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THERMAL SPRAYING – INTERDISCIPLINARY DOMAIN

Mihaela Popescu[1], Ibolyka Bran[1], Radu Alexandru Roşu[1], Carmen Opriş[1]
[1]Politehnica University of Timişoara, hela.popescu@yahoo.com

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Abstract: Thermal spraying is a domain used more and more due of its increased applicability in many domains as naval, railway, aeronautic, etc. In this paper is described the interdisciplinary of thermal spraying domain by participating of sciences and technologies, metallurgy, surface engineering, chemistry, automation, medicine, etc presenting some aspects of metallic, ceramic, composite cermets and biocompatible coatings. Also, are presented various research directions and interaction of international control and supervisory authorities, occupational supervisory (OSHA, IIS/IIW, EWF, ISO/EN).

1. Introduction

Thermal Spraying (TS) known a high applicability, because presents many advantages. Currently, there are many industries that are using thermal coating technologies to obtain characteristics required by the designers. Among the areas, most advanced domain where are using coated components are aerospace and automotive industries [2,6,9,15,16,17,18,19].

There are two major research and innovation directions of thermal coatings: obtaining new materials with increasingly characteristics and use of increasingly sophisticated technologies to improve the characteristics of the deposited layers. Also, there are made efforts to increase productivity, decreasing the costs, obtaining more robust technology. Thermal spray coating technologies of composite, cermet, ceramic or biocompatible materials are relatively new, due to the incompatibility between the deposition material and the basic material [7].

2. Types of coatings and their applicability

Deposition of diverse materials by thermal spraying processes presents the following advantages in comparison with the welding processes [16,17]:

- The piece temperature during the coating process remains lower (150-200°C), which does not lead to structural modifications or piece deformations;
- The quantity of deposited material is smaller and easier to control during the deposition process;
- It can be deposited layers with different thickness taking only measures to cool the part after prolonged deposition;
- the deposited layer is porous, allowing the storage of the lubricant, assuring a better lubrication;
- It can be obtained pseudoalloys materials that can not be realized in melt state, (aluminum with steel)
- The coatings can be made on any basic materials ensuring the desired roughness.

Some of the disadvantages of thermal spray coating processes are mentioned [18,19]:

- The deposited layer has a low resistance to bending and traction;
- impossibility to realize holes in the deposited layers;
- the coatings can not be linear solicited, the deposited material can crack;
- the technological process is not effective for small pieces, because much material is lost;
- Is necessary to ensure adequate environmental protection (ventilation, pollution protection).

Thermal properties of the coatings made with the same thermal spraying techniques are presented in Table 1.

Table 1. Coatings properties realized by thermal spraying

Process	Flame	Detonation	Plasma jet	Electric arc
Oxidation	High	Low	Low	Low
Porosity, %	5 – 15	0,25 – 5	0,5 – 10	3 – 10
Thickness, mm	0.1 – 15	0.05 – 0.3	0.05 – 1	0.1 – 50
Dilution, %	0,1 – 2	0	0 – 0.2	0
Adherence, N/mm^2	20	170	35 – 70	28

The advantages of thermal spraying are that it can be using advanced materials such as ceramic composite, cermet, shape memory alloys and producing thermal barrier coatings. Due to high temperature stability, low thermal conductivity and thermal shock resistance, the ceramic materials can be used as thermal insulation (zirconium oxide).

3. Converging concerns of TS

PT is characterized by a strong interdisciplinary, reflected by a strong involvement of many sciences and disciplines (Figure 1), but also of constant concern of many international authorities.

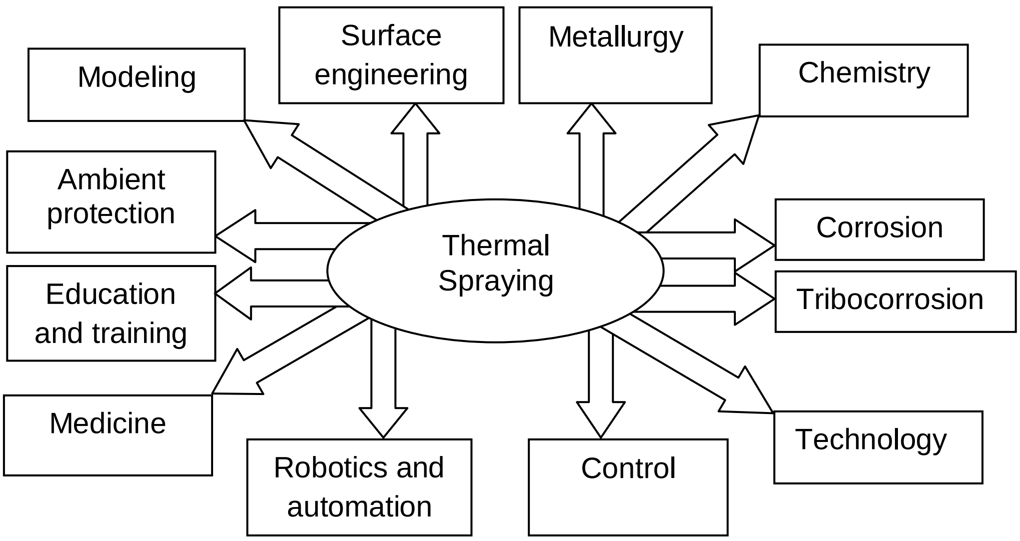

Figure 1. Thermal spraying interdisciplinary

3.1 TS interdisciplinary by involving science and disciplines

TS is the result of the domains interdisciplinary, of a sustained research & development work [2]:

- **Metallurgy**, including powder metallurgy, through his realizations participates to the development of the TS. If the initial applications were strictly to the realization of the wear resistant structures (hard loading for new parts or re-used components) with the implications of tribology, rapid prototyping and then a spectacular development for medical applications with biocompatible powder [1].
- **Surface engineering and coating technology** includes processes that can modify the surface behavior of materials in order to improve their performance, aesthetics and economic production. This means the modification of the surface of a component to give it different properties from those that one basic material. The goal may be to

increase corrosion resistance, reduce energy losses resulted from friction, reduce wear, the development of thermal barrier-type systems (with the role of thermal insulation) and also to ensure durability and operating performance of the basic material, obtaining biocompatible layers or realization of new parts by rapid prototyping. In order to protect the parts against wear and corrosion were developed cermet (ceramic-metal) composite coatings. The layers used in those areas are layers consisting of particles of WC or Cr_3C_2 distributed in a metal matrix which can be a pure metal or an alloy consisting of Ni, Cr, Co. Such layers are applied on the surface of components by thermal spraying technologies.

- **Tribocorrosion** is considered as surface transformation science as a result of mechanical disruption and chemical reactions that occur between elements of a tribosystem exposed to a corrosive environment [1]. Tribocorrosion process can be characterized by its synergy resulting from the coupling of mechanical and environmental effects [1]. This synergism leads to degradation and therefore to a loss of material. Friction induces tension in the materials and plastic deformation, residual stress and a variety of materials which can even cause structural changes [1]. Also, friction induces a local destruction of material surface layer formed by interaction with the environment. Tribocorrosion involves mechanical and chemical interactions between the surfaces which are in the presence of a corrosive environment.
- **Chemistry** is important due the reaction which appears at TS. It is described an example of dehydroxylation of hidroxyapatite at high temperatures. At higher temperatures, dehydroxylation occurs where hydroxyapatite gradually looses its hydroxyl (OH-) group. The dehydroxylation reaction occurs as two steps following the reactions in equation 1 and equation 2 [9].

$Ca_{10}(PO_4)_6(OH)_2 \rightarrow Ca_{10}(PO_4)_6(OH)_2$-2xOx أx + xH_2O (1)
(hydroxyapatite) → (oxyhydroxyapatite)

$Ca_{10}(PO_4)_6(OH)_2$-2xOx أx → $Ca_{10}(PO_4)$6O x أx + $(1-x)H_2O$ (2)
(oxyhydroxyapatite) → (oxyapatite)

Where أ is vacancy and $x < 1$

Decomposition

For temperatures below a certain critical point, HA retains its crystal structure during dehydroxylation and rehydrates on cooling. However, once the critical point is exceeded, complete and irreversible dehydroxylation results. This process is called decomposition. Decomposition of HA leads to the formation of other calcium phosphate phases, such as β-tri-calcium phosphate (β-TCP) and tetra-calcium phosphate (TTCP). The reactions involved in decomposition are presented in equation 3, 4 and 5 [9]. Firstly, oxyapatite transforms to tri-calcium phosphate, tri-calcium phosphate and tetracalcium phosphate both transform into calcium oxide.

$Ca_{10}(PO_4)_6$O x أx → $2Ca_3(PO_4)_2$ (β) + $Ca_4(PO_4)$2O (3)
(oxyapatite) → (tricalcium phosphate) + (tetracalcium phosphate)

$Ca_3(PO_4)_2 \rightarrow 3CaO + P_2O_5$ (4)
(tricalcium phosphate) → (calcium oxide) + (phosphorus pentoxide)

$Ca_4(PO_4)2O \rightarrow 4CaO + P_2O_5$ (5)

(tetracalcium phosphate) → (calcium oxide) + (phosphorus pentoxide)

- **Medicine** - Science and orthopedic surgery and the tribological aspects of bone implants, particularly hip and knee joints and dental implants are influenced by human body fluids at the interface [1]
- **Automation** - become a necessity in ensuring quality deposited layers and constant thickness (Figure 2).

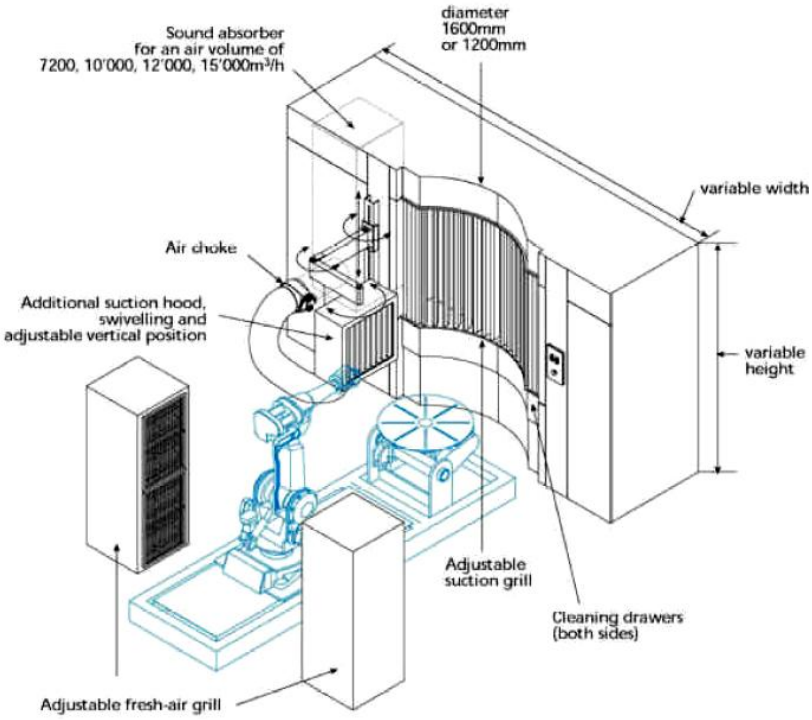

Figure 2. Work space of thermal spraying robot [20]

- **Ensuring quality** by non-destructive and destructive control has made possible the development of properly structures. International and European law (by continuous harmonization) have covered all aspects of TS for example (EN 657 and EN ISO 14917 wits powder–composition and technical supply conditions EN ISO 14232, thermal spraying-metallic inorganic coatings-zinc, aluminum and their alloys EN ISO 2063 and acceptance inspection of thermal spraying equipment EN ISO 14231).
- **Education and training.** Train staff in the sense of theoretical and practical knowledge, is made according to EWF guidelines. In a management system an important role plays the professional competence as a combination of staff knowledge and experience engaged in specific activities in a context where no production management system can be successful without the technical competence specifications. Training and continuing professional development is particularly important in thermal spraying. Under the authority of the European Welding Federation (EWF), based on continuity (standard courses: European Welding Engineer, International Welding Engineer, Welding Inspector, European Welding Technician, European Welding Specialist Practitioner, European Welder) are ongoing and courses in thermal spraying: The European specialist in thermal spraying (EWF-459r1-06) European thermal spraying (EWF-507r1-06) European thermal spray practitioner (EWF-592-01).
- **Modeling** with performant programs (DOE-Design Of Experiments, FEM-Finite Element Method, etc) help to comportment previsions of the pieces covered by PT.

- **Ambient environmental protection** of PT is imposed by the environment management (Figure 3).

Ambient protection at Thermal Spraying-measures

As environmental protection measures at thermal spraying can be listed as follows:
- adequate fire protection and portable fire extinguishers in the vicinity of spraying zone
- ensure adequate ventilation and filtration process of fine powders
- spraying cell must be constructed from noncombustible materials (the interior surfaces must be smooth, designed to prevent the deposits and to facilitate proper ventilation, cleaning and washing);
- spraying filters should be properly fitted to their supports
- mechanical ventilation adequate to remove flammable fuel vapors in a secure location
- prohibition of smoking in areas where exist flammable liquid fuels, solvents, adhesives, and in places where they are used, sprayed.

Figure 3. Systematization of the environmental protection measures

Exhaust ventilation systems required to TS (figure 4).

a) b)

Figure 4. The Praxair system: a) dry cartridge dust collector, b) acoustical enclosure

Exposure of the TS operators, compared with other joining methods: MMA, MAG, MIG, TIG is shown in Table 2 and Table 3.

Table 2. Exposure to welding fume, data period 1986 to 1996, at the person (PAS) [10]

Procedure	Sampling: at the person (PAS)					
	with capture²)			without capture²)		
	Number of mea-suring data	Frequency of exceeding for		Number of measuring data	Frequency of exceeding for	
		$6mg/m^3$ ³)	$3mg/m^3$ ⁴)		$6mg/m^3$ ³)	$3mg/m^3$ ⁴)
Manual metal arc welding	386	19	38	186	49	73
MAG welding	741	31	58	544	69	83
MIG welding	250	22	43	176	43	68
TIG welding	149	5	10	182	5	15
Thermal cutting (flame, plasma, laser cutting)	66	14	23	18	52	69
Thermal spraying (flame, arc, plasma spraying)	40	14	29	1	0	0

[1]) welding fume = fine dust
[2]) with/without extraction system
[3]) $6mg/m^3$ = limit value for respirable fraction in the period 1986-1996
[4]) $3mg/m^3$= indicative value for preventive occupational examinations according to BGI „Welfing fume"

Table 3. Exposure to welding fume, data period 1986 to 1996, stationary [10]

Procedure	Sampling: at the person (PAS)					
	with capture²)			without capture²)		
	Number of mea-suring data	Frequency of exceeding for		Number of measuring data	Frequency of exceeding for	
		$6mg/m^3$ ³)	$3mg/m^3$ ⁴)		$6mg/m^3$ ³)	$3mg/m^3$ ⁴)
Manual metal arc welding	45	4	8	41	4	19
MAG welding	187	5	16	110	14	29
MIG welding	58	2	23	52	7	24
TIG welding	39	0	1	35	4	9
Thermal cutting (flame, plasma, laser cutting)	33	0	11	13	18	26
Thermal spraying (flame, arc, plasma spraying)	28	15	19	0	-	-

[1]) welding fume = fine dust
[2]) with/without extraction system
[3]) $6mg/m^3$ = limit value for respirable fraction in the period 1986-1996
[4]) $3mg/m^3$= indicative value for preventive occupational examinations according to BGI „Welfing fume"

An evaluation of the measurements of welding fume exposure at workplaces with the respect to compliance with:

- the limit value then valid the respirable fraction of 6mg/m^3
- the indicative value for welding fume for preventive occupational medical examinations of 3mg/m^3

TS environmental protection must be ensured taking into account the relevant legislation in quality management and occupational health bodies Occupational Safety and Health Administration (OSHA) (figure 5).

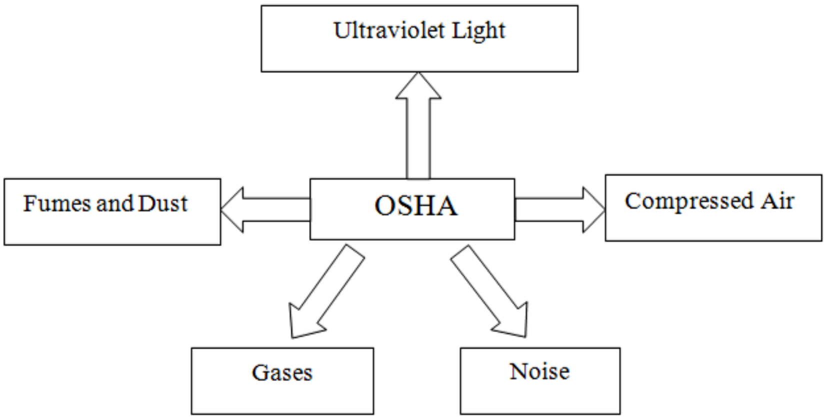

Figure 5. OSHA activities and preoccupations

After numerous researches and studies OSHA establish the exposure limits of the operators to avoid professional diseases.

Environmental protection particularized on TS processes. Thermal spraying produces large amounts of particulate hazardous substances, depending on the process used (table 4). Thus, emissions of hazardous substances are significantly lower in flame spraying than in arc spraying [10].

Plasma spraying produces the largest emission of hazardous substances compared to flame or arc spraying. Furthermore, the hazardous substances generated depend on the material and are exclusively emitted from the spraying material. The parent metal has no influence on the amount and the composition of the hazardous substance produced. In all spraying processes, welding fume and dust concentrations in the breathing zone exceed the general dust limit value for both A and E fractions, if there in so or insufficient capture and separation of hazardous substances. In general, spraying processes (especially plasma spraying) should be carried out in the closed booths so that the exposure of welders and others persons to fume, dusts and noise is reduced to minimum [10].

Flame spraying using wires and powder as spraying material generates gaseous and particle substances. The chemical composition of the particulate substances in fume/dust corresponds to the composition of the spraying material. In flame spraying, as in other oxy-fuel processes, generation of nitrous gases should be taken into account. During flame spraying with high alloy spraying material (Cr<27%, Ni<22%) high levels of dust emissions include also high proportions of nickel oxide [10]. In this process, nickel oxide concentrations considerably exceed 0,5mg/m^3. Chromium compounds may in addition be generated. It is assumed that a varied mixture of different chromium oxides is produced. This mixture is hardly soluble, also contains chromium and is regarded as carcinogenic. Nickel oxide is the key component when nickel and nickel alloys are used.

Table 4. Fume emissions at thermal spraying processes

Process	Spraying material	Welding fume/ key component
Flame spraying	Unalloyed, low-alloy steel (alloying components < 5%)	A, E dust[1)], nitrogen oxide
	Chromium-nickel steel	Nickel oxide, nitrogen dioxide
	Nickel and nickel alloys	Nickel oxide, nitrogen dioxide
	Aluminum base materials[3)]	A, E dust[1)], nitrogen oxide
	Lead alloys	Lead oxide, nitrogen oxide
	Copper and copper alloys	Copper oxide[2)], nitrogen dioxide
	Other non-ferrous metals and alloys	A, E dust[1)], nitrogen oxide
Arc spraying	Unalloyed, low-alloy steel (alloying components < 5%)	A, E dust[1)]
	Chromium-nickel steel	Nickel oxide
	Nickel and nickel alloys	Nickel oxide
	Aluminum base materials[3)]	A, E dust[1)]
	Copper and copper alloys	Copper oxide[2)]
	Other non-ferrous metals and alloys	A, E dust[1)]
Plasma spraying	Copper and copper alloys	Copper oxide[2)]
	Chromium-nickel steel	Nickel oxide
	Nickel and nickel alloys	Nickel oxide
	Cobalt base alloys	Cobalt oxide

[1]) Limit value for A dust (respirable dust)/welding fume and E dust (inhalable dust)
[2])Limit value for copper fume
[3])Aluminum-base materials (pure aluminum, aluminum alloys) limit value for aluminum oxide fume

Arc spraying produces large emissions of particles substances. For comparable spraying parameters and at approximately the same deposition rate, the emission of hazardous substances from aluminum wire is higher than that of zinc, chromium, nickel and aluminum bronze wires, where the emissions of hazardous substances are comparable. During arc spraying with chromium-nickel or nickel-base spraying materials, nickel oxide shall be considered as key component. The diameter of particles is usually smaller in arc spraying than in flame spraying, resulting in a larger respirable fraction.

Plasma spraying produces higher emissions of hazardous substances than flame or arc spraying with the same spraying materials, due to the use of a much higher spraying rate. Most of the plasma spraying processes are therefore carried out in enclosed systems (encapsulated systems). Nevertheless, there is still a health risk for the operator for the few manual spraying processes, if the high hazardous substance concentrations are not exhausted at source. Practice shows that the old TRK and MAK values can be substantially exceeded during plasma spraying with materials having higher proportions of critical materials (chromium, nickel, cobalt, etc) if no effective exhaust systems is in operation.

- Provisions relating to ergonomics (Figure 6)

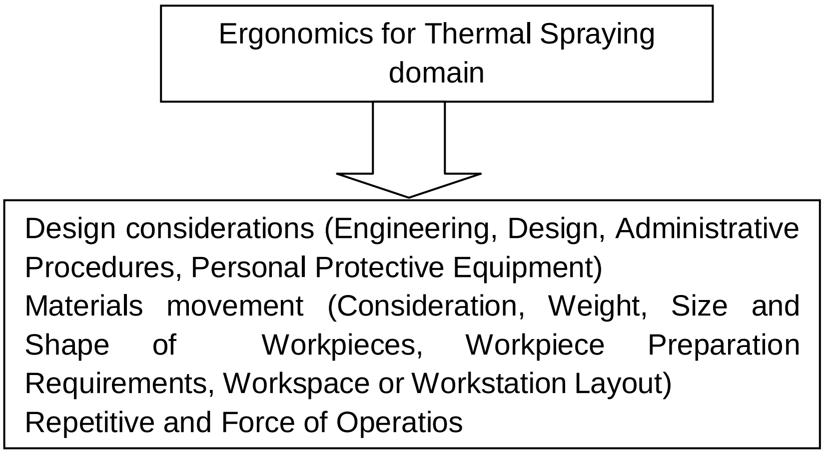

Figure 6. Provisions relating to ergonomics

3.2 TS Interdisciplinary by involvement of international organizations

International Institute of Welding (IIW / IIW) by IC Committees, respectively VIII provides the elaborations of the TS documents as the technological side and as well as occupational health. In Figure 7 are shown schematically the involvement of the international bodies on TS field.

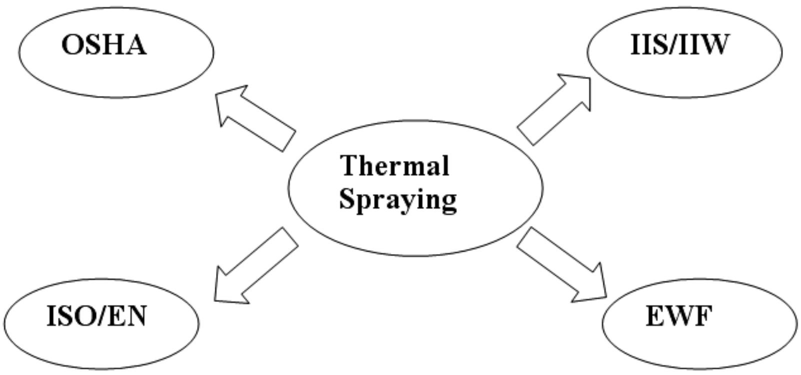

Figure 7. Involvement of the international bodies on TS field

4. Conclusions

4.1 It was described the elements related to development of inter-and multidisciplinary field of TS, indicating of the domains influences to ensure environmental protection

4.2 Multidisciplinary developing led to TS domain performance and to the ability to ensure quality coatings, according to all quality assurance requirements.

4.3 The obtained results by successive developments lead to the identification of potential new applications.

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