Plasma spraying as an advanced tool in surface engineering

H.-D. Steffens and M. Mack

Institute of Materials Technology, University of Dortmund, Germany

Abstract - Plasma Spray Technology may produce a variety of layers, free standing shapes and material composites made of metals, ceramics and cermets. Current developments show a refinement of the traditional applications - protective layers against wear, erosion, corrosion and high temperature load - as well as surface engineering in the fields of catalytic and electronic materials. Significant developments are going on for plasma-sprayed fibre-reinforced materials and fracture-toughened ceramics. Materials engineering by plasma spray methods is facilitated as plasma sprayed structures lend themselves easily to different methods of post-treatment.

INTRODUCTION

Advanced surface engineering means the design of a material composite according to a list of requirements - engineering demands, economical considerations and constraints given by environmental protection. In this, plasma spraying excels by its versatility and the wide range of materials to be processed. Traditionally, plasma spray coating technology is applied to produce protective layers against wear, erosion, high temperature corrosion, high temperature load and chemical attack. In the mid-sixties, plasma spraying took over from flame spraying and arc spraying in many of these applications (ref. 1). Today, plasma spraying has shown to be well suited for the production of advanced ceramics and covers an increasing range of electronic and catalytic materials. When applied to free standing shapes and spray material compacts, plasma spraying is in numerous examples competitive to sintering and powder-metallurgical techniques.
Advanced surface engineering, on the other hand, means control of the microstructure. As in other coating technologies, microstructural control is achieved only by the interplay of many process parameters, i.e. control is rather involved and indirect. Microstructural engineering is facilitated, however, as plasma sprayed structures lend themselves easily to various methods of post-treatment.
It is the aim of this review, to show some basics of microstructural control in plasma spraying and to illustrate current developments by selected application examples.

MATERIAL PROCESSING AND MICROSTRUCTURE

Plasma spray material processing consists essentially of two steps:
- injection of powder particles (size 10-100 μm) in a high temperature plasma. The powder particles are heated and accelerated to form fast molten droplets. One may use a plasma jet produced by an electric arc blown out through a confined water-cooled nozzle (D.C. spraying) or an inductively coupled plasma (R.F. spraying). (As the bulk of applications is still in the field of D.C. jets, most of the following report will apply to D. C. spraying).

- interaction of the molten droplets with the substrate (the true substrate or previous deposit), i.e. impact, spreading and solidification of the molten droplet.
Typical dwell times inside the plasma are in the order of milliseconds, spreading is accomplished within fractions of a microsecond and freezing

times are of the order 0.1 - 10 /us. Thus, plasma spraying implies non-equilibrium heating and solidification, allowing the production of meta-stable phases. Part of the expected future applications stems from the fact that plasma spraying is a rapid solidification technique (for possible applications see e.g. ref. 3).

Plasma–particle interaction

Particle Heating and Acceleration   The most decisive parameters on im-pact of the molten droplet are its specific heat content and its impact velocity. It is the task of the plasma processing step to provide a range as narrow as possible for both parameters. Starting already with a powder size distribution and, given a certain powder size, with a range of injec-tion velocities one inevitably obtains different trajectories through the plasma. It is the art of plasma engineering to provide e.g. D.C. jets with well developed velocity profiles which - at least in part - allow for the compensation of the lower temperature in the fringes by suitably higher dwell times. For heat transfer, not temperature on itself, but the tempera-ture dependency of heat conductivity (heat conducting potential, see ref. 4) is decisive, and therefore one may achieve a more homogeneous heat transfer profile by adding H_2, He or N_2 to the usual Ar plasma gas. In D. C. spraying, the design of the arc chamber determines the jet properties (see e.g. ref. 5). However, the plasma environment (either atmospheric, controlled atmosphere at 1000 mbar or low pressure) will change things sig-nificantly: in atmospheric plasma spraying (APS) the turbulent flow will strongly change isotherms, heat transfer characteristics and drag proper-ties as has been demonstrated recently by experimental investigations and theoretical models (refs. 6-9). Heat transfer and drag in so-called vacuum plasma spraying (VPS) is strongly reduced due to the non-continuum effects of the rarefied gas flow at typically 3 - 30 kPa (ref. 10). Measurements are so far confined to plasma temperatures and particle velocities, start-ing in APS (refs. 11, 12), where particle surface temperatures where deter-mined as well except close to the nozzle (ref. 11) and continuing to VPS recently (refs. 13-16). Up to now, no method has succeeded in measuring plasma velocities and the transport characteristics of the plasma are un-known to a large extent. There is still a clear need for modelling, and one sees growing activities in this field (refs. 10, 17-19). Parallel activi-ties are going on in the field of R.F. plasma spraying (refs. 20-22).

Particle-Plasma Mass Exchange   A further problem to be tackled by plas-ma engineering is the control on mass transfer to and from the particle. Superheated particles are desirable, but the evolving vapour cloud may sig-nificantly change drag and heat transfer and may eventually decrease plasma temperature. Oxidation in APS is clearly related to the turbulent flow and difficult to control. In spraying oxides under low pressure, the reverse problem may occur: oxygen depletion. There is still a lack in appropriate models for the chemical reactions between plasma constituents like hydrogen or oxygen and the hot particle surface.

Particle–substrate interaction

In recent theoretical work backed by experiments Houben (ref. 2) has shown that spreading of the molten particle takes place well before freez-ing. Following his approach, spreading is determined dominantly by shock wave dynamics and the related material parameters - in his calculations, he accounts for instantaneous pressures as high as 10^5 bar. Even in the relax-ation period governing the lateral outflow of compressed droplet material wetting parameters seem to be secondary. The spreading determines the size and shape of the resulting spray lamella, especially the area of close thermal contact. Freezing is governed by the rate of heat flow (cooling rate about 10^6 K/s) to the substrate, involving heat conducting properties of both spray material and substrate. Freezing dynamics determine grain growth and phase content. As the nucleation rate is strongly temperature-dependent, the heat flow rate determines grain shape as well: fine columnar growth is observed in most cases near a metallic substrate providing high heat flow, less elongated and larger grains are found e.g. in the middle and at the top of ceramic layers. This has been demonstrated in numerous examples, starting from the pioneering TEM-work of Safai/Herman (ref. 23) and McPherson (refs. 24, 25) up to recent cross-sectional TEM of sprayed TiC (ref. 26).

At the very moment of solidification, one finds - according to the cal-culations of Houben (ref.2) - a "hot" zone in the substrate (temperatures ranging from 300 °C up to the melting point of the spray particle). Its

width is about the lamella thickness. Hence, diffusion may still take place between the substrate and the spray material, controlled by the substrate thermal diffusivity. After cooling to the integral substrate temperature, thermal mismatch strains may result in microcracks already within the single splash.

Structure of sprayed layer

Besides the parameters already mentioned, surface temperature, substrate topography and the relative movement plasma/substrate govern the details of the growing lamellar structure. Surface temperature may be driven by deposition rate. The spreading does not result in a perfect lenticularly shaped splash, but shows rims, holes and elevations. On the other hand, the spreading may not penetrate to all cavities. Thus, there result pores and loose interlamellar contact (see e.g. ref. 25). Determining for the layer properties are mainly three features:
-    location and density of pores, pore shape and pore size
-    interlamellar contact and adhesion to the substrate, respectively
-    the distribution of residual stresses, mainly resulting from thermal mismatch. The former two determine electrical, thermal and mechanical properties of the layer, whereas the latter relates to crack resistivity and thermal shock/thermal fatigue resistance. There are interesting approaches to model crack resistivity from random deposition of lamellae (ref. 27) and from thermal dynamics during spraying (ref. 28). Stress profiles were as well modelled for wavy surface topography (ref. 29), simulating the rough surface of the usually grit-blasted substrate.

Adhesion is a question comprising residual stresses as well as lamella interface features and surface (oxide) chemistry. In this respect, plasma spraying does not differ substantially from other thermal spraying techniques, and many results of earlier work (ref. 30) are still found valid in recent investigations (refs. 31, 32).

Adhesion, residual stresses and pore content, however, may be fully dominated by the plasma process step: it has been nicely demonstrated by Brunet and Dallaire (ref. 33) for the case of spraying pure TiC, how strongly these three features may depend on powder size distribution.

'TRADITIONAL' APPLICATION FIELDS

Increasing demands in the field of protective layers against wear, erosion, high temperature load and high temperature corrosion have stimulated careful investigations in microstructure and their dependency on process parameters (see e.g. refs. 34, 35 for wear applications). In many cases, such as spraying dispersed hard phases embedded in a ductile matrix, the proper preparation of spray powder is decisive - whether fused or cladded, crushed or atomized.

High temperature wear and corrosion

Mould equipment in glass industry is subject to extreme thermal, corrosive and abrasive loads. Requirements are - besides excelllent thermal fatigue and shock resistance - a defined grain size and a non-porous, uniform surface texture after polishing. Oxide and carbide inclusions initiating thermal stress peaks must be avoided. Successful repair of glass rollers made from a Ni-based alloy by spraying a 5-10 mm thick layer of the substrate material at low pressure has been reported by Disam et al. (ref. 36). A uniform grain size and the required very low porosity was achieved (further improved by heat treatment) at the impressive powder feed rate of 15 kg/h.

The field of MCrAlY's sees elaborate investigations concerning the microstructure and the dynamics of yttria precipitation (ref. 37). There is increasing interest in spraying erosion resistant cermets made from MCrAlY and Al_2O_3, e.g. for use in pressurized fluidized bed coal combustion (ref. 38), again accompanied by thorough microstructural, X-ray and TEM-investigations.

A distinct example of surface engineering is reported by Dallaire (ref. 39): for the protection of graphite electrodes in steel melting he first sprays a 25-50 /um thick Ti-layer directly onto graphite, followed by 250-650 /um SiC grains embedded in Al. The titanium is meant as diffusion barrier, but on application one has to deal with the four materials phase diagram Al-C-Si-Ti at 2000°C: Dallaire finds best protection when there results a duplex layer, viz. dense Al_4SiC_4 covering graphite and Al-Ti-oxides sealing the surface. Formation of Al_4C_3 must be suitably prevented, e.g. by using uniformly large grains (about 50 /um) of SiC.

Thermal barrier coatings

Thermal stresses and phase dynamics are a long-standing research topic in thermal barrier coatings made of partially or fully stabilized zirconia. Thermal shock and fatigue behaviour is related to the profile of residual stresses evolving from as-sprayed microstructure. Under numerous research contributions one sees modelling of the stress profile (refs. 28, 29, 40), shaping stress-relieving structural details like pores or graded metal-ceramic interfaces by spray conditions (ref. 41) or allowing for vertical cracks while carefully avoiding lateral ones ("segmentation"). Hoel and Kvernes (ref. 42) have shown that in raising the fracture toughness by appropriate stabilizers it is indispensable to keep the Si-impurity level down. Promising experiences were made with the use of zirconia-MCrAlY-cermets in metal moulds for casting (see e.g. ref. 43).

In fusion plasma devices one faces a different kind of thermal shock problem: plasma disruptions may cause an energy flow as large as 20 MJ/m^2, lasting from 1 ms up to 100 ms. Protection of the steel vessel by plasma sprayed pure TiC layers is currently under investigation, testing plasma-sprayed layers by intense laser pulses (refs. 44, 45).

Chemical attack

Very dense layers, essentially pore-free, are required for protection against chemical attack. In a metal layer like Ti or Ta, any oxides, nitrides or carbides have to be precluded. Preparation of dense, corrosion resistant protective layers by low pressure spraying is currently investigated. Results for Ti and Ta obtained in our laboratory are quite promising, as are the results of Fukumoto et al. (ref. 46) for VPS-sprayed alumina. Matching powder size distribution carefully with plasma jet properties, however, is of crucial importance especially in this field. Goal of the investigations is in first instance corrosion resistance, but future use is anticipated for layers with <u>defined</u> electrochemical properties like the electrodes mentioned in the following section.

'ADVANCED' APPLICATION FIELDS

Under this heading we may summarize electronic and catalytic materials and the production of spray material composites, which may be reinforced by fibres or particulate matter.

Electrodes in water electrolysis

Electrocatalytic materials are required to reduce cell overvoltage in water electrolysis for H_2-production. As cathodes one uses porous Ni-structures (Raney-Nickel) produced by leaching out Al from sprayed NiAl-layers (refs. 47, 48). Spray engineering problem is to shape porosity as sprayed, lamellae size and interlock, adhesion, residual stresses and the distribution of the Al-rich phases in such a way as to guarantee large effective surfaces combined with excellent mechanical and thermal stability of the active layer. Henne et al. (ref. 47) have demonstrated, how confined particle flow and raised particle acceleration brought about by a LAVAL-nozzle may improve results. As anodes, Co-based mixed oxides of the spinel and perovskite type are used. Spraying these materials under reduced pressure in order to ensure purity, one faces the problem of oxygen depletion. Thus, the possibility to spray with O_2 addition instead of H_2 must be investigated. In a similar case, viz. when spraying ZrN, Fauchais and coworkers (ref. 49) used a controlled Ar/N_2 atmosphere at 900 mbar in order to prevent the nitride powder from N_2 depletion. Last not least the precious oxide material forces one to optimize spray deposition efficiency distinctly above the 50-60% value reported in previous publications (ref. 50).

Advanced ceramics

The problem of oxygen depletion is a well known drawback in plasma-spraying spray compacts or layers of high T_c-superconducting materials (refs. 51, 52). Superconducting properties have to be restored by a heat treatment in O_2. Because of the phase transformations experienced on the passage through the plasma, there is even no need to use powder with superconducting properties (ref. 52). Addition of O_2 to the plasma and its influence on YBaCu-oxide phase content is currently under investigation at several laboratories.

Superconductors are one example for plasma-sprayed materials in electronic applications. Currently, various materials like (doped) silicon (ref. 53), Fe_2O_3 (ref. 54) and TiO_2 (ref. 55) to be used in semiconductor or photovoltaic applications are considered possible candidates for plasma spray processing and investigated. For thick-film dielectrics, the use of plasma-sprayed alumina is standard industrial application (ref. 56), and possibly plasma-sprayed spinel will follow (see e.g. ref. 57). It is evident, that electrical conductivity and dielectric properties of the sprayed layer depend strongly on pore (size) distribution, lamellae thickness and interlamellar contact. The content of metastable phases (well known for the case of alumina) will matter as well.

To the materials engineering of advanced ceramics belongs as well the production of zirconia coatings with enhanced fracture toughness for use at ambient temperatures (ref. 58). So far, microstructural control of grain size is not sufficient to use any other stabilizer than ceria. (Besides that, grain size in plasma sprayed coatings is usually too small to ensure a proper amount of transformable tetragonal phase, see e.g. ref. 42). One may expect growing activities in this field, which - for plasma spraying - is a rather new topic.

Free standing shapes

Formation of free spray compacts, made up only from uncontaminated spray material, is an advantage above vapour deposition or crucible melting methods when processing (doped) silicon or precious oxides. Free standing shapes have proven their worth when fabrication of ceramic parts with complex (inner) geometry is required (ref. 59). In the production of large, thin-walled ceramic or high-melt metal parts plasma spraying is the method to be preferred. Impressive achievements are seen in the production of alumina parts: a water-stabilized plasma jet with up to 200 kW power, fed at rates up to 30 kg/h, is used to produce tubes of 2 m diameter up to 10 m length and a variety of complex shapes (ref. 60). Spray engineering has to prevent crack formation due to thermal stresses, even if dense compacts with low porosity are required. In metal applications, mostly sprayed at reduced pressure, purity of the sprayed compact may be an advantage above powder-metallurgical processing.

Fibre-reinforced materials

Plasma spraying excels by the flexibility to produce any combination of ceramic/metal, metal/metal and ceramic/ceramic compounds. Here, adhesion of the sprayed matrix to the fibres has to be optimized by a careful choice of matrix powder size distributions (as compared to fibre diameter and - for discontinous fibres - fibre aspect ratio) and spray conditions. When using carbon-containing fibres in a metal matrix, appropriate diffusion barriers have to be applied first by coating the fibres before spraying.
Berndt and Yi (ref. 61) have investigated the coating microstructure for different systems, dealing extensively with the engineering of composite powders, containing cladded discontinous ceramic fibres. Various fibre diameter distributions (0.5 - 20 /um) were used. The fibre morphology is found to be retained in the sprayed structure.

We have dealt with continous fibres in our laboratory (range 10-100 /um) and experienced that spreading characteristics of the matrix droplets had to be optimized in order to overcome shadowing effects. The use of still thinner continous fibres (< 5 /um) will be a forthcoming application of RF-spraying: such fibres may be vulnerable to high impact velocities. Therefore, the low velocities of the usually strongly superheated particles (leading to fine spreading) in RF-spraying will be advantageous.

POST-TREATMENT

The microstructure of as sprayed layers may benefit from posttreatment. A <u>heat treatment</u> may induce grain growth and initiate precipitations. To this aim, MCrAlY coatings are heat treated. Eaton and Novak (ref. 62) have reported beneficial effects when sintering sprayed zirconia coatings (fully and partially stabilized) at 1100 - 1500 °C: the structure transforms from a mechanically interlocked lamellae network to a chemically bonded system. Interlamellar porosity is changed to spherical porosity. Silicon impurity, again, plays a decisive role in this densifying effect.

Hot isostatic pressing usually results in complete closure of pores
(ref. 63). The interdiffusion between substrate and layer has to be care-
fully controlled: it may be beneficial in improving the adhesion, but
detrimental, when the diffusion leads to the formation of undesired inter-
metallic phases. Ref. 63 reports that oxide lamellae produced in APS may
act as a diffusion barrier preventing substrate constituents from
deteriorating a FeCrAlY-layer.

Shot peening and related techniques will compact the surface and change
the residual stress profile near the surface (ref. 64). There is still a
need for investigations which determine the proper shot peening parameters
for different coating materials and coating microstructures.

Remelting of the layer surface by electron and laser beams ("glazing"
the surface) is currently under extensive investigation (see e.g. refs. 65,
66). From the published results (and our own experience, too) glazing
ceramic layers by laser beams shows still serious drawbacks: deep cracks,
produced by thermal stresses and large pores brought about by vapour bub-
bles seem difficult to avoid. Success may perhaps be reached for ceramics
with sufficient thermal diffusivity. On the contrary, laser remelting of
high melt metallic layers like low pressure sprayed Ta, performed in our
laboratory, showed very promising improvement in corrosion resistance.

Sealing of the surface has been tried as well by adding a CVD or PVD
layer (ref. 67, sealing APS sprayed alumina by a CVD alumina-titania-
layer). One certainly has to use plasma-assisted CVD, in order to avoid the
high deposition temperature of conventional CVD. For the corrosion resis-
tance of vapour-deposited layers it is decisive to avoid the formation of a
columnar structure showing voids in between the columns. To which extent
this may be achieved, must be the subject of further investigations. In
special cases, e.g. in electronic applications, vapour-deposited layers may
act as a smooth, well adherent contact surface on a plasma-sprayed oxide
dielectric.

CONCLUSIONS

General features

Plasma spraying as a tool in advanced surface engineering excels by the
nearly unlimited choice of materials and its low geometrical constraints.
It provides an efficient and fast deposition which lends itself easily to
automation. Scaling-up from laboratory experiments to industrial production
is quite straightforward. For the production of graded or multi-component
layers, plasma spraying offers a flexible one-step-process. By spraying
under controlled atmosphere or under reduced pressure one may realize
layers or solid compacts of low impurity content. Due to rapid solidifica-
tion, applications involving metastable phases and amorphous materials like
metallic glasses may be expected. An additional advantage is the possibili-
ty to perform various methods of post-treament on the sprayed structure.

Problems to be solved

Things to be improved may be summarized under two topics: to facilitate
microstructural control and to raise deposition efficiency.

For improved deposition efficiency, a better control of powder injec-
tion is desirable. To a large extent, spray loss results from unmelted par-
ticles leaving the jet at the fringes. Proper injection and control of tur-
bulence must aid to keep the injected particles inside the central region
of the jet. In VPS applications, laminar jets are preferable. Much may be
done, given a fixed material system, by proper "powder engineering", i.e.
matching powder morphology and powder size distribution to the characteris-
tics of the jet. In addition to the existing plasma-particle models, there
is a need to model high powder load. Lee and Pfender (ref. 19) have shown
for APS that plasma temperature and plasma acceleration may drop signifi-
cantly already for powder flow rates in the order of one third of the plas-
ma gas flowrate.

Precondition for improved microstructural control is a better under-
standing of plasma-particle interactions: heating, acceleration and mass
exchange. Especially the problem of oxygen depletion needs to be tackled,
as many of the advanced materials are oxides, but require to be sprayed in
an inert or low pressure environment in order to avoid contamination. Ac-
cess to new fields in microstructural plasma spray engineering will open
up, if one succeeds to provide a narrow range of impact velocities and a
narrow range of heat contents on impact under conditions of controlled
plasma chemistry.

REFERENCES

1. A. Matting, <u>Brit. Weld. J.</u> <u>13</u>, 526-532 (1966).
2. J. M. Houben, Ph.D. Thesis, Technical University of Eindhoven, (1988).
3. H. Warlimont, <u>Angew. Chem. Adv. Mater.</u> <u>101</u>, 971-974 (1989).
4. X. Chen and E. Pfender, <u>Plasma Chem. Plasma Process.</u> <u>2</u>, 185-212 (1982).
5. P. Fauchais, J.F. Coudert, A. Vardelle, M. Vardelle, A. Grimaud, P. Roumilhac, Proceedings NTSC 1987 Orlando/USA, ed. D.L. Houck, pp. 11-19(1987).
6. A. Capetti and E. Pfender, <u>Plasma Chem. Plasma Process.</u> <u>9</u>, 329-341 (1989).
7. Y.P. Chyou and E. Pfender, <u>Plasma Chem. Plasma Process.</u> <u>9</u>, 291-328 (1989).
8. R. Spores and E. Pfender, <u>Surf. Coat. Technol.</u> <u>37</u>, 251-270 (1989).
9. Ph. Roumilhac, J. F. Coudert, J. Leger, A. Grimaud, P. Fauchais and M. Ducos, Proc. 1st Plasma-Technik-Symposium Lucerne/Switzerland 1988, ed. H. Eschnauer, vol. I pp 105-119 (1988).
10. E. Pfender, <u>Pure Appl. Chem.</u> <u>57</u>, 1179-1195 (1985).
11. P. Fauchais, A. Vardelle, M. Vardelle, J.F. Coudert and J. Lesinski, <u>Thin Solid Films</u> <u>121</u>, 303-316 (1984).
12. J. Lesinski and M.I. Boulos, <u>Plasma Chem. Plasma Process.</u> <u>8</u>, 113-132 (1988).
13. M. F. Smith, Proc. 1st Plasma-Technik-Symposium Lucerne/Switzerland 1988, ed. H. Eschnauer, vol. I pp. 77-85 (1988).
14. W. Mayr, R. Henne, Proc. 1st Plasma-Technik-Symposium Lucerne/ Switzerland 1988, ed. H. Eschnauer, vol. I pp 87-97 (1988).
15. H.-D. Steffens, M. Mack and R. Lauterbach, Proc. 1st Plasma-Technik-Symposium Lucerne/Switzerland 1988, ed. H. Eschnauer, vol. I pp. 67-76 (1988).
16. H.-D. Steffens, M. Mack and R. Lauterbach, Proc. 1st Int. Conf. on Plasma Surface Engineering, Garmisch-Partenkirchen/Germany 1988, eds. E. Broszeit et al., pp. 1235-1242 (1989).
17. I. Groma and B. Veto, <u>Int. J. Heat Mass Transfer</u> <u>29</u>, 549-554 (1986).
18. A.H. Dilawari and J. Szekely, <u>Plasma Chem. Plasma Process.</u> <u>7</u>, 317-339 (1987).
19. Y.C. Lee and E. Pfender, <u>Plasma Chem. Plasma Process.</u> <u>7</u>, 1-27 (1987).
20. J. Mostaghimi, P. Proulx and M.I. Boulos, Plasma Chem. Plasma Process. 4, 199-217 (1984).
21. P. Proulx, J. Mostaghimi and M.I. Boulos, <u>Plasma Chem. Plasma Process.</u> <u>7</u>, 29-52 (1987).
22. J. Lesinski and M.I. Boulos, <u>Plasma Chem. Plasma Process.</u> <u>8</u>, 133-144 (1988).
23. S. Safai and H. Herman, <u>Thin Solid Films</u> <u>45</u>, 295-307 (1977).
24. R. McPherson, <u>Thin Solid Films</u> <u>83</u>, 297-310 (1981).
25. R. McPherson and B.V. Shafer, <u>Thin Solid Films</u> <u>97</u>, 201-204 (1982).
26. G. Veilleux, R.G. Saint-Jacques and S. Dallaire, <u>Thin Solid Films</u> <u>154</u>, 91-100 (1987).
27. O. Knotek and R. Elsing, <u>Surf. Coat. Technol.</u> <u>32</u>, 261-271 (1987).
28. D.S. Rickerby, G. Eckold, K.T. Scott and I.M. Buckley-Golder, <u>Thin Solid Films</u> <u>154</u>, 125- 141 (1987).
29. G.C. Chang, W. Pucharoen and R.A. Miller, <u>Surf. Coat. Technol.</u> <u>32</u>, 307-325 (1987).
30. A. Matting, H.-D. Steffens, <u>Metall</u> <u>17</u>, 583-593 & 905-922 & 1213-1230 (1963).
31. C.C. Berndt and R. McPherson, <u>Surf. J. Intl.</u> <u>1</u>, 49-52 (1986).
32. S. Kitahara and A. Hasui, <u>J. Vac. Sci. Technol.</u> <u>11</u>, 747-753 (1974).
33. C. Brunet and S. Dallaire, <u>Surf. Coat. Technol.</u> <u>31</u>, 1-10 (1987)
34. A.R. Nicoll, <u>Surf. Coat. Technol.</u> <u>30</u>, 223-242 (1987).
35. J.R. Lindgren and W. R. Johnson, <u>Surf. Coat. Technol.</u> <u>32</u>, 249-260 (1989).
36. J. Disam, A. Sickinger, V. Wilms and G. Johner, Proceedings 1st Int. Conf. on Plasma Surface Engineering, Garmisch-Partenkirchen/Germany 1988, eds. E. Broszeit et al., pp. 355-364 (1989).
37. B. Gudmundsson and B.E. Jacobson, <u>Thin Solid Films</u> <u>173</u>, 99-107 (1989).
38. B. Gudmundsson, B.E. Jacobson, L. Berglin, L.L'Estrade and H. Gruner, Proc. 1st Plasma- Technik-Symposium Lucerne/Switzerland 1988, ed. H. Eschnauer, vol. I pp. 173- 179, (1988).
39. S. Dallaire, <u>Surf. Coat. Technol.</u> <u>32</u>, 141-152 (1987).
40. H.-D. Steffens, Z. Babiak and U. Fischer, Proc. 2nd Int. Conf. on Surface Engineering Stratford-upon-Avon 1987, ed. I.A. Bucklow, pp. P41/1-12 (1987).
41. H.-D. Steffens and U. Fischer, <u>Surf. Coat. Technol.</u> <u>32</u>, 327-338 (1987).
42. R.H. Hoel and I. Kvernes, Proc. NTSC, Orlando/USA 1987, ed. D.L. Houck, pp.291-296 (1987).

43. T. Oka, J. Takeuchi, Y. Harada and H. Nakahira, Proc. 1st Plas ma-Technik-Symposium Lucerne/Switzerland 1988, ed. H. Eschnauer, vol. I pp. 173-179, (1988).
44. S. Dallaire and R. G. Saint-Jacques, <u>Surf. Coat. Technol.</u> <u>33</u>, 319-326 (1987).
45. P. Groot, J.G. van der Laan, L. Laas, M. Mack and M. Dvorak, Proc. Euro pean Ceramic Society Conf. Maastricht, (1989).
46. M. Fukumoto, M. Ortiz and I. Okane, Proc. ISPC-8 Tokyo 1987, pp. 1934-1939 (1987).
47. R. Henne, M. von Bradke, G. Schiller, W. Schnurnberger and W. Weber, Proc. 1st Plasma-Technik-Symposium Lucerne/Switzerland 1988, ed. H. Eschnauer, vol. I pp. 225-235 (1988).
48. D. Chuanxian, Zh. Yefang, Q. Jianzhong, L. Huling and H. Bingtang, Proc. 1st Plasma-Technik-Symposium Lucerne/Switzerland 1988, ed. H. Eschnauer, vol. I pp. 237-245 (1988).
49. F. Derradji, F. Kassabji and P. Fauchais, <u>Surf. Coat. Technol.</u> <u>29</u>, 291-301 (1986).
50. G. Wuest, S. Keller, A.R. Nicoll and A. Donnelly, <u>J. Vac. Sci. Technol.</u> <u>A3</u>, 2464-2468 (1985).
51. L. S. Wen, S.W. Quian, Q.Y. Hu, B.H. Yu, H.W.Zhao, K. Guan, L.S. Fu and Q.Q. Yang, <u>Thin Solid Films</u> <u>152</u>, L143 - L145 (1987).
52. Y. Arata, A. Ohmori and S. Sano, <u>Transact. Jap. Weld. Res. Inst.</u> <u>2/ 1988</u>, 173-175 (1988).
53. R. Suryanarayanan, G. Brun and A. Akani, <u>Thin Solid Films</u> <u>119</u>, 67-73 (1984).
54. L. Parent, J.P. Dodelet and S. Dallaire, <u>Thin Solid Films</u> <u>154</u>, 57-64 (1987).
55. R. Wang and C.H. Henager, <u>J. Electrochem. Soc.</u> <u>126</u>, 83-85 (1979).
56. L. Pawlowsky, <u>Surf. Coat. Technol.</u> <u>35</u>, 285-298 (1988).
57. H.G. Wang and H. Herman, <u>Ceram. Bull.</u> <u>68</u>, 97-102 (1989).
58. G. N. Heintze and R. McPherson, Proc. NTSC, Orlando/USA 1987, ed. D.L. Houck, pp.291-296(1987).
59. R. J. Quentmeyer, G. McDonald and R. C. Hendricks, <u>J. Vac. Sci. Technol.</u> <u>A3</u>, 2450-2455 (1985).
60. S. Schindler and W. Schultze, Proc. 1st Plasma-Technik-Symposium Lucerne/Switzerland 1988, ed. H. Eschnauer, vol. I pp. 181-191 (1988).
61. C.C. Berndt and J.H. Yi, <u>Surf. Coat. Technol.</u> <u>37</u>, 89-110 (1989).
62. H.E. Eaton and R.C. Novak, <u>Surf. Coat. Technol.</u> <u>32</u>, 227-236 (1987).
63. C. Burman, T. Ericsson, I. Kvernes and Y. Lindblom, <u>Surf. Coat. Technol.</u> <u>32</u>, 127-140 (1987).
64. J.S. Eckersley and R. Kleppe, <u>Surf. Coat. Technol.</u> <u>33</u>, 443-451 (1987).
65. R. Streiff, M. Pons and P. Mazars, <u>Surf. Coat. Technol.</u> <u>32</u>, 85-95 (1987).
66. N. Iwamoto and N. Umesaki, Proc. NTSC Orlando/USA 1987, ed. D. L. Houck, pp. 357-363 (1987).
67. T. Mäntylä, P. Vuoristo and P. Kettunen, <u>Thin Solid Films</u> <u>118</u>, 437-444 (1984).