JTTEE5 12:234-239

Metallurgical Characterization and Determination of Residual Stresses of Coatings Formed by Thermal Spraying

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(Submitted 24 February 2001; in revised form 26 February 2002)

This work presents an experimental determination of residual stresses in 35CrMo4 (Euronorm) low alloyed steel substrates with thermally sprayed coatings. Two different materials were separately deposited. The first one consisted of a blend of two superalloys: Cr-Ni steel and Cr-Mn steel, designated 55E and 65E, respectively. The second material was molybdenum. In a first part, basic characteristics of the deposited layers (metallographic analysis, hardness, and adhesion) are presented. In a second part, the determination of the residual stresses, in both substrate and thermal sprayed layers is performed using an extensometric method in combination with a simultaneous progressive electrolytic polishing. The influence of a nickel-aluminum (80:20%) bond-coat and/or a post-annealing at 850 °C in air for 1 h is studied.

Keywords adhesion, coatings, extensometry, interface, layer removal, metallography, microhardness, residual stresses

1. Introduction

The purpose of any surface treatment is to improve a specific property, but the process systematically generates residual stresses, which influence the global behavior of the obtained structure.[1,2] Depending on the stress distribution within the material and its application, this influence may be considered favorable or unfavorable. Therefore, the stress determination is important, not only at the surface, but also at a certain depth to know the total stress field.

This work presents metallurgical characterization and determination of the residual stresses in a 35CrMo4 steel that has been coated using thermal spray techniques. Two types of coating materials were used. The first one is a combination of two wires: a Cr-Ni steel designated by 55E and a Cr-Mn steel designated as 65E. They are co-sprayed using an Arc Spray 234 (Metal Spray Co. Ltd, Auckland, New Zealand) electric arc gun. The second material is molybdenum wire with the designation 99E. It is deposited by a Mark 62 (Metal Spray. Co. Ltd.) flame spray gun.

These two spray processes are particularly used to resurface and renovate worn mechanical parts surfaces. Electric arc and flame depositions constitute two possibilities in competition for these applications.

The first part of this work consists in a basic characterization of the samples by metallographic study followed by adhesion tests and microhardness profiles.

The second part is focused on the experimental determination of the residual stresses in the substrate and deposited layers with an extensometric method and a gradual electrolytic polishing.

The influence of an 80Ni-20Al bond coat and a post-annealing in air at 850 °C for 1 h is analyzed.

2. Experimental Techniques

2.1 Materials and Spraying Conditions

The substrate was a 35CrMo4 (Euronorm) steel with area dimensions of 60 × 40 mm and a thickness of 4 mm. The thickness of the top deposits was about 0.4 mm. The Ni-Al bond coat was about 0.2 mm thick. It was deposited by the electric arc gun

Table 1 Chemical Composition, wt.%, of the Wires Used

	Wt.%							
Wire	**Fe**	**C**	**Cr**	**Ni**	**Mn**	**Al**	**Si**	**Mo**
75E				79.2		19.4	0.1	
55E	66.8	<0.03	20.1	8.2	2.88	0.24	0.64	
65E	94.1	0.21	2.2		2.03	0.23	0.35	
99E								99.2

Table 2 Thermal Spray Conditions of (a) the Steels, 55E + 65E, and Ni-Al, 75E, and (b) Molybdenum, 99E

(a) Parameter	Value
Spraying pressure	3×10^5 Pa
Generator voltage	30 V
Current intensity	100 A
Spraying distance	140 mm
Wires diameter	1.6 mm
(b) Parameter	**Value**
Acetylene pressure	10^5 Pa
Oxygen pressure	1.6×10^5 Pa
Speed of wire moving	0.065 m/s
Spaying distance	140 mm
Wire diameter	2 mm

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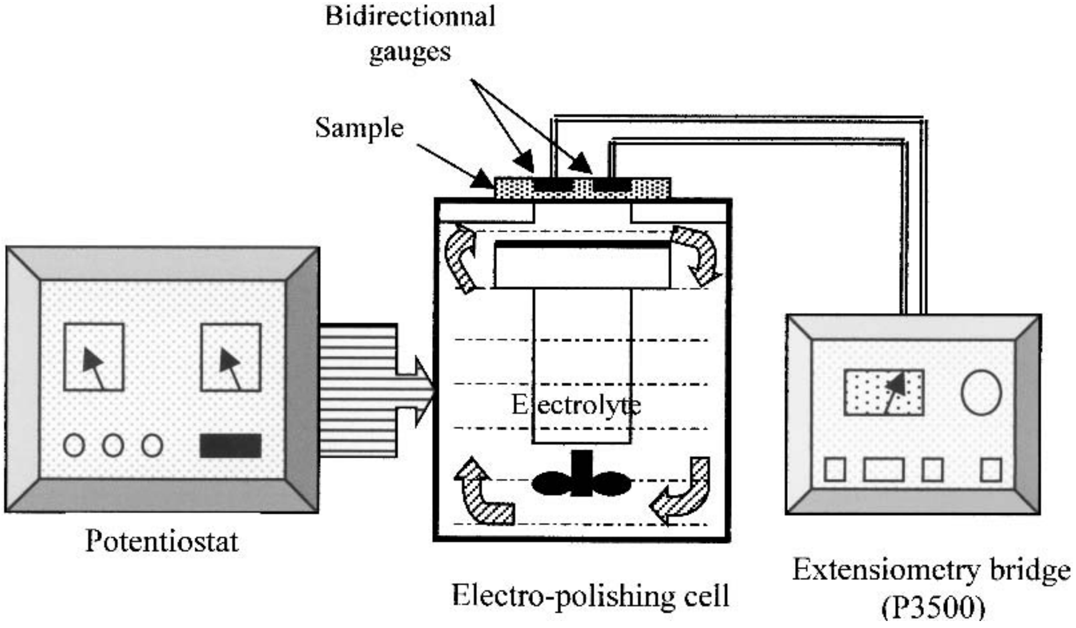

Fig. 1 Experimental procedure for determining the residual stresses

using 75E designated wire. Selected samples (with and without bond coat) were annealed for 1 h at 850 °C in air to study the influence of such annealing. The chemical compositions of the wires used are presented in Table 1.

Prior to the deposition, the samples were cleaned, degreased and grit blasted according to the usual standard.[2-4] For all the specimens, a roughness value Ra of about 7 μm, which is suitable for a good mechanical adhesion of the deposit, was obtained.[5] Table 2 presents the thermal spray parameters.

2.2 Metallurgical Characterization Techniques

The metallographic study was focused on the substrate-deposit interface to examine the diffusion and adhesion phenomena at the interface. Nital (5%) was used to etch the samples and reveal the microstructure near to the substrate-layer interface.

A tensile test was used to measure the adhesion of the deposited material on the substrate. The coated sample was glued to a virgin substrate with a Cyanocrylate TB-1702 (Threebond Co., Ltd. Tokyo, Japan) glue,[3] and the tensile force needed for separation was measured. The two surfaces to be glued were initially polished. The adhesion of different coatings with their substrates is estimated as the stress value when the decohesion starts taking place.[3] Failure often occurred within the glue and only a part of the deposit was removed, particularly for the annealed samples. A ±10% error is taken in the adhesion stress measurements.

The HV microhardness is calculated by averaging the results of three tests made at each point across the layers of the different samples and the error is estimated to be ±5%.

2.3 Residual Stresses Determination Procedure

The determination of residual stresses for the different samples is based on the measurement of deformations during electro-chemical controlled thinning of the deposits.[6,7] The procedure (Fig. 1) consists in measuring micro-deformations using a bi-directional extensometric gauges glued on the substrate side of the materials. Very thin layers of the deposits are removed by electrochemical polishing across the sample surface. Longitudinal and transversal deformations $\varepsilon_{\mathrm{Long}}$ and $\varepsilon_{\mathrm{Trans}}$ are instantaneously measured after each removal.[2,6,8]

Table 3 Young's Modulus of the Used Materials

Material	*E*, GPa
35CrMo4	208
(55E + 65E)	82
Molybdenum	424
Ni-Al bond-coat	89

The electrochemical machining was performed by a DISA Electropol Mark 5 of Struers Instruments, Copenhagen, Denmark electropolishing machine using a 50 g/l sodium chloride (NaCl) solution. The temperature was maintained below 40 °C so additional thermal or mechanical stresses were not generated during the electrochemical machining process.

The optimal electropolishing parameters were determined by preliminary studies and are $I = 4A$ and $V = 20V$ which, for our specimen geometry, achieved a machining speed of about 3-5 μm/min (depending on the layer type). Under these conditions, the polishing was uniform and removed the as-received surface roughness of the coatings. The thickness of each removed layer was about 50 ± 5μm.

The stress distribution that was originally in the material may be calculated from the stress history as material is removed. The principle of this measurement method is based on the evaluation of the stress rearrangement, which takes place when a small thickness of deposit is removed from the surface. The related displacements along the faces opposite to the machining direction are measured by CEA-XX-125UT-120 strain gauges

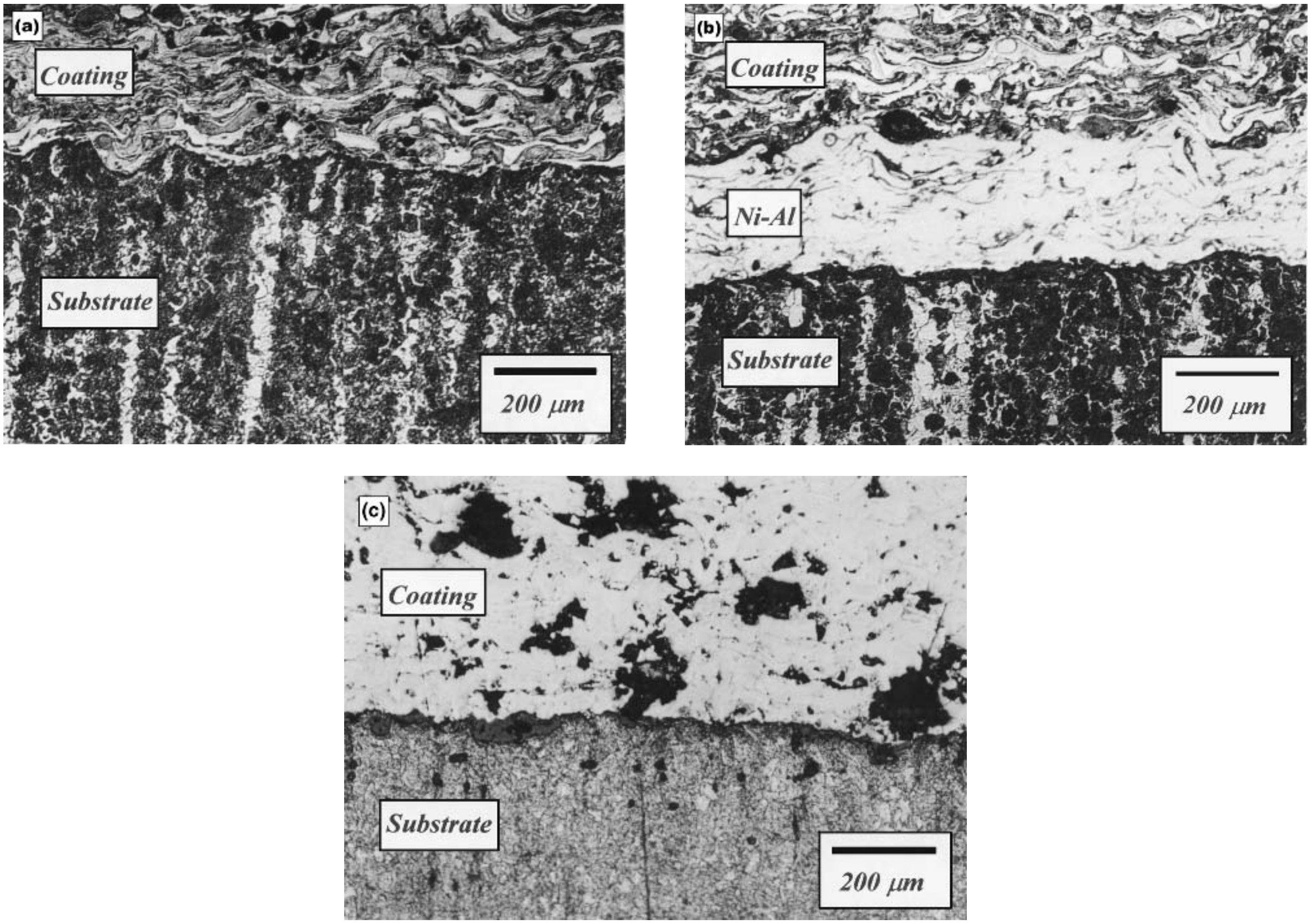

Fig. 2 **(a)** Metallographic analysis of the 35CrMo4 /(55E + 65E) single-layer coating; **(b)** metallographic analysis of the 35CrMo4/Ni-Al/(55E + 65E) two-layer coating; **(c)** metallographic analysis of the 35CrMo4/molybdenum single layer coating

(Vishay Micromeasurements Group, NC) connected to a P3500 Vishay (Micromeasurements Group, NC) extensometer bridge. The deduced micro-deformation values $\Delta\varepsilon_{\mathrm{Long}}$ and $\Delta\varepsilon_{\mathrm{Trans}}$ are loaded into a program that calculates the residual stress distribution in the sample.[1,2,9] The determination of the Young's modulus E of the used materials [35CrMo4, 80Ni-20Al, (55E + 65E), and 99E], needed for this computation procedure, was done in a series of experimental studies using a test based on the magnetic resonance method.[10,11] It can be noticed that as increases the Young's modulus, then the material is oxidized; and as E decreases then the material becomes more porous. These two opposing trends give rise to values presented in Table 3.

Samples can be divided into two groups, depending on whether the coating composition consisted of 55E + 65E or molybdenum. Each group comprised four different sample types: substrate (35CrMo4)/deposit (55E + 65E or molybdenum); substrate (35CrMo4)/bond coat (Ni-Al)/deposit (55E + 65E or molybdenum); substrate (35CrMo4)/deposit (55E + 65E or molybdenum) annealed in the air at 850 °C for 1 h; and substrate (35CrMo4)/bond coat (Ni-Al)/deposit (55E + 65E or molybdenum) annealed in the air at 850 °C for 1 h.

The results are presented to demonstrate how the residual stresses evolve from the surface of the deposit into the substrate, at which point they converge to zero. Deformations measurements and residual stresses determination are made to an accuracy of ±10%.

3. Results and Discussion

3.1 Metallographic Analysis

Figure 2 shows that deposits contain pores and a significant fraction of oxides as would be expected with an atmospheric thermal spray process. However, the deposit-substrate interfaces or bond coat-deposit-substrate interfaces are well defined and of high metallurgical quality.

The post-annealed samples revealed a more homogenous distribution of inclusions and smaller sized carbides and oxides.

3.2 Coating Adhesion

The values obtained for the as coated samples of the first group (74 MPa in case of steel coating and 68 MPa in case of molybdenum) confirm that grit blasting has given a good mechanical adhesion as well.

The results presented in Fig. 3 confirm the beneficial role of

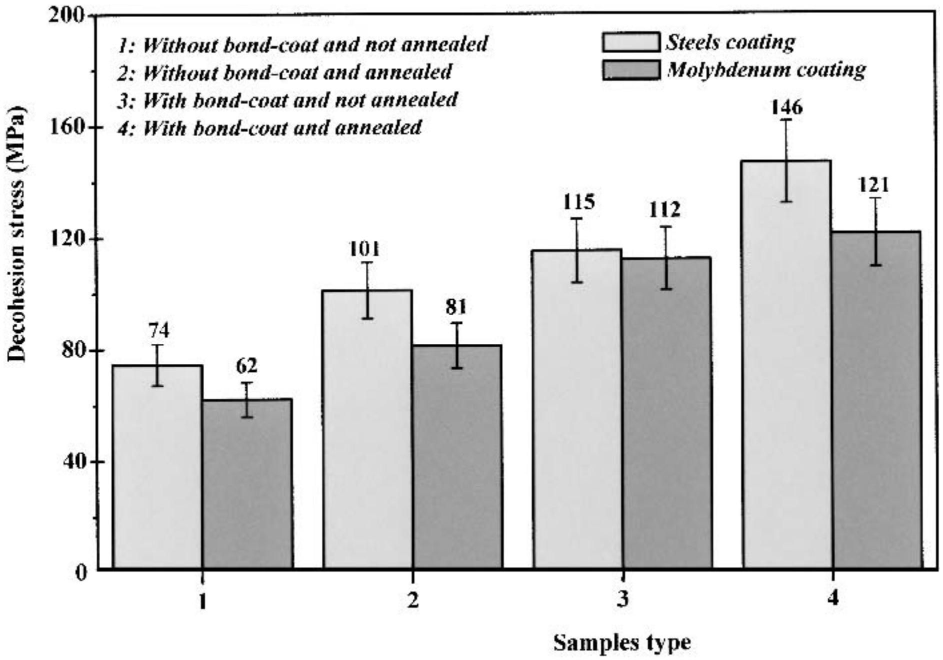

Fig. 3 Coating adhesion according to the samples types

the Ni-Al bond coat and the post-annealing. The combination of these two factors permits approximately doubling of the adhesion stress for samples bond coated and annealed by comparison with samples without bond coat and not annealed. Failure stresses pass from 74-146 MPa for (55E + 65E) steel coating and from 68-121 MPa in the case of molybdenum coating.

3.3 HV Hardness Profile

The hardness values of the substrate vary between 250 and 270 $HV_{0.1}$ for all non-annealed samples and the annealing at 850 °C raised this hardness to about 300 $HV_{0.1}$. Heat treatment has induced austenization of the 35CrMo4 substrate and the transformation during cooling in air leads to a slightly finer, so a little more harder microstructure compared with the initial alloy.

Tables 4 and 5 show that hardness of deposits for all samples decreases after annealing, especially for molybdenum, which changed from about (1700-1800 $HV_{0.15}$) to about 1300 $HV_{0.15}$. For steel deposits, hardness decreased from ~470 to ~420 $HV_{0.1}$. However, Ni-Al bond coat hardness has increased from about 350 to about 450 $HV_{0.1}$ after annealing whatever the superficial layer.

3.4 Residual Stresses Distribution

Figures 4 and 5 show respectively the variation of the deformations ε_{Long} and ε_{Trans} and the corresponding residual stresses σ_{Long} and σ_{Trans} across the thickness of the substrate that was only grit-blasted and without any deposit.

The obtained curves are classic.[2,11] In fact, the grit blasting created a compressive superficial zone of about 250 μm. The generated compressive residual stresses have an average value of about −350 MPa with a peak of more than −700 MPa at a depth of about 100 μm.

Table 4 HV Microhardness of the (55E + 65E)/Ni-Al/35 CrMo4 Samples

Layer Type	Position, mm	Not Annealed Sample HV	Annealed Sample HV
55e + 65e	0.1	495	412
	0.2	416	376
	0.3	445	406
Ni-Al	0.45	358	449
	0.55	362	469
Substrate	0.8	255	288
	1.2	248	293
	1.6	252	280
	2	238	285

Table 5 HV Microhardness of the 99E/Ni-Al/35CrMo4 Samples

Layer Type	Position, mm	Not Annealed Sample HV	Annealed Sample HV
Molybdenum	0.1	1700	1324
	0.2	1780	1400
	0.3	1750	1346
Ni-Al	0.45	324	445
	0.55	286	489
Substrate	0.7	250	280
	0.9	244	275
	1.2	248	268
	1.6	254	286
	2	248	295

For each sample type, longitudinal and transversal residual stresses σ_{Long} and σ_{Trans} are very similar. So, only σ_{Long} (for example) will be presented in the following figures for clarity of presentation. For the first samples type, 35CrMo4/(55E + 65E) (Fig. 6), the stresses are compressive at the surface and are

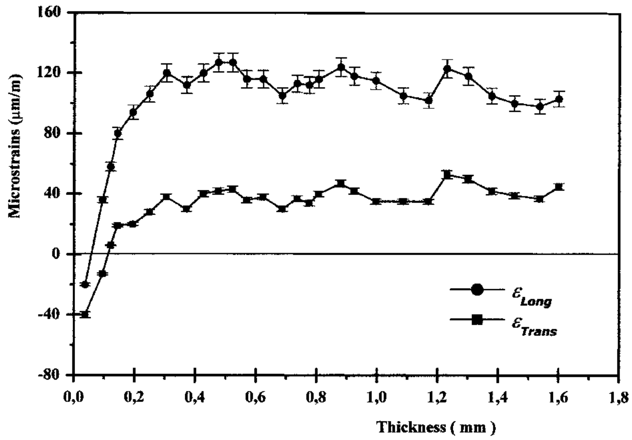

Fig. 4 ε_{Long} and ε_{Trans} microstrains distribution of the grit blasted 35CrMo4 substrate

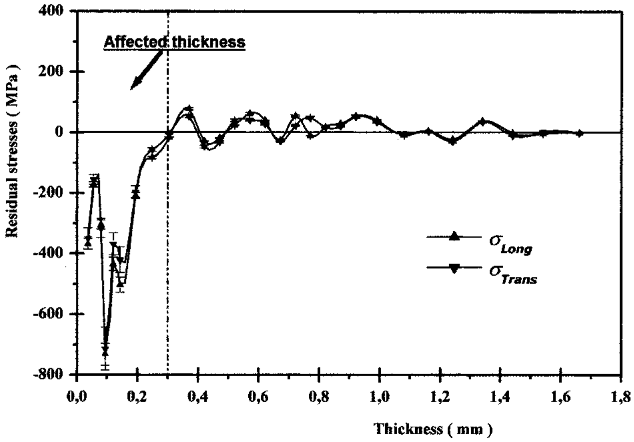

Fig. 5 Residual stresses profile of the grit blasted 35CrMo4 substrate

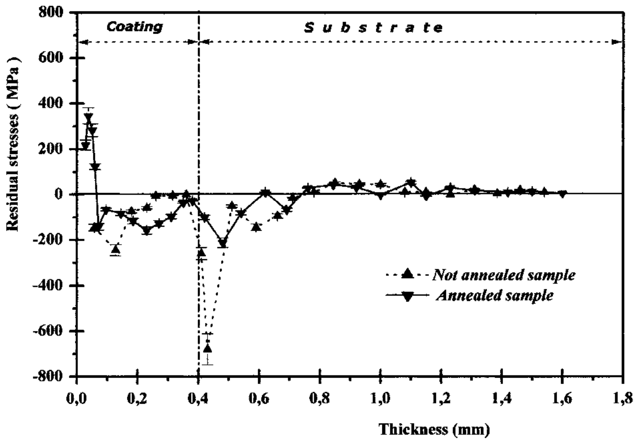

Fig. 6 Residual stresses profile of the (55E + 65E)/35CrMo4 sample

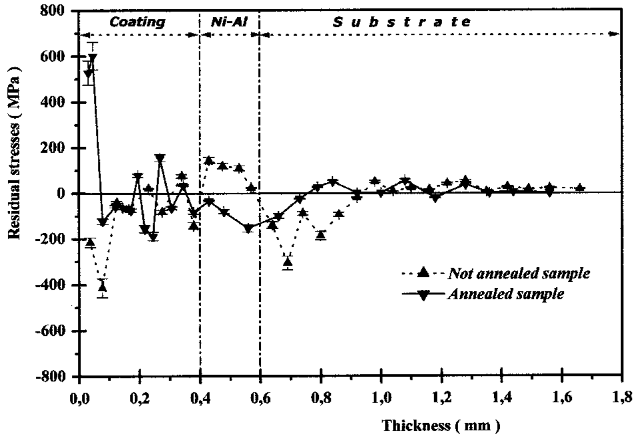

Fig. 7 Residual stresses profile of the (55E + 65E)/Ni-Al/35CrMo4 sample

abruptly more compressive towards the interface in the top layers of the substrate. This compression zone of the substrate has a thickness of about 300 μm and it can be divided into a high-compression zone (−700 MPa) and a less-compression zone (−150 MPa).

The high value of the stresses is mainly due to the severe surface roughness (7 μm) generated by the grit blasting.

The post-annealing has reduced the overall stresses in the sample. Within the deposit, nearby the surface, the stresses became tensile. In the substrate, the compression zone was about 200 μm and the residual stresses are lower than before annealing.

The presence of the Ni-Al bond coat (Fig. 7) has reduced the variation in residual stresses. The bond coat is in tension, (about +170 MPa). The stresses in the coating are more or less scattered but globally in compression with a maximum peak of about −400 MPa at 100 μm from the surface. The substrate can also be divided into a highly compressed zone (−380 MPa) and a lower one (−200 MPa). Taken as a whole, the bond coat contributed to decrease the stresses in the first zone.

After post-annealing, the residual stresses of bond-coated samples are in tension at the surface and then vary between tension and compression between the two extreme values of about ±200 MPa. The high value at the surface (+600 MPa) might possibly be associated with the superficial oxidation of the coating during heat treatment in air. The thickness of the affected zone is about 200 μm.

Concerning molybdenum deposits (Fig. 8 and 9), the residual stresses are weaker, more homogeneous and peaks are smaller compared with samples with (55E + 65E) coating. Nevertheless, the effect of Ni-Al bond coat and/or annealing is similar to the first group specimen. The thickness of the affected zone in the substrate is about 200 μm too. These lower residual stresses are partially due to the thermal contraction difference between molybdenum coating and 35CrMo4 steel substrate (thermal expansion coefficient of molybdenum is about twice and a half lower than steel's).[12] Also, at the distance of 140 mm, the flame spray procedure induces heating of successive layers when deposited so the obtained coating is globally relaxed.

On the other hand, initially in tension, the bond coat is in compression after annealing.

The variations of the residual stress levels in the coatings are partially due to the thermal spray procedure. On impact with the substrate, the molten particles, moving at velocities in the range 100-600 ms^{-1}, flatten to form "splats," cool down by heat trans-

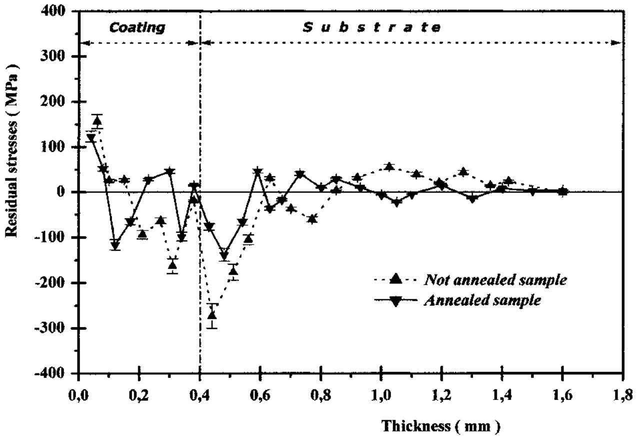

Fig. 8 Residual stresses profile of the molybdenum/35CrMo4 sample

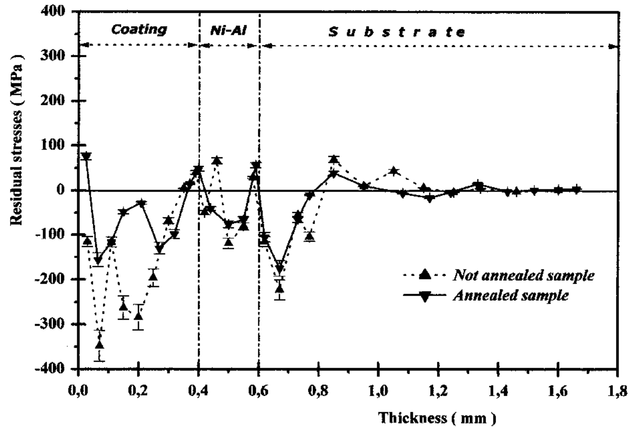

Fig. 9 Residual stresses profile of the molybdenum/Ni-Al/35CrMo4 sample

fer to the underlying material, and solidify in strongly non-equilibrium conditions.[13,14] Also, phase transformations in both coating and substrate lead to refined microstructures and a more homogenous distribution of inclusions, carbides and oxides. This can decrease the residual stresses level of the hole sample.[15]

4. Conclusion

The metallographic analysis shows coatings with cavities, pores and oxides, while the interfaces are clear.

In the case of molybdenum coating, the post-annealing does not have a great effect, either on the hardness or on the residual stresses profiles. The adhesion was improved by metallic bonds formed at the interface by diffusion.

The post-annealing is beneficial for (55E + 65E) coating: the hardness has not decreased, residual stresses are attenuated, and adhesion is improved for the same reasons as molybdenum coating case.

The adhesion became better after post-annealing when the sample contains the Ni-Al bond coat as well. The residual stresses are attenuated and became in tension.

The two used thermal coating processes could not eliminate totally the grit blasting effect (residual stresses always in compression). However, the residual effect is more important in the case of electric arc process than that of the flame.

References

1. M. Laracine, C. Bignon, M. Lormand, A.B. Vannes, and C. Bedrin: "Determination of Residual Stresses in Multimaterial, Multilayer Pieces-Adaptation to Ceramic Coatings," *Ann. CIRP,* 1991, *40*(1), pp. 535-39.
2. V. Guipont: "Experimental Determinations of Residual Stresses in Materials Realized by Brazing," Ph.D. Thesis. No. 94-50, 1994, E.C. Lyon, France (in French).
3. N. Mesrati, D. Nguyen, and D.Treheux: "Role of Zinc and Silver on the Adhesion of a Projected Zirconia on an Aluminum-Silicon (12%) Alloy," *Rev. Métall.* 1993, *12,* pp. 1673-80 (in French).
4. O. Kesler, J. Matejicek, S. Sampath, S. Suresh, T. Gnaeupel-herold, P.C. Brand, and H.J. Prask: "Measurement of Residual Stress in Plasma-Sprayed Metallic, Ceramic and Composite Coatings," *Mater. Sci. Eng.,* 1998, *257,* pp. 215-24.
5. J. Lesage, D. Chicot, D. Judas, M. Zampronio et al.: "Interfacial Indentation Measurements of Adhesion of Thermal Sprayed NiCr Coatings," *Matér. Tech.,* 1999, *9-10,* pp. 29-34 (in French).
6. M. Laracine, C. Bignon, M. Lormand, J. Hernandez et al.: "On a Method of Determination of Residual Stresses in Multilayers: Application to Trimetallic Structures Elaborated by Laser Treatment," *J. Phys*., 1987, *12,* pp. 147-50.
7. L. Castex: *Stresses Redistribution in a Plate After Layers Removal,* ENSAM, Paris, 1986.
8. D. Kaplan: *Residual Stresses Measurements by Drilling and Layers Removal,* IRSID documentation, 1983 (in French).
9. R.T.R. McGrann, D.J. Greving, J.R. Shadley, E.F. Rybicki et al.: "The Effect of Residual Stress in HVOF Tungsten Carbide Coatings on the Fatigue Life in Bending of Thermal Spray Coated Aluminum," *J. Therm. Spray Technol.,* 1998, *7*(4), pp. 546-52.
10. S. Li: "Damage Mechanisms of Abradable Materials for Turbines: Experiments and Simulations," Ph.D. Thesis, No. 98-41, 1998, E.C. Lyon, France (in French).
11. Y.C. Kim, K.H. Chang, and K. Horikawa: "Characteristics of Residual Stress Generated by $MoSi_2$ Plasma Thermal Spraying," *J. Jpn. Welding Soc.,* 1998, *12,* pp. 867-71.
12. M. Winter: http://www.webelements.com/ document, 2001.
13. I. Iordanova, K.S. Forcey, B. Gergov, and V. Bojinov: "Characterization of Flame-Sprayed and Plasma-Sprayed Pure Metallic and Alloyed Coatings," *Surf. Coat. Technol.* 1995, *72,* pp. 23-29.
14. I. Iordanova and K. S. Forcey: "Texture and Residual Stresses in Thermally Sprayed Coatings," *Surf. Coat. Technol.,* 1997, *91,* pp. 174-82.
15. F. Kroupa: "Residual Stresses in Thick, Nonhomogeneous Coatings," *J. Therm. Spray Technol.,* 1997, *6*(3), pp. 309-19.