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A complex investigation of structure and properties of thermally sprayed Ni and Cu-based coatings

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Résumé. — Plusieurs méthodes expérimentales, notamment analyse par rayons X, microscopie optique et électronique, mesure de la porosité et interférence d'ondes thermiques sont appliquées afin de rechercher les propriétés des couches métallisées par projection thermique. Certaines conclusions concernant l'influence de la composition chimique et de la technologie sur la structure et les propriétés mécaniques et physiques des couches sont présentées.

Abstract. — A number of experimental methods including X-ray analysis, optical and electron microscopy, porosity measurements and thermal wave interferometry are applied for investigation of the properties of thermally sprayed coatings. Some conclusions about the influence of the chemical composition and the technological parameters on the structure and mechanical properties of the coatings are drawn.

1. Introduction.

Thermal spraying is used to produce metal, metal-ceramic or ceramic coatings by impact of molten or semi-molten particles on a metal substrate, which may have a flat or a more structured surface texture. The coating's composition and properties can be the same, or different, from those of the substrate. Materials to be sprayed usually are in form of wire, powder or rod.

The thermally sprayed coatings are chosen with appropriate mechanical, thermal, anti-corrosion, electrical, etc. properties.

The correlation between the wear-resistance, microstructure and other coating's properties has previously been investigated [1]. Other studies have been performed on the bonding mechanism between the sprayed coating and the substrate [2, 3]. The thermal diffusivity and thermal effusivity coefficients as well as the thermal conductivity and the specific heat of the coatings have been estimated in [4, 5]. The influence of the coating properties on the sensitivity of the thermal-wave testing techniques is investigated in [4]. A comparison of coating microstructure on the propagation of thermal and ultrasonic waves is made in [6]. Microstructure, composition, micro- and macrostrains in layers of nitrocarburized iron and steel has been investigated in [7] by the

means of optical and electron microscopy and X-ray analysis. However, a survey of the literature revealed that the number of papers describing the results obtained by a more wide ranging investigation of a number of properties of the flame sprayed coatings is quite restricted.

The purpose of this paper is to report on the application of a variety of experimental methods to investigate the properties of the flame sprayed coatings, the mechanisms of their formation and the dependence of the coating's properties on some technological parameters of the spraying process.

2. Preparation of coatings and experimental methods for their characterization.

2.1 PREPARATION OF SAMPLES. — The coatings were applied by the MOGUL U-10 equipment for thermal spraying using powders produced by the « INTERWELD » firm, Austria. The scheme of the equipment used is shown in figure 1. Principally the equipment acts as follows: the flame of the thermal gun results from the burning of acetylene and oxygen passing through the nozzles of the gun. The coating powder is transported into the flame by the transport gas. For some of the samples an air jet has been also blown through the nozzles at angle 10° to

Fig. 1. — Block-diagram of the equipment for thermal spraying of powders.

the sprayed beam. This air jet envelopes the flame and changes its gas-dynamic parameters and the velocity of the powder particles. The technological parameters were as follows :

- $P_{C_2H_2} = 0.09-0.10$ MPa (pressure of acetylene) ;
- $P_{O_2} = 0.18-0.20$ MPa (pressure of oxygen) ;
- $P_{tr.gas} = 0.05-0.06$ MPa (transport gas pressure) ;
- powder grain size — $45 - 90 \mu m$.

The chemical composition of the used powders is given in table I.

Table I. — Chemical composition of used powders, according to the firm — producer « INTERWELD ».

mark	chemical composition, wt %							
	Fe	Si	Ni	Cr	Al	B	Cu	WC, W ₂ C*
MOGULM-48	1.00	0.80	57.00	3.90	1.90	0.60	—	34.80
MOGULM-135	—	—	3.80	—	9.80	—	86.40	—

(*) WC and W₂C are mechanically mixed in the powder.

The samples were prepared in the form of tablets (Fig. 2). The coatings were applied on mild steel substrates (diameter 22 mm, thickness 3 mm), which

Fig. 2. — Shape and dimensions (in mm) of the samples.

were previously grit blasted by corundum. After spraying, the coatings were polished parallel and perpendicularly to their flat surfaces. Three samples S1, S2 and S3 with a coating thickness of 1 mm were prepared (Tab. II).

In order to etch the polished surfaces for the metallographical analysis, the following reactants were used :

- for sample S1 and S2 — 20 ml HNO₃ + 2 drops HF ;
- for sample S3 — 30 ml NH₄/25 %/ + 30 ml H₂O₂ (3 %) + 30 ml H₂O.

Table II. — Samples for the investigations.

sample	powder	P _{air} *, MPa
S1	MOGUL M-48	—
S2	MOGUL M-48	0.18-0.20
S3	MOGUL M-135	0.18-0.20

(*) air jet pressure.

Samples S1 and S2 were etched for 15 s at room temperature by dipping the samples into the solution and washing in water afterwards. Sample S3 was etched at room temperature, the reactants being applied in this case by cotton wool for 5 s, followed by water rinsing.

2.2 EXPERIMENTAL METHODS. — The following methods were used :

- metallographical analysis ;
- X-ray analysis ;
- measuring of the relative porosity ;
- SEM (scanning electron microscopy) ;
- interferometry with thermal waves.

By the metallographical analysis the microstructure was investigated and the microhardness was estimated. The Vickers microhardness was measured by applying the 100 g load for a loading time of 10 s. Hundred measurements were made to obtain good statistics for drawing the microhardness distribution curves.

Phase analysis by X-ray diffraction was performed using a diffractometer with a CoK α characteristic X-ray beam and a scanning angle 2θ from 20° to 120°. In this way, information about the composition and the crystal structure of the coatings was obtained.

The relative porosity was estimated by hydrostatic weighing of the coating after its separation from the substrate. This involved drying, covering the coating with a thin vaseline film, hanging on a thin thread, and weighing in air and in water.

The porosity p (%) was estimated by the following formula :

$$p = \left(1 - \frac{\frac{W_z \rho_v}{\rho_z}}{W - W' - \frac{W_c \rho_w}{\rho_c} - \frac{W_v \rho_w}{\rho_v}} \right) 100.$$

where :

ρ_z : density of the coating material ;

ρ_w : density of distilled water ;

ρ_c : density of metal thread, used for the hanging of the coatings ;

ρ_v : density of the vaseline ;

W_z : the coating weight in air ;

W_c : weight of the part of the metal thread, which is under water ;

W_v : weight of vaseline film applied on the coating ;

W : weight of the sample with the vaseline film and the metal thread in air ;

W' : weight of the sample with the vaseline, hung on the thread in water.

By SEM mapping it was possible to determine the following : the average chemical composition of the coatings ; the average chemical composition of each type of the grains observed metallographically and also of parts of the grains ; the distribution of the main chemical elements in the coating.

The schematic diagram of the photoacoustic experimental setup is shown in figure 3. A plexiglass cell, designed as a Helmholtz resonator with an about 2 cm³ sample chamber volume and a condenser microphone Brüel & Kjær 4166 were used. The beam of a 50 mW He-Ne laser was interrupted by a computer controlled mechanical chopper in the frequency range 13-250 Hz and fell unfocused onto the sample. The amplitude and the phase of the photoacoustic signal were registered by a PARC 5301 lock — in amplifier and were sent to a computer through a RS 232 C interface. The samples

used in this case are identical to S1 and S2 but their diameter is 14 mm.

3. Experimental results and discussion.

The microstructures of the samples S1, S2 and S3 are shown in figure 4. It is obvious, that the microstructure of S3 is more homogeneous and with less porosity than S1 and S2. Three grain types were observed in S1 and S2 :

— grains with inhomogeneous microstructure, containing inclusions in the volume with the form of rods or rocks (defined as A in Fig. 4) ;

— grains with a complicated form without formations, appearing as bright regions (type B in Fig. 4) ;

— grains with inhomogeneous microstructure, consisting of regions containing dot — like formations (type C in Fig. 4).

In sample S2, some of the grains have a perfectly spherical shape as can be seen from figure 4. It is supposed, that they correspond to the already described type C grains, but are formed from such powder particles, for which the technological parameters were not suitable to cause their melting. The spherical grains are observed over the whole S2 coating surface, and quite rarely over the S1 coating surface.

In figure 5 the Vickers microhardness distribution curves for different types of grains and for the whole observed surface are shown. It is obvious that in samples S1 and S2 the regions with inclusions in the form of rods or rocks (type A, Fig. 4) have the lowest values of the microhardness. The highest values of the microhardness are observed in the grains with dot — like formations inside them and for spherical grains (type C, Fig. 4). The microhardness values in S1 and S2 are much more inhomogeneous than those in S3. This inhomogeneity is more pronounced for S2. The average value of the microhardness for S1 and S2 is higher than for S3.

The results from the X-ray diffraction analysis are given in table III. The data for pure Ni and pure Cu in the table are taken from a reference book. The experimentally obtained diffracted beam angles for the investigated samples have been corrected by the data for a quartz monocrystal standard, whose diffraction pattern has been registered at exactly the same conditions as for the investigated specimens. This procedure was followed to exclude the systematical error when the diffraction pattern was taken. From the X-ray data it is obvious, that the obtained coatings have a polycrystalline structure and all the registered diffraction peaks follow strictly those of the basic materials (Ni or Cu). As it could be seen from table III, the diffraction peaks of the investigated samples are shifted to smaller θ angles in comparison with those for pure Ni or Cu. The

Fig. 3. — Block-diagram of the photoacoustic experimental equipment for thermal wave interferometry.

Fig. 4. — Microstructure of the coatings-cross-section (X 300). a) for sample S1 : A-grains with inclusions in the form of rods ; B-grains with complicated shape without formations ; C-grains with dot-like formations. b) for sample S2 : A-grains with inclusions in the form of rocks ; B-grains with complicated form without formations ; C-grains with dot-like formations. c) for sample S3.

Fig. 5. — Vickers microhardness distribution curves (A, B, C, as in Fig. 4 ; S-summary). a) for sample S1 ; b) for sample S2 ; c) for sample S3.

Table III. — *X-ray diffractometry investigations by CoK α beam.*

sample	θ , deg										
pure Ni	23.45	26.10	27.35	30.55	40.90	45.90	49.65	52.77	57.40	61.65	66.85
S1, S2	23.44	26.06	27.38	30.50	40.85	45.88	—	—	57.38	—	—
pure Cu	22.85	25.40	26.65	29.70	39.35	44.45	48.00	50.95	55.25	59.10	63.70
S3	22.56	25.36	26.31	29.26	38.76	43.70	47.25	49.88	54.13	57.82	—

applied X-ray phase analysis does not show any evidence of the existence of more than one phase. Probably the main phases of the polycrystalline coatings formed are solid solutions on the base of nickel or copper respectively. If other phases exist, their quantity is obviously smaller than a few volume percents and so are not sufficient to be registered by this method. The shift of the diffraction peaks from the positions for pure Ni or Cu could be connected with the existence of different atoms in the lattice of Ni or Cu forming the solid solutions or with the residual stresses arising as a result of the difference between the thermal properties of the coating and substrate.

The first reason for the observed shift is more probable for the sample S3 which contains 14.38 wt % Al (see Tab. IV). The atomic radius of the latter ($r_{\text{Al}} = 1.43 \text{ \AA}$) is bigger than the atomic radius of Cu ($r_{\text{Cu}} = 1.28 \text{ \AA}$) and could be the reason for the observed shift to smaller θ . The comparison between the atomic radii of Ni and the alloying elements in samples S1 and S2 shows that such a shift of X-ray peaks connected with this difference should not exist. A rough estimation of the sum of the main residual stresses ($\sigma_1 + \sigma_2$), based on the shift of the X-ray peaks and performed following the procedure described in [8], gives the maximum values of $(\sigma_1 + \sigma_2) \sim 1\,000 \text{ MPa}$. These values are higher than the observed by other authors [7, 8], but the performed in this work estimation is not accurate enough and aims only to show the probable reason for the observed shift of the X-ray peaks.

In figure 6 the characteristic $K\alpha$ X-ray maps, obtained by the SEM, are shown. On the maps, the white dots show the presence of a chemical element, and the black regions — its absence. The distribution of the elements with the highest concentration in the initial powders (Ni and Cr for S1 and S2, and Cu and Al for S3) was investigated. From figure 6a and figure 6c it is obvious, that the basic metal is more homogeneously distributed in sample S3. In this sample the Al-distribution is comparatively homogeneous too, while the Cr-distribution in S1 is quite inhomogeneous.

Table IV. — *Chemical composition of the different types grains *, wt %.*

sample	type grains HV **, kg/mm ²	Al	Si	Cr	Fe	Ni	Cu
S1	average	4.63	5.15	10.30	2.67	77.25	—
	A HB = 131.41	6.80	0.98	0.50	0.25	91.47	—
	B HB = 820.38	—	5.60	19.90	3.94	70.56	—
	C	—	6.69	13.97	3.62	75.73	—
	HB = 1 036.69	—	—	—	—	—	—
S2	average	5.14	5.39	10.14	3.34	75.98	—
	A HB = 331.99	—	1.22	0.17	1.13	97.98	—
	B HB = 925.69	—	6.53	14.62	4.13	74.12	—
	C	—	6.25	16.78	3.85	73.12	—
	HB = 1 062.24	—	—	—	—	—	—
S3	average HB = 179.60	14.38	—	—	1.32	2.77	81.54

(*) A, B, C as in figure 4.
(**) Vickers microhardness.

The mean chemical composition of the different types of the grains observed metallographically, estimated by the SEM $K\alpha$ mapping, are given in table IV. In the same table, the mean values of the Vickers microhardness are given. As it follows from the table, the grains in the Ni-based coatings which showed the higher values of the microhardness have higher concentrations of Si, Cr and Fe at the expense of Ni. From the comparison of the data in figure 6 and table IV with those in figure 5 it follows, that the more pronounced inhomogeneity of the chemical composition in S1 and S2 in comparison with sample S3 is the reason for the wider scattering of the Vickers microhardness values in the Ni-based coatings than in the Cu-based.

a)

b)

c)

d)

Fig. 6. — Characteristic X-ray maps of the samples, obtained by SEM. a) for sample S1-Ni ; b) for sample S1-Cr ; c) for sample S3-Cu ; d) for sample S3-Al.

The increased concentration of Cr in the C-type grains of samples S1 and S2 probably is the reason for the increase of the melting point temperature of the powder particles, from which the C-type grains have been formed. Introducing an air jet during the coating procedure, as was done for sample S2, sharply decreases the probability for melting of the powder particles before they reach the steel surface. This is considered to be the reason for the formation of the spherical grains. As it follows from table IV the C-type grains have the highest value of the Vickers microhardness and increased concentration of Cr and Si. Obviously their increased microhardness is due to the increased melting point temperature of the particles because of the increased Cr and Si concentrations.

The higher homogeneity of the microstructure and microhardness in S3 is due to the more favourable thermophysical properties of the basic coating metal (Cu) — i.e. the lower melting point temperature and higher thermal conductivity (with respect to the Ni-based coatings). Aluminium, which is the next in concentration after Cu in the MOGUL M-135 Powder (see Tab. I) has thermal properties similar to copper. This fact probably leads to melting of all the powder particles before they reach the surface of the steel sample and to a better thermal contact between the grains of the coating during cooling. As a result the coating, produced from the Cu-based powder, has more homogeneous structure, chemical composition and properties. The lower melting point temperature of the MOGUL M-135 powder particles and the better thermal contact between them after impact surface, could be the reasons for the formation of a denser coating than the one produced from the MOGUL M-48 powder.

The results from the quantitative estimation of the porosity are given in table V. It is obvious, that the relative porosity of sample S3 is considerably lower than that of samples S1 and S2. From the data in table V it follows, that the introduction of an air jet into the flame affects the microhardness, microstructure and chemical composition homogeneity of the coating, but does not affect the porosity values.

By the thermal wave interferometry, a difference of the thermophysical properties of samples S1 and S2 has been established.

Table V. — *Porosity of the coatings.*

sample	relative porosity, %
S1	17.13
S2	17.80
S3	8.81

Fig. 7. — Phase difference as a function of the modulated frequency. (*) for sample S1 ; (x) for sample S2. Parameters for the theoretical curve : 28 μm thickness of the good thermal conductive layer and 7 μm — for the poor thermal conductive layer ; 10/1 — ratio of the thermal conductivities of the two layers.

In figure 7, the phase difference between the investigated samples and a blackened optical glass, used as a reference sample, as a function of the modulated frequency is shown. According to the Rosencwaig — Gersho theory [9] the phase difference between two homogeneous opaque thermally thick samples is 0°. This holds true to a great extent for S1. The normalized phase of S2 changes significantly below 50 Hz. Some of the possible reasons for the photoacoustic behaviour of S2 may be :

- at these frequencies S2 becomes thermally thin ;
- presence of pores and inclusions ;
- presence of thermal barriers between the particles.

In the first case one can find out from the thermal parameters, obtained in [5], that even at 10 Hz the thermal diffusion length in the coating is more than 10 times smaller than its thickness. The presence of pores is found not to affect significantly the photoacoustic signal in this case [5]. Thus the phase shift is attributed to the thermal barriers (domains with very low thermal conductivity) between the different grains. Since the deposited grains have an elongated form, coatings with similar structure can be modelled by a layered structure. The behaviour of the layered structures is described by the Opsal — Rosencwaig model [10].

The continuous curve in figure 7 gives the results from the Opsal — Rosencwaig theory with appropriate parameters.

The data from figure 7 show the existence of greater thermal barriers in S2 than in S1 sample. These thermal barriers are supposed to be due to the particles, which have reached the steel surface in an unmolten state and have formed the spherical grains observed in figure 4.

From the SEM data (see Tab. IV) it follows, that WC and W_2C were not observed in the composition of the applied coatings for S1 and S2, although their quantity in the initial powder was high enough (see Tab. I). The X-ray analysis data did not show WC, W_2C -peaks either (see Tab. III). This is the reason to assume that during the applied technological regimes WC, W_2C -particles do not stick on the surface and do not take part in the formation of the coating.

4. Conclusions.

4.1. A number of methods for a wide ranging investigation of the structure and some physical and mechanical parameters of thermally sprayed coatings have been applied. These techniques give information about the influence of the chemical composition and some technological parameters of the process of formation of the coatings and their properties.

4.2. The coating produced from the Cu-based powder, is more homogeneous compared with those produced from the Ni-based powder, it has a lower

porosity and with lower average values of the Vickers microhardness.

4.3. The higher homogeneity of the Cu-based coating is due to the higher homogeneity of its chemical composition and to the more suitable thermo-physical parameters of copper in comparison with nickel. These parameters allow all the particles in MOGUL M-135 powder to be molten during the spraying process and lead to a better thermal contact between the coating grains formed on the surface of steel and finally to a higher density of the coating.

4.4. All the investigated coatings have a polycrystalline structure and their X-ray diffraction peaks correspond to the peaks of the basic metal (Ni or Cu), but shifted to lower angles θ . The last phenomenon is probably due mainly to the residual stresses arising during the growth of the coatings. An accu-

rate estimation and analysis of the residual stresses is going to be done in our future work.

4.5. The Ni-based coatings, which have been sprayed with or without an air jet, have equal porosities, but different thermophysical properties. This difference is connected with the existence of thermal barriers between the polycrystalline grains. These thermal barriers have an influence on the thermal wave interferometry signal and are supposed to be due to the grains, which have been formed from the unmolten powder particles.

4.6. By the applied technological regimes the WC and W₂C particles, which exist in the MOGUL M-48 powders, do not adhere to the steel surface and do not take a part in the coating formation procedure.

References

- [1] CHUANXIAN D., BINGTANG H., HUILING L., *Thin Solid Films* **118** (1984) 485.
 - [2] KITAHARA S., HASUI A., *J. Vac. Sci. Technol.* **11** (1974) 747.
 - [3] DALLAIRE S., *Thin Solid Films* **95** (1982) 237.
 - [4] MORRIS J., PATEL P., ALMOND D., REITER H., *Surf. Coat. Technol.* **34** (1988) 51.
 - [5] VELINOV Ts., GERGOV B., BRANSALOV K., *Rev. Phys. Appl.* **25** (1990) 817.
 - [6] PATEL P., ALMOND D., *J. Mat. Sci.* **20** (1985) 955.
 - [7] ROZENDAAL H. C. F., COLIJN P. F., MITTEMEIJER E. J., *Surf. Eng.* **1** (1985) 30.
 - [8] TAILOR A., X-ray metallography (John Wiley and Sons, Inc. New York — London) 1961.
 - [9] ROSENCWAIG A., GERSHO A., *J. Appl. Phys.* **47** (1976) 64.
 - [10] OPSAL J., ROSENCWAIG A., *J. Appl. Phys.* **53** (1982) 4240.
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