, time 1000 h, air). The erosion and abrasion test confirm good properties of all studied materials, and they show slightly better erosion resistance of the hybrid sprayed coatings as compared to the HVOF coatings. The results were obtained within the statistic range of error.

Acknowledgment

A part of this study was performed within the projects S/WM/1/2013 financed from the science fund by The Polish Ministry of Science and Higher Education.

References

1. Song Y., Lv Z., Liu Y., Zhuan X., Wang T.J., *Effects of coating spray speed and convective heat transfer on transient thermal stress in thermal barrier coating system during the cooling process of fabrication*, Applied Surface Science, **324**: 627–633, 2015, doi: 10.1016/j.apsusc.2014.10.157.
2. Wielage B., Pokhmurska H., Student M., Gvozdeckii V., Stupnyckyj T., Pokhmurskii V., *Iron-based coatings arc-sprayed with cored wires for applications at elevated temperatures*, Surface and Coatings Technology, **220**: 27–35, 2013, doi: 10.1016/j.surfcoat.2012.12.013.
3. Hanson T.C., Settles G.S., *Particle temperature and velocity effects on the porosity and oxidation of an HVOF corrosion-control coating*, Journal of Thermal Spray Technology, **12**(3): 403–415, 2003, doi: 10.1361/105996303770348276.
4. Tarasiuk W., Szczucka-Lasota B., Piwnik J., Majewski W., *Tribological properties of super field weld with micro-jet process*, Advanced Materials Research, **1036**: 452–457, 2014, doi: 10.4028/www.scientific.net/AMR.1036.452.
5. Oksa M., Turunen E., Suhonen T., Varis T., Hannula S.P., *Optimization and characterization of high velocity oxy-fuel sprayed coatings: techniques, materials, and applications*, Coatings, **1**(1): 17–52, 2011, doi: 10.3390/coatings1010017.
6. Szymański K., Hernas A., Moskal G., Myalska H., *Thermally sprayed coatings resistant to erosion and corrosion for power plant boilers – a review*, Surface and Coatings Technology, 2014, doi: 10.1016/j.surfcoat.2014.10.046.

7. Gorlach A., *Evaluation of the HVAF thermal sprayed coating*, Research and Development (R&D) Journal of the South African Institution of Mechanical Engineering, **24**(3): 4–8, 2008, http://www.saimeche.org.za/?page=RD_2008.

8. Zurecki Z., Ghosh R., Mebrahtu T., Thayer M.J., Stringer S.R., *Automated substrate cooling system for HVOF coating operations*, [in:] E. Lugscheider [Ed.], *Air Products & Chemicals*, Maastricht, Netherlands, 2008.

9. Ghosh R., *Cryogenic nitrogen gas cooling for thermal spray coatings*, Spraytime, **14**(4): 2–4, 2007.

10. Fauchais P., Vardelle A., *Thermal sprayed coatings used against corrosion and corrosive wear* [in:] H.S. Jazi [Ed.], *Advanced Plasma Spray Applications*, ISBN 978-953-51-0349-3, 2012, © The Author(s), CC BY 3.0, http://www.intechopen.com/books/advanced-plasma-spray-applications/thermal-sprayed-coatings-usedagainst-corrosion-and-corrosive-wear, 2012.

11. Węgrzyn T., Piwnik J., Łazarz B., Hadryś D., *Main micro-jet cooling gases for steel welding*, Archives of Metallurgy and Materials, **58**(2): 555–557, 2013.

12. Szczucka-Lasota B., Szymański K., *The selected tribological and structural properties of protective coatings obtained by different methods*, Solid State Phenomena, **246**: 81–84, 2016, doi: 10.4028/www.scientific.net/SSP.246.81.

13. Mrowec S., Werber T., *Gas metal corrosion* [in Polish: *Korozja gazowa metali*], Śląsk, Katowice, 1975.

14. Węgrzyn T., Piwnik T., Wieszała J., Hadryś D., *Control over the steel welding structure parameters by micro-jet cooling*, Archives of Metallurgy and Materials, **57**(3): 679–685, 2012, doi: 10.2478/v10172-012-0073-9.

15. Hadryś D., Węgrzyn T., Piwnik J., *The effect of different micro-jet streams number on plastic properties of welds*, Archives of Metallurgy and Materials, **60**(3): 1617–1622, 2015, doi: 10.1515/amm-2015-0282.

16. Hadryś D., Piwnik J., Węgrzyn T., Łazarz B., *Coefficient of restitution and plastic strain for impact of elements welded with micro-jet cooling*, Transport Problems, **9**(2): 61–68, 2014.

Received October 24, 2016; accepted version October 29, 2016.