

Study of adhesion of PROTAL[®] copper coating of Al 2017 using the laser shock adhesion test (LASAT)

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Surface preparation of substrates is a major stage in thermal spraying as it greatly influences coating adhesion. Standard grit-blasting creates roughness but also often leaves grit inclusions at the substrate surface, which are detrimental for coating quality. In contrast, the use of smooth substrates involves improvements in metallurgical adhesion. This work deals with the use of substrate pre-heating and of the PROTAL[®] process ('PROjection Thermique Assistée par Laser') to promote metallurgical adhesion. PROTAL is based on substrate laser treatment prior to spraying to achieve an oxide-free interface and, under specific conditions, which modifies the substrate morphology. A metallurgically reactive system (i.e., copper sprayed onto Al 2017) was selected to be suitable for controlling metallurgical features at the coating-substrate interface (mainly pores, intermetallic phases and pre-existing cracks). These were shown to depend on substrate roughness and on the substrate temperature during the first spraying pass.

LASer shock adhesion test, namely LASAT, was developed to enable morphological and metallurgical features of as-sprayed interfaces to be studied separately. The existence of a critical roughness for anchoring (CRA) and of an adhesion transition temperature (ATT) could be assumed. As for metallurgical properties, interface intermetallics and pre-existing cracks were shown to be detrimental for adhesion. Moreover, LASATesting succeeded in showing that adhesion of PROTAL coatings is better than that of APS-only coatings.

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1. Introduction

Improvements in plasma spraying might mean those in substrate surface treatments prior to spraying. A major step forward in this field would be the dropping of standard grit blasting, which often leaves harmful grit residues at the substrate surface [1]. This contamination is detrimental for the coating quality, especially onto ductile materials (e.g., aluminum alloys), primarily due to a related reduction of adhesion to the substrate.

Moreover, no more grit blasting in the spraying route would meet the increasing demand for spraying onto 'smooth' substrates [2] including Al-based substrates especially [3]. This is required to decrease coating surface roughness and/or when using fine powders. However, for metallic materials, the use of smooth

substrates involves improvements in metallurgical diffusion to compensate the lack of mechanical anchoring. The present study deals with 2 different processes for promoting interfacial diffusion. As diffusion is a thermally-activated phenomenon, the first process is a purely thermal process which consisted in pre-heating merely the substrate surface. Various types of substrate pre-heatings were tested to obtain different interfaces.

The second process consisted of a thermo-physico-chemical treatment, based on laser irradiation just prior to spraying, namely PROTAL[®] (French acronym for 'PROjection Thermique Assistée par Laser,' i.e., 'Laser-Assisted Thermal Spray') [4]. This mainly results in the cleaning of the substrate surface due to the removal of diffusion barriers (e.g., oxides,

contaminants . . .) [5]. Under specific conditions, PROTAL treatment may also modify the substrate morphology [5]. This allowed the study of the influence of substrate roughness on coating adhesion.

A metallurgically-reactive system, i.e., copper sprayed onto aluminum-based substrates, was selected to achieve various types of coating-substrate interfaces, depending on substrate preparation and on the thermal cycles they underwent. Copper coatings are widely used for industrial applications, e.g., for electrical or heat conduction [6]. The main stages in this research work concerned the processing of the copper coatings (including substrate preparation), the study of the substrate surface after PROTAL treatment, morphological and metallurgical interface analyses (including quantitative characterization) and adhesion testing of the samples. For the latter, the laser shock adhesion test (LASAT) [7, 8] was previously shown to be suitable for studying local adhesion and for determining the influence on adhesion of metallurgical features at the interface. It was confirmed that when using smooth substrates, coating adhesion depends on the interface quality dramatically, down to a low scale [9]. Relationships between metallurgical and morphological interface properties, substrate cleanliness and coating adhesion, are discussed in the light of a previous study of air plasma-sprayed (APS) samples [9], which were considered as references.

2. Materials and methods

2.1. Powder and substrates

AISI Al 2017 (AU4G in the French standards) $25 \times 25 \times 3 \text{ mm}^3$ and $60 \times 15 \times 3 \text{ mm}^3$ substrates were coated with a commercial Cu powder (METCO 55, $-90 + 45 \text{ }\mu\text{m}$) using respectively air plasma spraying and PROTAL process. They were not grit-blasted but polished down to $3 \text{ }\mu\text{m}$ diamond paste ($R_a \approx 0.03 \text{ }\mu\text{m}$) before spraying.

2.2. Plasma spraying

To obtain different metallurgical states at the coating-substrate interface, various numbers of torch passes were tested for pre-heating the substrate. The substrate temperature was measured using a thermocouple in contact with the uncoated surface of the aluminum substrate.

2.2.1. Air plasma spraying

Plasma spraying provides copper powder with thermal and kinetic energies from the plasma generated by an electric arc. The melted particles impinge on the substrate to build-up the coating. In the air plasma spraying (APS) mode, the coating is achieved at the ambient atmosphere.

Some of the spraying experiments were performed in the CAPS unit ('Controlled Atmosphere Plasma Spraying') of the C2P ('Center for Plasma Processing') in Evry (France), using the APS mode coupled with conventional air cooling of the substrates. Standard spraying conditions for Cu were used (set of parameters '1' in Table I).

Specimens were pre-heated with 2, 3 and 9 plasma torch passes before spraying. The adhesion of plasma-sprayed coatings was shown to depend directly on metallurgical characteristics of coating-substrate interfaces, as already shown in an earlier study [9]. The maximum substrate temperature during the first spraying pass, which was used for the designation of the samples (Table II), is a key parameter for heat transfers through the copper-aluminum interface therefore for coating adhesion. One may notice that the first spraying pass temperature of the sample pre-heated with 9 torch passes is lower than the temperature of the sample pre-heated with 3 torch passes. This results from different cooling times prior to the spraying.

TABLE I APS spraying conditions for copper coatings

Spraying parameters	1	2
Arc current	600 A	600 A
Arc voltage	70 V	70 V
Plasma gas flow rate	Ar = 80 l·min ⁻¹ , H ₂ = 10 l·min ⁻¹	Ar = 80 l·min ⁻¹ , H ₂ = 10 l·min ⁻¹
Injector diameter	1.8 mm	1.8 mm
Carrier gas flow rate	Ar = 3 l·min ⁻¹	Ar = 3 l·min ⁻¹
Powder feed rate	30 g·min ⁻¹	30 g·min ⁻¹
Spraying distance	140 mm	140 mm
Torch speed	300 mm·s ⁻¹ (Pre-heating) 300 mm·s ⁻¹ (CAPS spraying)	300 mm·s ⁻¹ (Pre-heating) 450 mm·s ⁻¹ (PROTAL spraying)

TABLE II Designation of the samples and experimental conditions

Samples	Spraying mode	Number of pre-heating passes	Average maximum temperature during the first spraying pass (°C)	Spraying parameters (Table I)
A-248	APS	2	248	1
A-270	APS	3	270	1
A-265	APS	9	265	1
A-208	APS	3	208	2
P-208	PROTAL	3	208	2
P-237	PROTAL	9	237	2

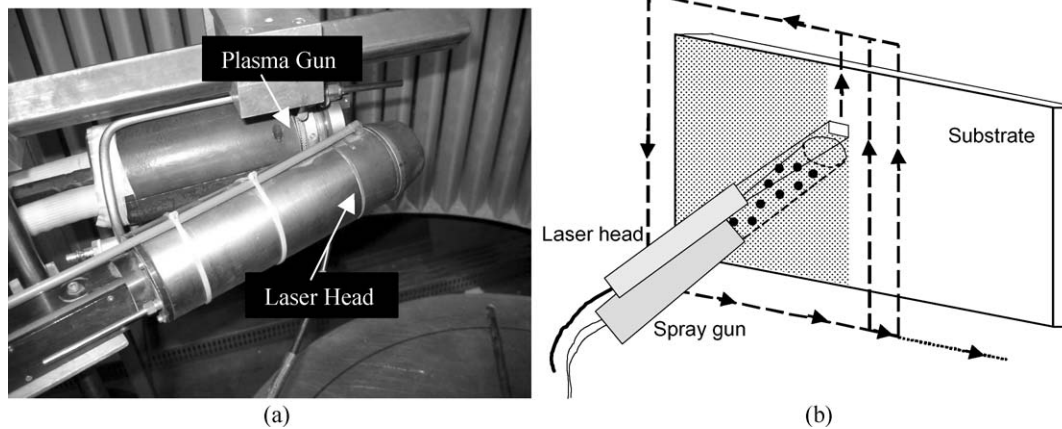


Figure 1 PROTAL process: (a) experimental set up and (b) spot arrangement.

2.2.2. PROTAL

Specimens were coated in APS facilities at Sulzer Metco in Wohlen (Switzerland) coupled with a Q-switched Quantel Nd: YAG laser. These result in the PROTAL device (Fig. 1a). Two optical fibers, integrated in the laser head, can deliver an average power of 40 W at the 1.064 μm wavelength. Pulse duration is close to 10 ns and its frequency was set at 120 Hz. The laser is associated to the plasma gun to form a rectangular-shape laser spot. The geometrical positioning between the plasma and laser guns (Fig. 1b) was achieved in such a way that the laser treatment precedes the spraying deposition immediately. The principle of PROTAL process is that the particles are expected to impinge on a surface free of oxides and contamination (dust, oils . . .) [5].

Standard spraying parameters (conditions number '2' Table I) were applied to pre-heat with 3 and 9 torch passes and to coat the aluminum-alloy substrates. The conditions were similar to those used for APS in CAPS (see Section 2.2.1 and Table I) except for the torch speed when spraying. This speed was taken 1.5 times that for conventional APS to be also appropriate as the laser traverse speed in the irradiation conditions used (i.e., pulse duration and frequency). The last three samples described in Table II were achieved that way. One may notice that the first spraying pass temperatures attained by the samples sprayed using the PROTAL system (P-typed samples) are lower than the first spraying pass temperatures of the substrates coated in APS mode (A-typed samples). The temperature difference was due to a higher torch speed during the PROTAL deposition and to a stronger air circulation and exhaust in PROTAL chamber than in CAPS unit. For all that, to attempt a comparison between APS and PROTAL modes, the air-sprayed A-208 sample was achieved without laser treatment, in the PROTAL chamber and applying precisely the same spraying conditions as the ones used to obtain the PROTAL-processed samples (Table II).

2.3. LASATesting

All the laser shock adhesion tests were performed at the CLFA laser center ('Coopération Laser Franco-Allemande'), in Arcueil. The samples were tested in vacuum using a Nd: YAG laser delivering 10 ns Gaussian pulses at the 1.064 μm wavelength. The laser

focused on a 1 or 2 mm diameter spot at the surface of the substrate with a wide range of laser power densities (5 to 300 GW/cm^2).

Irradiating the surface of a substrate with a high power laser generates a shock wave, the propagation of which leads to tensile stresses at the coating-substrate interface [7]. Doppler laser interferometry using a VISAR ('Velocity Interferometer System for any Reflector') was applied to the coating surface to measure its velocity as a function of time [8].

3. Results

3.1. Surface state of a PROTAL laser-processed substrate

After PROTAL laser preparation, the surface of the Al 2017 substrate showed a repeated irradiation pattern which resulted from the scanning of the laser pulses (Fig. 2). The spatial energy distribution in every elementary spot was heterogeneous deliberately to achieve different surface states on a single specimen, hence with the same spraying conditions.

Scanning electron microscope (SEM) observations of the surface of as-irradiated substrates showed that the laser-processed pattern exhibited 3 areas (Fig. 3).

On so-called 'smooth' areas, initial polishing scratches vanished (Fig. 3a and b). Laser energy was high enough to allow shallow re-melting of the aluminum surface.

The energy deposited onto 'intermediate' areas enabled low-melting point phases (dust, impurities . . .) to evaporate. Surrounding superficial liquid was ejected due to vapor pressure, which formed craters and droplets (Fig. 3c). Initial pores at the substrate surface or slightly underneath might lead to similar phenomena. Part of the laser beam was reflected within the pore, which provoked preferential energy absorption and to the evaporation from the pore walls.

'Rough' areas were those for which a high energy was deposited by laser irradiation, allowing evaporation of the aluminum alloy and formation of craters all over the substrate surface (Fig. 3d).

The PROTAL laser treatment led to new surface states that were expected to promote the bonding of the plasma-sprayed coatings on the substrate from the eliminating of contaminations and of oxide layers

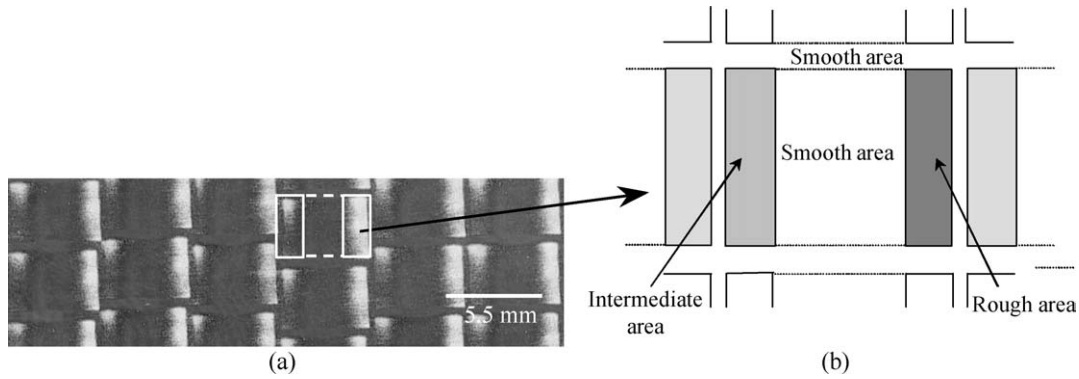


Figure 2 (a) Optical view of Al 2017 substrate surface after PROTAL laser treatment. (b) Schematic illustration of the corresponding pattern on the substrate.

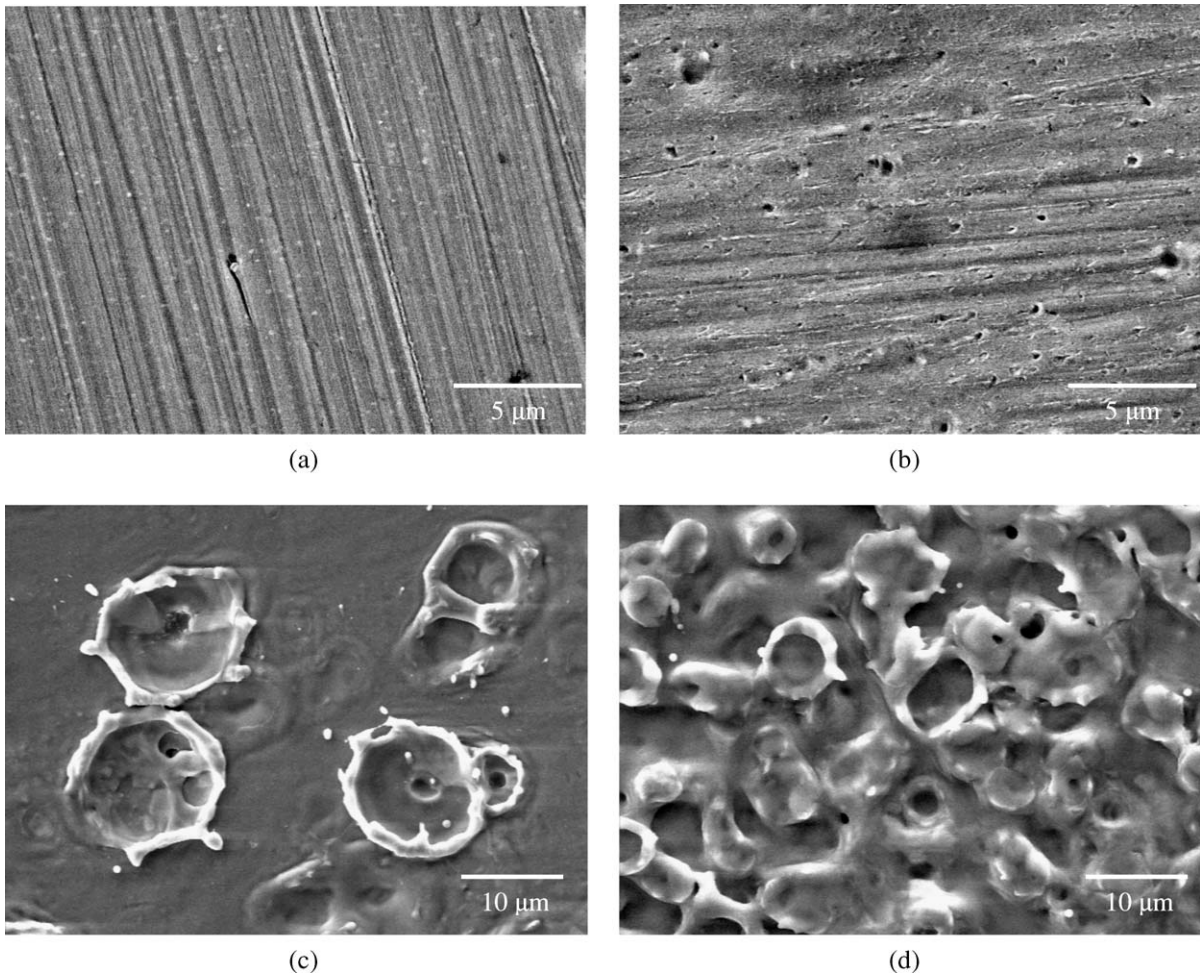


Figure 3 SEM images of the surface of Al 2017 substrates: (a) as-polished, (b) as-laser processed, smooth, (c) as-laser processed, intermediate and (d) as-laser processed, rough.

(if any) in addition to some superficial melting of the substrate. It could be deduced from kinetic and geometric considerations that the substrate temperature increase, due to laser irradiation, was a rapid phenomenon (during about 20 ns only) [4]. The laser treatment could not therefore change the heat transfers from spraying, which occurred 45 ms after the laser preparation.

3.2. Coating-substrate interface

Optical cross-section observation of PROTAL-processed samples (namely PROTAL samples) after spraying allowed discrimination between smooth

(Fig. 4a) and rough (Fig. 4b) copper-aluminum interfaces. Intermediate interfaces were not however easy to locate. Morphological and metallurgical features of smooth and rough interfaces will be therefore mainly studied. As-sprayed APS and PROTAL interfaces exhibited cracks (Fig. 4b), intermetallic phases and interface porosity (Fig. 4c). These were quantified for every sample to be linked to substrate roughness and to coating-substrate adhesion. The overall content and average length of intermetallics and cracks resulted from measurements of unetched cross-section (over 4 cm typically) from optical microscopy.

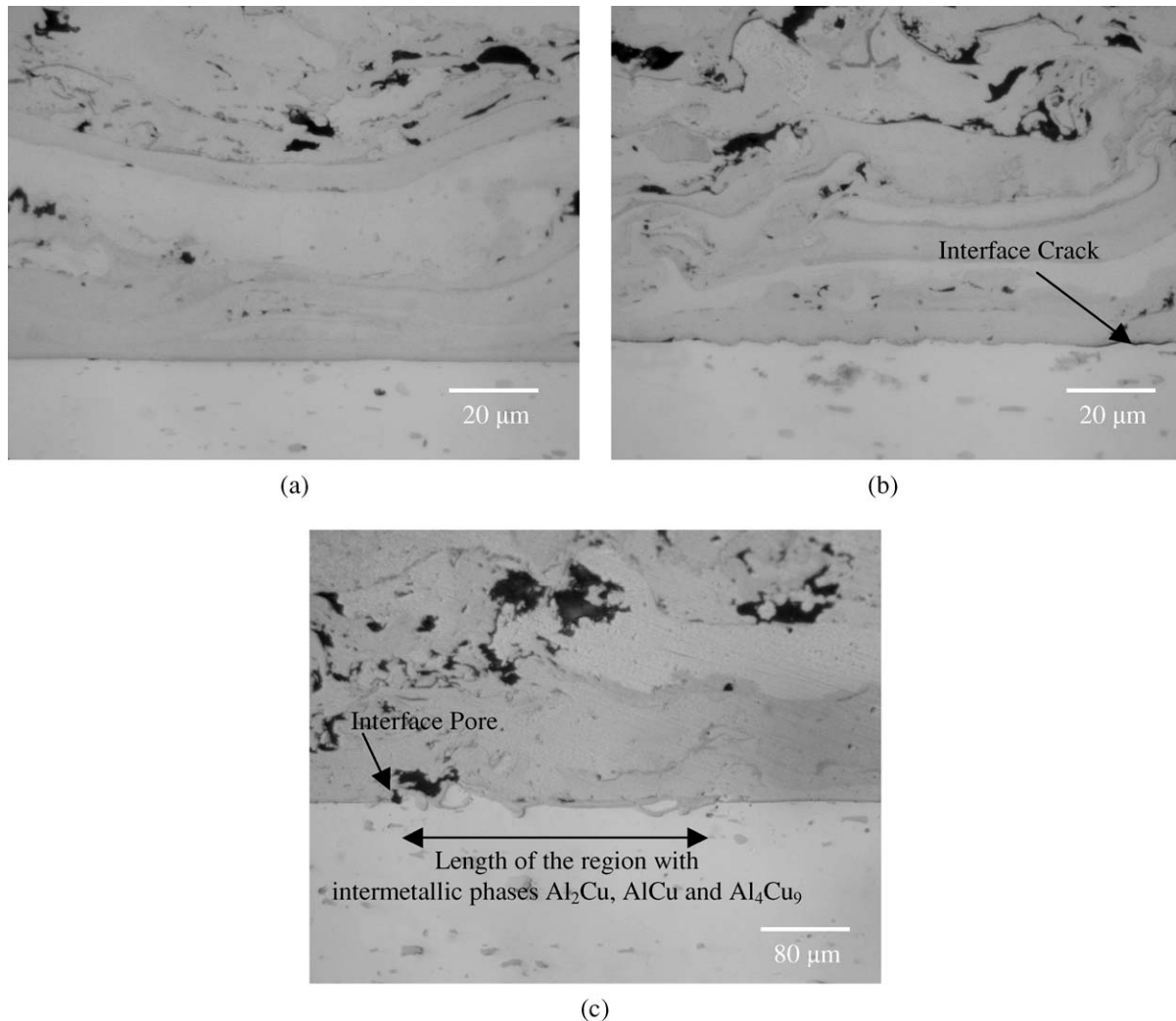


Figure 4 Optical cross-section views of P-237: (a) smooth and (b) rough interfaces and of (c) P-208 smooth interface.

3.2.1. Interface morphology

Confocal imaging was carried out on PROTAL laser-processed substrates (Fig. 5). Experiments showed that the rather low laser energy deposited onto smooth areas was not sufficient to modify substrate roughness. However, the laser irradiation which led to rough areas corresponds to an increase in the aluminum alloy roughness compared to that of unprocessed substrates, which were coated to obtain the A-typed samples. For every sample, PROTAL laser treatment therefore generated various substrate roughnesses which ranged, as for Ra, from 0.03 to 0.4 μm . Coating-substrate interfaces (Sections 3.2.2 and 3.2.3) related to the coating-substrate adhesion were therefore studied (Section 3.3) as a function of substrate morphology, excluding metallurgical features.

3.2.2. Interface metallurgy

A preliminary study of A-248, A-270 and A-265 [9], showed that intermetallic phases formed unevenly at the coating-substrate interface during the air plasma spraying of copper onto aluminum alloy. The same intermediate phases (Al_2Cu , AlCu and Al_4Cu_9) were obtained at coating-substrate interfaces after PROTAL spraying (in gray in Fig. 4c).

Intermetallics quantification showed that the overall intermetallics contents were lower in PROTAL interfaces than in APS interfaces (Fig. 6). This may be explained by a lower substrate temperature at the first spraying pass when coating using PROTAL. As shown in a previous study of A-typed samples [9], intermetallics formation is a thermally-activated phenomenon which directly depends on substrate temperature at the first stage of spraying.

However, a higher intermetallics content in rough interfaces compared to smooth interfaces in P-208 sample cannot be attributed to the average substrate temperature. It may rather be explained by a more efficient removal of oxides in rough substrate areas (which were laser-treated more severely) and by local temperature rises due to substrate roughness [10]. Substrate morphology may actually allow thermal inertia in valleys and substrate temperature should be locally higher than that in the smooth areas during the first copper particle impacts.

For P-237 sample, the substrate morphology seems to have no significant effect on intermetallics formation. The quantified intermetallics regions (Fig. 6) had to be at least 10 μm long to be detected in optical microscopy. However, further post-spraying metallurgical investigation showed that smaller intermetallics regions

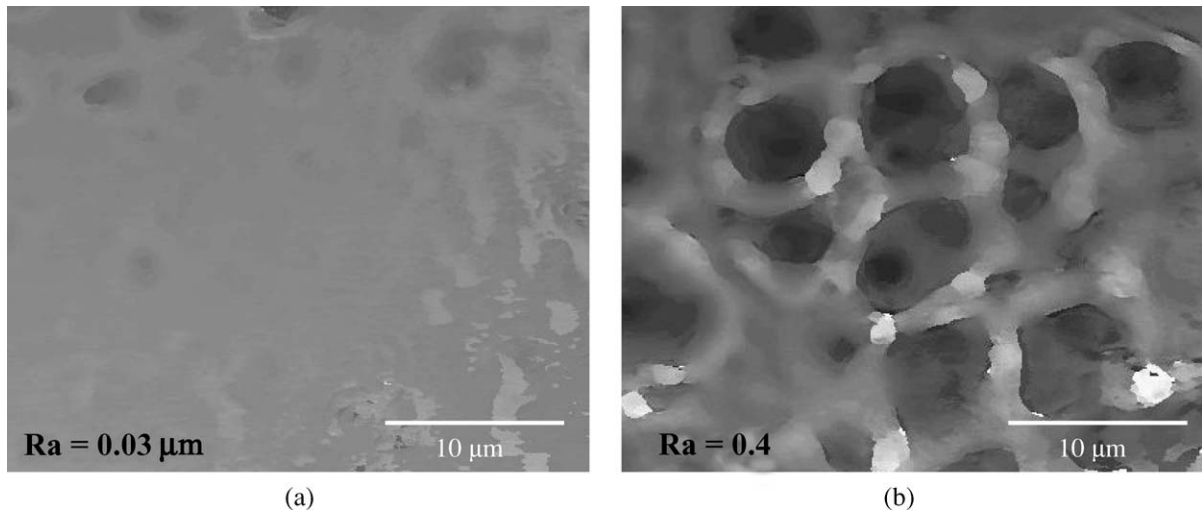


Figure 5 Confocal imaging of: (a) smooth and (b) rough surfaces. Deep areas appear in dark and shallow areas in bright.

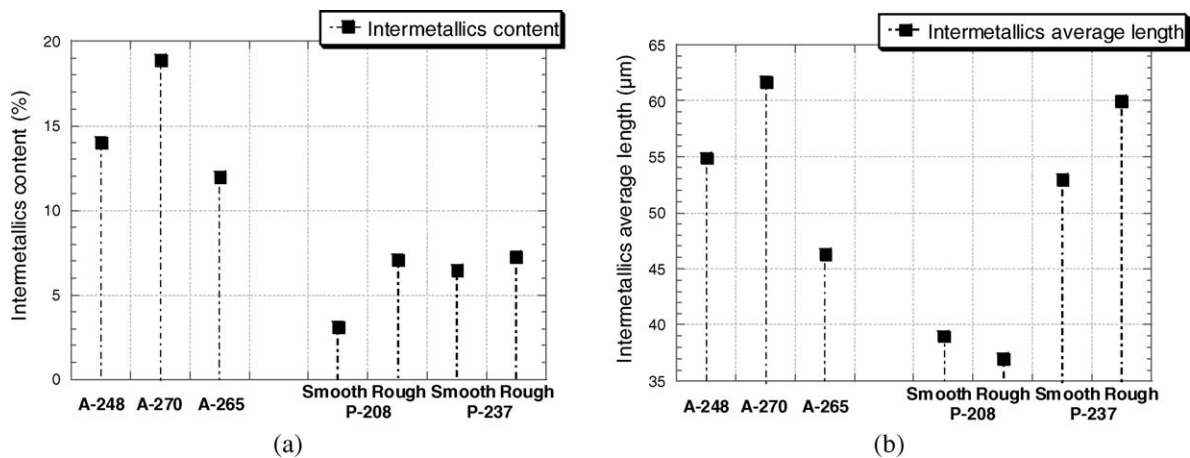


Figure 6 (a) Interface intermetallics content and (b) average length for A and P-typed samples for various pre-heating conditions.

also formed, mainly in rough areas (Fig. 7). This ascertains the assumption for a better oxide removal in rough areas and of heat confinement at the substrate surface due to topography.

3.2.3. Interface pre-existing cracking and porosity

Conventional optical observation of unetched APS and PROTAL samples showed post-spraying cracks and pores at the Cu-Al 2017 interfaces. For quantifying of these defects at the interface (Fig. 8), cracks were considered to be strictly different from porosity, i.e., that swallowed pores due to cracking were neglected. Interfacial pores were therefore all the scarcer as pre-existing cracks are frequent.

Moreover, in smooth interfaces, cracks tended to be all the more frequent as the average substrate temperature during the first spraying pass is low. For the studied system, as could be expected, metallurgical adhesion through diffusion was therefore shown to be a thermally-activated phenomenon.

In PROTAL-processed rough areas, mechanical adhesion led to a lesser interface cracking compared to that in smooth areas.

3.3. Coating-substrate adhesion

To determine the adhesion threshold for all the previously-studied interfaces, laser shocks were applied to samples using different laser power density levels. The de-bonding limit, i.e., when exceeding the interface strength, was determined from the analysis of the coating surface velocity profiles. Below and above the laser shock adhesion threshold, two types of velocity signals were obtained actually (Fig. 9).

Both velocity curves showed peaks in amplitude, which corresponded to the interaction of the shock wave with the coating surface. Above the adhesion threshold (e.g., for a 16 GW/cm² laser power flux in P-208 sample), the time elapsed between the first two peaks is the time necessary for the wave to propagate through the copper coating and go back. The shock wave reflected on the void which was created at the first interaction with the interface. The numerous subsequent peaks can be explained by reflections due to bi-dimensional effects. These were caused by the rather small beam spot area (1 mm in diameter) applied to a comparatively thick material (600 μm).

Below the adhesion threshold (for a 5 GW/cm² laser flux onto P-208 sample), the velocity profile turned to zero amplitude after the first peak, which left the

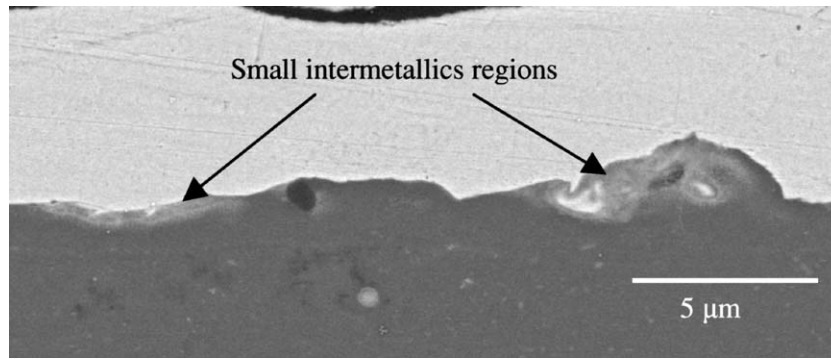


Figure 7 Cross-section SEM images of P-208 rough interfaces.

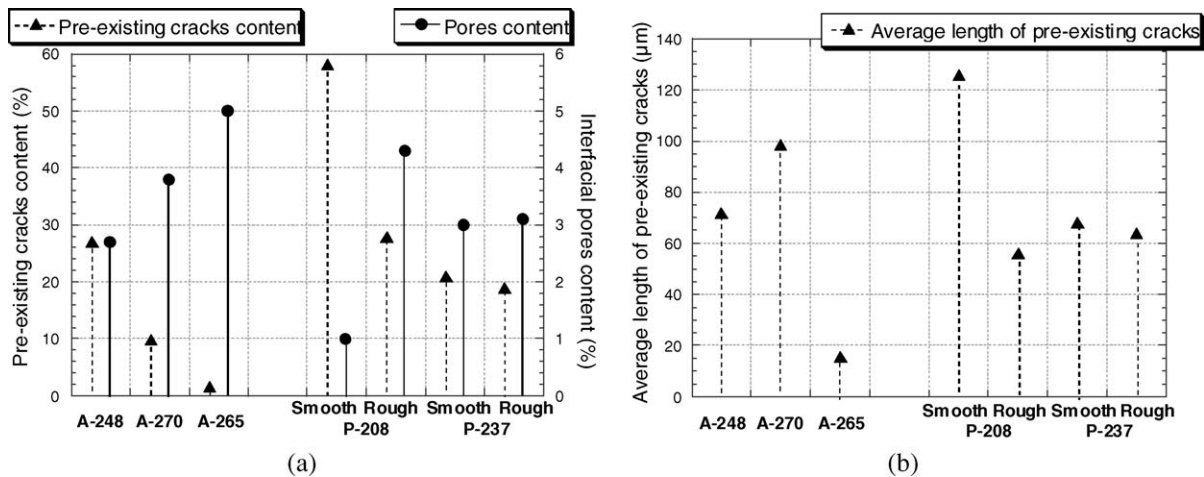


Figure 8 (a) Interfacial pre-existing cracks and pores content and (b) pre-existing cracks average length for A and P-typed samples with various pre-heating conditions.

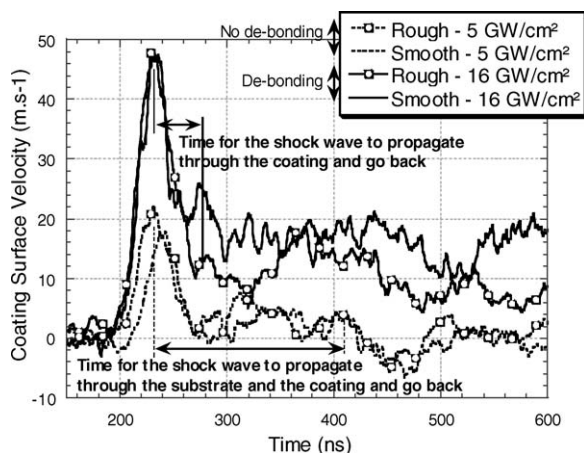


Figure 9 Coating surface velocity vs time VISAR profiles, below and above the laser shock adhesion threshold for P-208.

second peak slightly forward. The time between the two peaks corresponds to that necessary for the shock wave to propagate through the substrate and coating and go back. The interface was therefore not damaged because the wave went through.

LASATesting allowed to determine adhesion levels in local areas. Smooth and rough interfaces in PROTAL-processed samples were therefore located and tested separately. Substrate roughness, due to laser treatment, did not influence significantly shock wave propagation as the velocity profiles showed sim-

ilar shapes for rough and smooth PROTAL interfaces (Fig. 9).

The interpretation of the velocity profiles was ascertained by systematic metallographic observation of cross-sections of all the laser-shocked specimens (Fig. 10). Undamaged or de-bonded interfaces were observed respectively below and above the adhesion threshold.

Coating-substrate adhesion thresholds were determined by testing the interfaces for various laser power densities. Sample P-237, which underwent 9 plasma torch passes for pre-heating, showed a higher adhesion than that of P-208, which was pre-heated with 3 torch passes (Fig. 11). In addition, laser-treated smooth and rough interfaces showed the same adhesion threshold for all samples.

LASATesting was not applied to APS A-208 sample because the copper coating could not be bonded to the substrate. The same spraying conditions as for P-208 sample were used except that no laser treatment was applied to the substrate before spraying.

4. Discussion

Coating-substrate adhesion results from metallurgical and morphological combined effects that occur at the interface when spraying. The use of polished substrates, deliberate heterogeneous laser treating and of local adhesion testing (LASATesting) allowed, to a certain

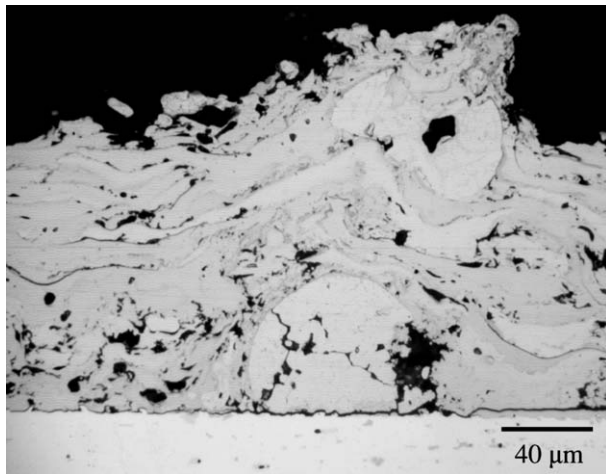


Figure 10 Optical cross-section view of P-208 damaged interface due to laser shock (at 16 GW/cm²).

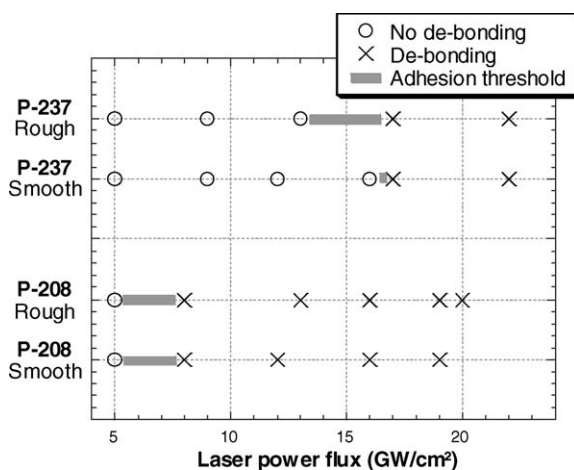


Figure 11 Influence of laser power density in laser shock adhesion test of PROTAL-processed samples.

extent, the de-coupling of interface metallurgy and substrate morphology influences.

4.1. Substrate morphology

As-sprayed interface properties of high first spraying pass temperature samples (e.g., P-237) were studied (Figs 6 and 8). This showed that smooth and rough areas exhibited comparable contents and sizes of intermetallics, cracks and pores. Since these areas were in a single sample, the two types of corresponding copper-aluminum interfaces were metallurgically similar. They only differed by the initial substrate morphology.

Laser shock adhesion tests of smooth and rough areas, showed no significant effect of substrate roughness on copper-aluminum adhesion (Fig. 11). PROTAL-treated substrates roughness was in too low and narrow a range (i.e., from 0.03 to 0.4 μm) to promote mechanical anchoring, which would have improved coating adhesion. Moreover, aluminum roughness led to the formation of small intermetallic regions in the valleys at the aluminum surface (Fig. 7). The presence of these brittle phases is detrimental for coating adhesion [9] and might have counterbalanced any beneficial substrate roughness effect. This suggests the existence of a 'Critical Roughness for Anchoring' (CRA). Below the

CRA, coating adhesion is not improved because the influence of small intermetallics prevails that of roughness. In contrast, above CRA, mechanical anchoring is predominant, which promotes the interface resistance.

CRA results from competing morphological (mechanical anchoring) and metallurgical (intermetallics) effects, which can be both significant when involved copper and aluminum. More generally, CRA depends on the nature of the materials of the coating-substrate system. As for topography, CRA is not only influenced by the value of the average roughness, Ra, but also by the substrate roughness profile and this depending on size of the sprayed powder.

4.2. Interfacial metallurgy

4.2.1. Cracking and intermetallics

For low first spraying pass temperatures (e.g., for P-208 sample), similar adhesion levels of the rough and smooth areas (Fig. 11) can be attributed to the competition of four interfacial characteristics after spraying, i.e., small intermetallics, substrate roughness, pre-existing cracks and elongated intermetallics.

The presence of small intermetallics regions should reduce effects of the aluminum morphology in rough areas. In addition, long and rather numerous cracks along the smooth interface lower the coating-substrate resistance (Fig. 8) and the frequent elongated intermetallics at the rough interfaces are also preferential sites for initiating cracks (Fig. 6).

The lower adhesion of samples with low pre-heating temperatures (P-208) compared to that of higher temperatures (P-237) are also caused by metallurgical features at the copper-aluminum interface. For high first spraying pass temperatures, a rather high content of pores and cracks impairs coating adhesion. Moreover, in rough areas, intermetallics are fairly small but numerous (Fig. 6b).

4.2.2. Substrate cleanliness

When pre-heating is carried out at too low a temperature and no laser pre-treatment is applied to the substrate (i.e., for APS A-208 sample), the coating shows no adhesion. This may be attributed to possible pollution and to the presence of a passivation film of oxide onto the aluminum substrate prior to air plasma spraying. A thin alumina layer plus contamination consist of actual obstacles to heat transfers and material transport between copper and aluminum and therefore result in barriers to metallurgical adhesion.

The higher adhesion of PROTAL coatings achieved at similar low substrate temperatures (P-208) shows the efficiency of laser pre-spraying treatment to leave an oxide- and contamination-free substrate surface that promotes metallurgical adhesion.

4.3. Adhesion transition temperature

Results of LASATesting of coated smooth substrates (Section 3.3 and [9]) as a function of the maximum substrate temperature during the first spraying pass (Fig. 12) may result in the definition of one may call an 'Adhesion Transition Temperature' (ATT).

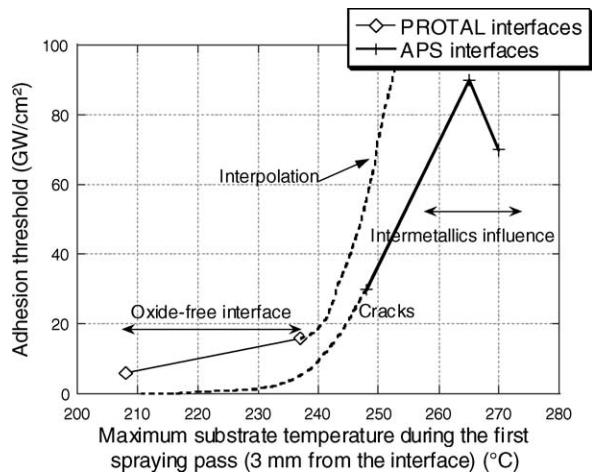


Figure 12 Influence of the substrate temperature on adhesion for APS and PROTAL coatings sprayed onto smooth aluminum.

Below ATT (for substrate temperatures below 250°C when APS coating of Cu onto Al 2017), adhesion is mainly governed by the presence of pre-existing interface cracks. At the transition (i.e., around 265°C for APS interfaces) substrate temperature is high enough to promote purely metallurgical adhesion (as no mechanical anchoring could occur on smooth aluminum substrates). This increases copper-aluminum adhesion dramatically. Above ATT, when metallurgically reactive materials are involved, substrate temperatures may lead to the formation of intermediate phases, which may be detrimental for coating adhesion, as shown in this study for copper plasma-sprayed onto an aluminum-based substrate. At high substrate temperatures, the adhesion level decreases because it is mostly influenced by the higher intermetallics content at the interface [3]. However, for purely diffusional systems, coating adhesion should be all the higher as the substrate temperature during the first spraying pass increases.

A better substrate cleanliness, due to the use of PROTAL process in particular, may reduce ATT by promoting metallurgical adhesion (Fig. 12).

More generally, above ATT, adhesion is mainly influenced by metallurgical features. Below ATT, mechanical anchoring is the predominant phenomenon for coating adhesion (Fig. 13). Increasing adhesion for low temperatures requires the use of roughened substrate above CRA.

5. Conclusion

LASER shock adhesion testing (LASATesting) was shown to be suitable to determine the influence of metallurgical features of plasma-sprayed materials interfaces on adhesion. For this, smooth surface substrates were used to involve no morphological effects.

PROTAL laser treatment and substrate pre-heating were studied to achieve metallurgically-different interfaces, free of oxide films and contamination and with a controlled substrate roughness.

A thorough metallographic investigation into interfaces after PROTAL spraying showed a rather intri-

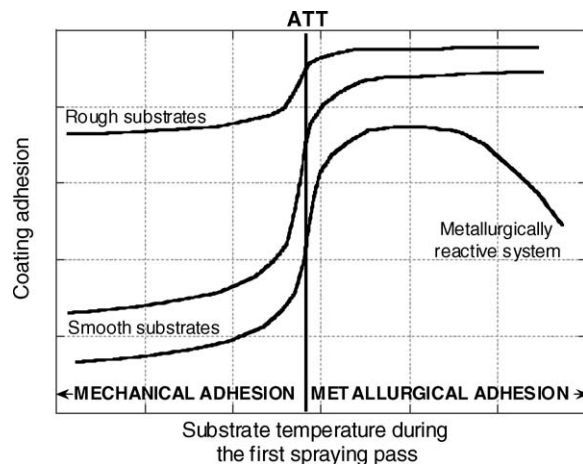


Figure 13 Diagram showing ATT on model curves.

cate copper-aluminum interface. The content of post-spraying intermetallics and interfacial cracks were shown to depend on substrate roughness and on the substrate temperature during the first spraying pass.

LASAT could be applied to rough interfaces successfully. Moreover, the feasibility of local adhesion testing was demonstrated. These two major capabilities of LASAT could be exploited especially when applied to PROTAL-processed coatings which exhibited small-sized areas of various roughnesses. LASATesting therefore allowed morphological and metallurgical features of as-sprayed interfaces to be studied separately.

Substrate roughness from PROTAL treatment showed no significant effect on coating adhesion because this roughness remained low. The existence of a 'critical roughness for anchoring' (CRA) was therefore suggested. Below the CRA, aluminum roughness has no effect on coating adhesion. Further experiments will be done to determine the effects of powder size (e.g., using nanometric particles) and roughness profiles on CRA for the Cu-Al system.

As for metallurgical properties, interface intermetallics and pre-existing cracks were shown to be detrimental for adhesion. In addition, the removal of the aluminum oxide film from the substrate due to superficial laser treatment was assumed to explain the better adhesion of PROTAL coatings compared to that of APS-only coatings. To confirm this, further studies, however, are required to go into surface oxidation and the physical chemistry processes that are involved in PROTAL treatment. Among these, an investigation using advanced surface analysis is in progress.

The existence of one may term as an 'adhesion transition temperature' (ATT) was also claimed. More generally, this ATT concept might be useful to characterize a given coating-substrate system for experimental spraying/materials parameters, primarily substrate roughness and powder size.

The determination of ATT and CRA for various materials systems and substrate preparation (in particular PROTAL laser treatment) could be useful tools to achieve optimal adhesion conveniently for industrial applications, e.g., those involving Cu-based coatings and Al-based substrates.

Acknowledgments

The French Ministry of Education and Research is gratefully acknowledged for supporting the LASAT project. The authors would like to thank Mrs F. Le Strat from GIE REGIENOV (Guyancourt, France), Mrs B. Dumont from KME/Tréfimétaux (Sérifontaine, France) and Mr J. P. Rozenbaum from APS PLETECH (Marne La Vallée, France) for financial support and helpful discussions. Many thanks also to Messrs. P. Zürcher and C. Märki from SULZER METCO (Wohlen, Switzerland) and Mr. F. Borit from the 'Ecole des Mines de Paris' for sprayings.

References

1. N. IWAMOTO *et al.*, The Effect of Pretreatments of Metals on Bond Adhesion, Int. Thermal Spray Conference "ITSC 1983," Essen (1983) p. 18.
2. X. Q. MA, F. BORIT, V. GUIPONT and M. JEANDIN, *J. Adv. Mater.* **34** (2002) 52.
3. D. COOK, M. ZALUZEC and K. KOWALSKY, Development of Thermal Spray for Automotive Cylinder Bores, Int. Thermal

- Spray Conference "ITSC 2003," Orlando, edited by C. Moreau and B. Marple (ASM Int., Materials Park, OH, USA, 2003) p. 143.
4. C. CODDET *et al.*, *J. Therm. Spray Techn.* **8**(2) (1999) 235.
 5. F. FOLIO, J. MICHLER and G. BARBEZAT, *Surf. Eng.* **17**(6) (2001) 490.
 6. J. HAYNES and J. KARTHIKEYAN, Cold Spray Copper Application for Upper Stage for Upper Rocket Design, Int. Thermal Spray Conference "ITSC 2003," Orlando, edited by C. Moreau and B. Marple (ASM Int., Materials Park, OH, USA, 2003) p. 79.
 7. C. BOLIS *et al.*, "Developments in Laser Shock Adhesion Test (LASAT), Int. Thermal Spray Conference "ITSC 2002," Essen, edited by E. Lugsheider *et al.* (ASM Int., Materials Park, OH, USA, 2002) p. 587.
 8. M. BOUSTIE *et al.*, *Europ. Phys. J.* **AP5** (1999) 149.
 9. S. BARRADAS *et al.*, Study of the Role of (Cu, Al) Intermetallics on Adhesion of Copper Plasma-Sprayed onto Aluminum using LAser Shock Adhesion Testing (LASAT), Int. Thermal Spray Conference "ITSC 2002," Essen, edited by E. Lugsheider *et al.* (ASM Int., Materials Park, OH, USA, 2002) p. 592.
 10. D. BOUCHARD *et al.*, *Metall. Mater. Trans. B.* **32B** (2001) 111.

*Received 21 July
and accepted 23 December 2003*