Problems encountered in the development of locally shielded plasma spray devices

PROBLEMS ENCOUTERED IN THE DEVELOPMENT OF LOCALLY SHIELDED PLASMA SPRAY DEVICES.

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SUMMARY.
The main problems encountered in the development of locally shielded plasma spray devices are described. Stream patterns inside a tube and the detrimental influence of spray vapour and secondarily adhering particles on the structure of a deposit are shown. Commercial available Mo powders turned out to be not directly fitted to meet the requirements of high quality work with a shielding tube due to their large amount of volatile, vapour producing elements. A narrow tube type seems to offer the possibility of working up coarse grains at a free standing distance of 15 mm without extra sheath gas consumption. This tube requires additional care for proper injection of the spray powder.

1. INTRODUCTION

To avoid contamination of spray particles by the surrounding air during plasma spraying, essential three types of equipment can be applied:
- an inert gas or vacuum chamber in which the material to be coated is placed, ref. 1-2-3
- an inert gas tent into which operator and workpieces embark, ref. 4
- an inert gas shroud around the plasma jet which prevents penetrating of air into the stream of hot gas and particles, ref. 5.

This last equipment offers a mean of shielded spraying that does not require large investments. It is a versatile method with respect to parts geometry and size. The operation costs and the effectiveness of this shrouding equipment are strongly dependent on the shielding gas consumption. In ref. 5 a laboratory device has been described that gives full protection against contamination at a rather low shielding gas consumption level of 25-50 Nl/min. However the free standing distance between shielding tube and substrate is limited to approximately 5 mm. This may be considered as not really fit for practice. So we worked on the development of shrouding tubes with a free distance of at least 10 mm.

Among others, two basic problems were encountered:
The first problem mainly is the establishment of stabil gasstreams inside the tube.
The second problem is the interaction of spray vapour and secondarily adhering particles with the substrate.

2. STREAM PATTERNS INSIDE A WIDE BODY SHIELDING TUBE.

Previous to the detailed describtion of stream patterns related to a certain tube type, it may be worthful to dedicate some explanation to the basic choice of size and shape. Okada and Maruo[6] introduced in 1968 a device shown in detail in fig. 1. The shielding tube is a cone with a top angle of approximately 22°. The shielding gas is supplied in a ringshaped cover around the tube. The overall width of the device is 200 mm, the free standing distance is small. This device certainly is a serious attempt to make shrouding equipment for practical purposes. The arrangement partly shows the same construction features as the movable welding booth for titanium.

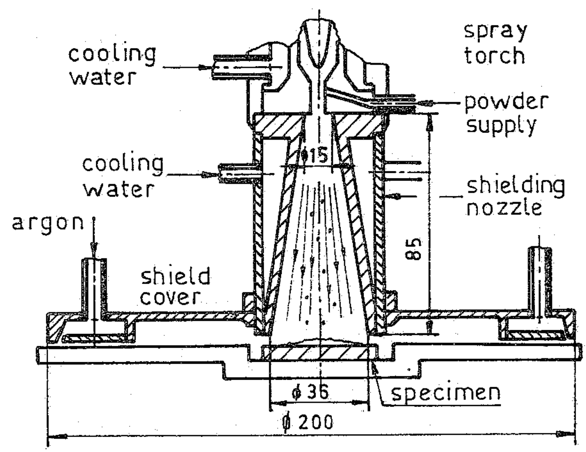


Fig. 1 ref 6

Shielding device acc. Okada and Maruo.

Fig. 2 shows a patented device by Guest and Ford[7]. The sheath gas is feeded through a spiral passage at a rate of 366 l/min, thus causing a vortical flow of the gas shield. The gap between the mouth of the tube and the substrate is 10-20 mm.

Fig. 3 shows a device presented at the 8th Thermal Spraying Conference [5]. This diffusor type was operated with a free gap of 5 mm and a gasconsumption of 25-50 Nl/min.

In these wide body shielding tubes the basic problem with respect to the gas flow inside is formed by the zone of sub-pressure that is created by the fast flowing plasma jet. The momentum equation applied on the control volume indicated in fig.4 reveals:

$$p_2 - p_1 = \frac{\rho v_1^2 A_1 - \rho v_2^2 A_2}{A_2} \qquad (1)$$

The continuity equation is:

$$v_1 A_1 = v_2 A_2 \qquad (2)$$

Combining (1) and (2) yields:

$$p_2 - p_1 = \rho v_2 (v_1 - v_2) > 0 \qquad (3)$$

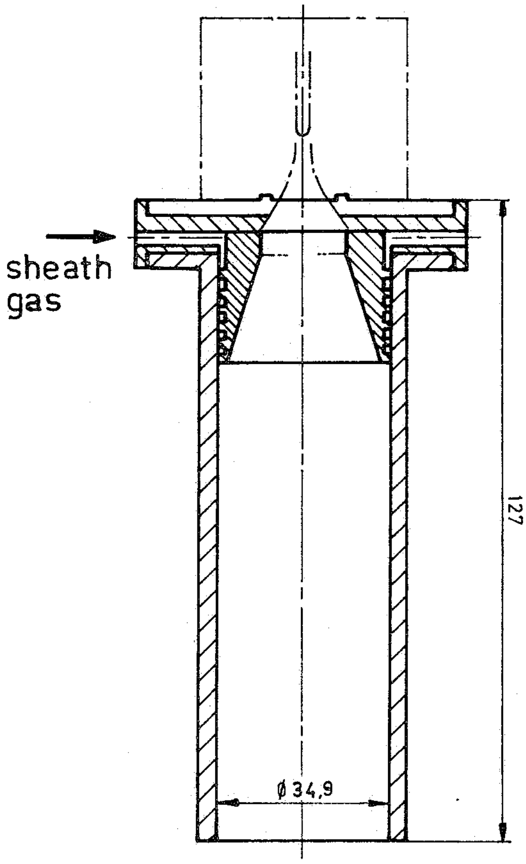


Fig. 2 ref. 7

Shielding device acc. Guest and Ford.

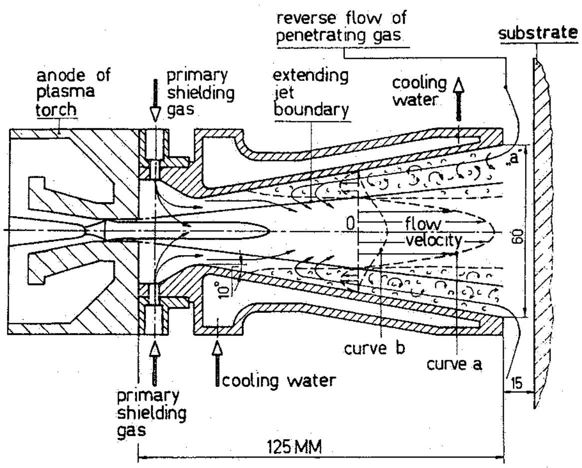


Fig. 3

Shielding device acc. Houben and Zaat

This under-pressure causes a back stream of penetrating air along the tube wall that is mixed up with the plasma jet, see fig. 3. The back stream of air certainly can be suppressed by a limited size of the tube mouth.

However, there were three arguments to accept a wide body tube in the first instance as a shielding device. First, the diverging jet of spray particles required a certain minimum inner size to avoid adhering of particles to the inner wall. Secondly, when the outstreaming plasma jet is closely surrounded by the inner wall of a shielding tube with a wide angle ($\sim 20^{\circ}$), to avoid particle adherence such as given in fig. 5, the plasma flame interacts with the tube wall and the backstream of air, causing an instable flickering jet and a wide cone of inhomogeneously heated particles. It turned out, that a certain free space around the jet was necessary to stabilize the plasma flame and the particle stream. The third argument is derived from the problems of injection low melting point materials in a plasma surrounded by a narrow tube. To avoid melting of the spray material before it has left the injection mouth-

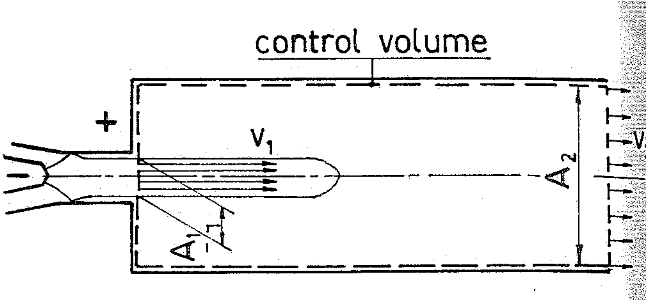


Fig. 4

Jet pumping action of the plasma

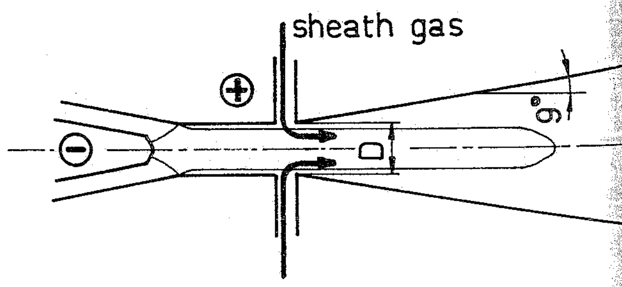


Fig.5

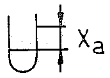
Instable configuration of a wide body tube.

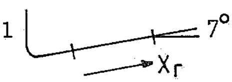
piece, a certain free distance between the outer diameter of the plasma and the injection bore is required.

In consideration of these arguments we came a.o. to the test arrangement of fig. 6. The pressure-taps I, II, III and IV are fitted to measure the static pressure difference with the surrounding atmosphere, indicated by a U-type manometer. The pressure difference x_a is given in mm ethylalcohol. The watercooled Pitot tube, mounted in a bore of the substrate measures the total pressure profile of the exhaust plane. The sites are indicated by the numbers 0-6 . The Pitot tube is connected with an inclined plane manometer tube.

Table 1: Pressure measurements x_a and x_r inside the shielding tube

Condition	A		B				C		D	
			$s_{1-1,5}$		s_{1-3}					
Pressure tap position	x_a	x_r	x_a	x_r	x_a	x_r	x_a	x_r	x_a	x_r
I	-190		-380		-152		-215		-90	
II	-190		-330		-150		-215		-90	
III	-185		-260		-142		-210		-85	
IV	-165		-200		-128		-190		-65	
0 ≙ centerline										>0
1										
2								>0		
3		>0		>0		>0				
3,5										<-570
4										
4,5										
5		-55				-50		-260		>0
5,5										
6		-55		-55		-50		-260		

x_a : mm ethyl alcohol 

x_r : mm ethyl alcohol 

During the tests the plasma torch was operated at a power level of 22 kw (500A and 44 V over the electrodes). The arc gasconsumption was 50 Nl/min argon and 16,8 Nl/min hydrogen. The free standing distance between tube exit and substrate was 15 mm. Successively pressure measurements were carried out under the following varying operating conditions:

A: the burning plasma torch without any further completion of sheath gas.

B: added to A, feeding of sheath gas(air) through bores indicated in fig. 6 as $S_{1-1,5}$ and S_{1-3}. $S_{1-1,5}$ represents a conical arrangement of 1,5 mm bores, whereas S_{1-3} is an axial arrangement of 3 mm bores.

C: added to A, feeding of sheath gas through bores S_2.

D: added to A, feeding of sheath gas through bores S_3.

The amount of sheath gas, if supplied, was 400 Nl/min. In table 1 the measurements are filed. In fig. 6 the pressure profiles are sketched.

In additional measurements we tried to determine whether the static under-pressure always measured at the taps I-II-III-IV was related to a reverse stream of air originating from the surrounding atmosphere. By means of small Pitot pressure taps at position I and IV we could ascertain this reverse stream. In these first round measurements the uncooled Pitot taps often broke down because of superheating. For this reason the dynamic pressure measurements are not yet well established regarding the thickness of the reverse stream. So, these figures are not mentioned here. Nevertheless we can sketch the partly quantitive picture (fig. 6) of the positive flow boundary under different circumstances A, B and C. Test situation D has been left out for lack of hard information at this moment.

Based on fig. 6, the accessory graph and the additional dynamic pressure measurements, we can make the following concluding remarks concerning the stream patterns inside the tube.

1. There is a reverse stream of penetrating air along the wall.
2. When shielding gas is feeded through bores $S_{1-1,5}$ the positive stream boundary moves slightly outwards, but the increased under-pressure at positions I-II-III and IV indicates an increased reverse stream velocity. If the feeding bores are enlarged to 3 mm and placed axially instead of conically a great deal of the jet pumping action of the shielding gas has been

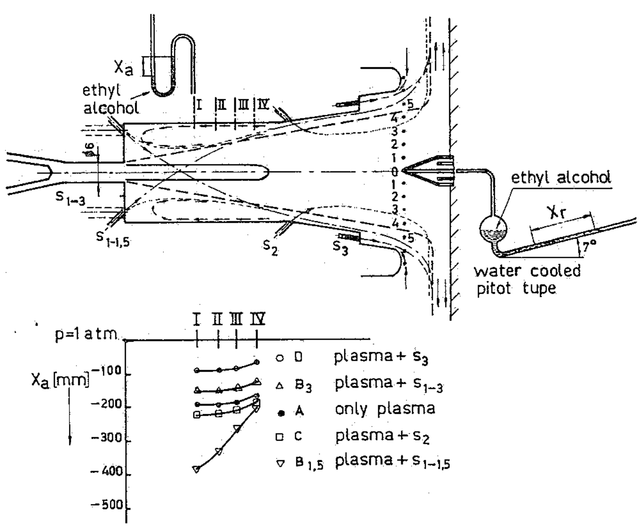


Fig 6

Pressure profiles and stream patterns inside a wide body tube

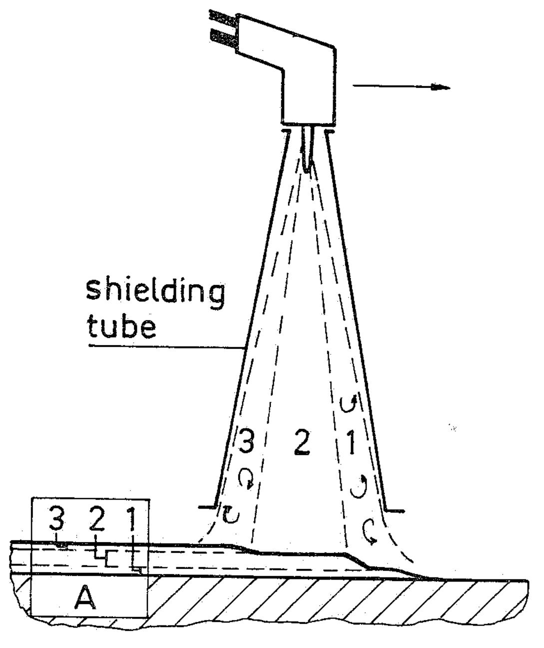


Fig. 7a

taken away, see curve B 1,5 and B 3 in fig.6.

3. Pressure profile D following from feeding the sheath gas in position S_3 , also shows a smaller under-pressure backwards in the tube compared to reference curve A. So it might be expected that feeding shielding gas in position S_3 also is advantageous regarding the suppressing of the reverse stream.
4. Feeding in position S_2 causes more under-pressure than curve A and a contraction of the positive flow. This seems to be the most unfavourable way to the stagnation of the reverse stream.
5. From the additional measurements we could determine only a minor influence on the stream pattern when the substrate has been taken away. The vicinity of the substrate represents a slight extra flow resistance for the reverse stream but is not of such a crucial importance as has been turned out in the device of fig. 3 with a free gap of 5 mm between tube and substrate.
6. The main conclusion is: the penetrating air stream can partly be suppressed by feeding sheath gas in position S_1 and S_3. This partly shielding effect only can be achieved with the considerable amount of 400 Nl/min shielding gas. Other ways must be found to make such a a diffusor type shielding tube fit for economical practice. Research is still in progress.

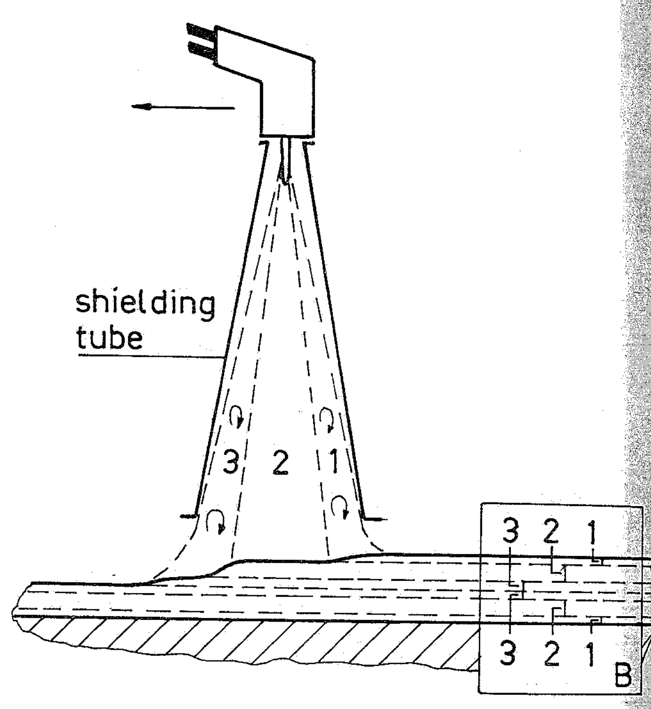


Fig. 7b

Schematic structure of a sprayed deposit regarding vapour deposition and secondarily adhering particles.

Table 2: Chemical analysis of commercial available Mo-samples, S-Mo and M-Mo. The original material ≙ o.m.; the bulk sprayed deposit ≙ b.d. and the surface of the bulk deposit ≙ s.d.

wght %	S - Mo			M - Mo		
Element	o.m.	b.d.	s.d.	o.m.	b.d.	s.d.
Mo	≤ 99,44			≤ 99,75		
W	0,085	0,10	0,10	0,055	0,070	0,06
Fe	0,085	0,070	0,10	0,015	0,020	0,070
Ni	0,055	0,040	0,055	0,020	0,015	0,015
Si	0,0035	0,001	0,002	0,0025	0,0009	0,0007
Mg	0,0025	0,0003	0,001	0,0004	0,00008	0,0002
Al	0,003	≤ 0,001	0,003	≤ 0,001	≤ 0,001	≤ 0,001
Cu	0,001	0,0007	0,003	0,0004	≤ 0,0001	≤ 0,0001
Co	0,003	0,001	0,002	≤ 0,001	≤ 0,001	≤ 0,001
B	0,0004	≤ 0,0001	≤ 0,0001	≤ 0,0001	≤ 0,0001	≤ 0,0001
Mn	0,0002	0,00006	0,0001	≤ 0,00005	≤ 0,00005	0,0001
Pb	≤ 0,0002	≤ 0,0002	≤ 0,0002	≤ 0,0003	≤ 0,0002	≤ 0,0003
Cr	0,0015	≤ 0,001	0,002	≤ 0,001	≤ 0,001	≤ 0,001
C	0,046	0,019	0,0185	30-33 ppm	22-24 ppm	41-44 ppm
O_2	0,25	0,86	2,3	0,155	1,2	1,8

3. INTERACTION OF SPRAY VAPOUR AND SECONDARILY ADHERING PARTICLES WITH THE SUBSTRATE;

These interaction phenomena turned out to be of crucial importance for plasma spraying with a shielding tube. During spraying quite a lot of vapour is produced. Besides there are many so called secondarily adhering particles. In the first collision, they rebound from the substrate, are picked up again by the gases and swept to the surface for the second time, being captured by the main stream of particles.

The vapour is coming from volatile materials or pollutions in the spray particles and from vaporizing superheated spray material itself. All the vapour is guided to the substrate surface by the tube wall (Without a tube, a great deal of the vapour would evade into the atmosphere not contacting the substrate surface). The vapour will condens on the surface . It forms a small film of high pollution concentration before and after every pass of the spray jet, thus affecting the coherence between the subsequently deposited layers.

Basically the same phenomena regarding vapour deposition and secoundary adherence occur when spraying with a very narrow spray jet of particles (which can be achieved by special injection techniques, ref.8) in absence of the shielding tube. Extra spray vapour then is produced by the reaction of material with the atmosphere. In this report we will not further distinguish between spraying with or without shielding tube regarding vapour and secondary adherence. Schematically the following picture about the structure of a deposit can be drawn.

The first pass of the torch causes a deposit according to fig. 7, detail A. The reverse stroke of the torch yields the structure of detail B. The spray zones are indicated as :1 vapour, 2 particles + vapour, 3 vapour. From detail A and B it is clear that a single layer of vapour deposition will be present between the substrate and the sprayed deposit and there will be a double layer of vapour deposition between the particular spray deposits.

The increased surface concentration of volatile elements coming from the original material has been proved by chemical analysis of:

- the original material (o.m.) before spraying,
- the bulk deposit (b.d),
- the removed contaminated surface of the deposit (s.d).

Two commercial available fractions of molybdenum, marked as S-Mo and M-Mo, have been put to the test. In table 2 the results of the chemical analysis are listed. Besides the elements mentioned in the table, As,Ag,Sn,Re, Na, K and S have been traced,but the amounts were too low for proper indication. Note that all materials except for W and Re have vapour pressures > 1 bar at the melting point of Mo. Fig. 8, based on table 2 will make clear what effects due to vapour-substrate interaction occur. Some general remarks can be made

- A falling line, going from o.m. to b.d., means that material has been vaporized.
- A rising line, going from b.d. to s.d., means that the vaporized material has been partly condensed on the surface. If s.d. % > o.m.% a very heavy vapour deposition occured.
- The increased Fe content is probably originating from the substrate and the scraping tool; the increasing W amount is supposed to be cathode material. The high O_2 content is partly due to reaction of Mo with air.
- The percentages for the surface material (s.d.) must be considered as relative values because the mass of the scraped off material varies over the different samples submitted to the analysis.

We did quite a lot of work to determine the origin of the spray vapour. Just to glance at these investigations a characteristic example of the original S-Mo is shown in photo 1 and 2. The particles are mixed up with a dark phase not being pure Mo. From photo 1, it is clear that not all of the particles are polluted. This means however that other particles are very heavily polluted to make up for the mean value that is detected

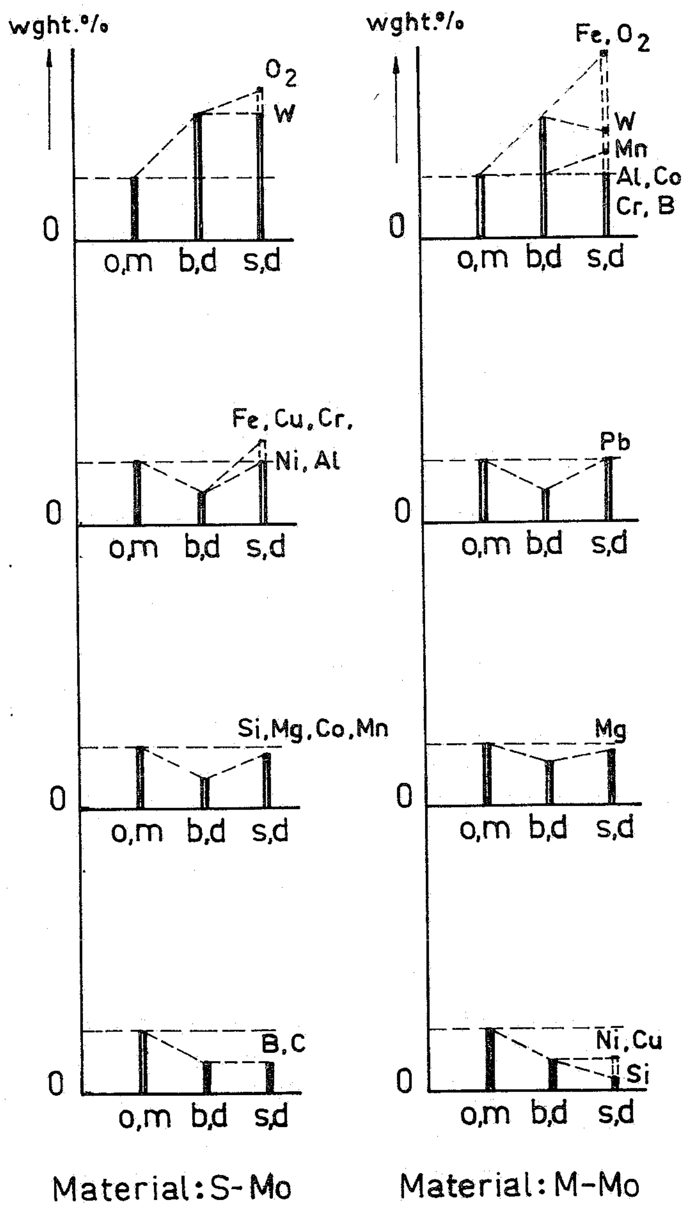


Fig.8

Concentration of elements in:
o,m: original material before spraying
b,d : bulk deposit.
s,d : surface of bulk deposit.

in a chemical analysis. In photo 3 the cross section of the same S-Mo is shown after purifying at high temperature in an inert atmosphere, followed by rapid cooling. The dark phase of the original powder has vanished. We see only the grain boundaries of very small cristals.

The purifying operation was followed by chemical analysis of the powders with respect to the significant pollutions O_2, C and Fe, see table 3.

Table 3: Chemical analysis of M-Mo after purifying.

Element	O_2 wght %	Fe wght %	C ppm
original mat	0,183	0,015	70
purified 1x	0,053	0,009	13
2x	0,036	0,003	9
3x	0,028	0,0035	7
4x	0,021	$\leq$ 0,001	7
5x	0,022	$\leq$ 0,001	6

From photo 1, 2 and 3 and the figures of this table it was clear to us that commercial available Mo powder was not fitted for scientific investigations regarding the development of shielding devices and the causality of spraying technique and deposit structure.

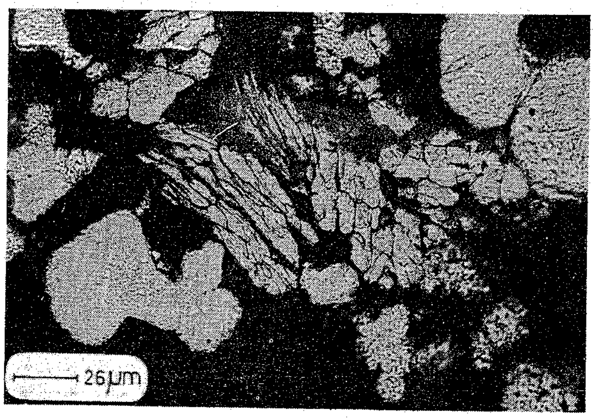


Photo 1: Original S-Mo, mixture of pure and polluted particles.

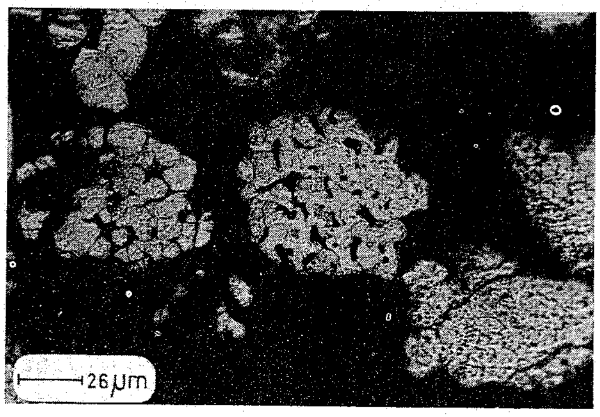


Photo 2: Original S-Mo, heavily polluted.

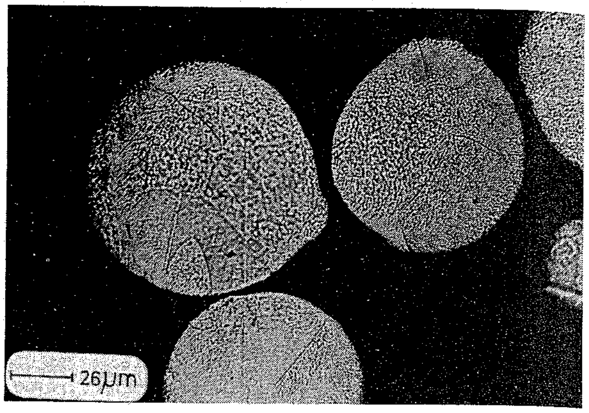


Photo 3: Cross section of purified and spheroidized Mo.

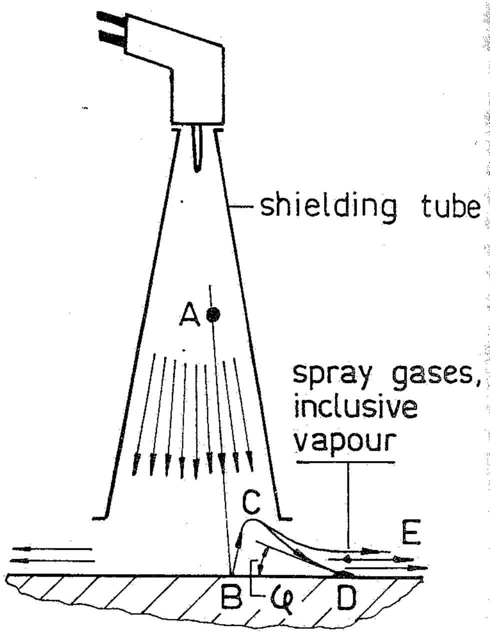


Fig. 9

Secondarily adherence of a spray particle.

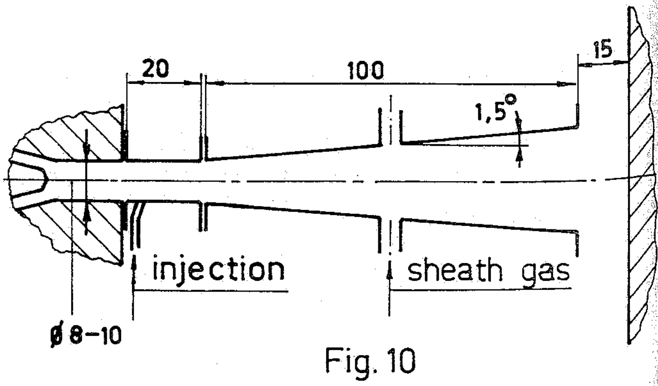


Fig. 10

Narrow shielding tube

Thus far we traced the spray vapour interaction with a substrate. The other detrimental effect, especially on the interface of two adfacent layers in a deposit,is due to in the first collision non-adhering particles. These particles rebound inside the shielding tube of which a great deal will be picked up by the exhausting spray gases and be smashed once again to the surface, however at a considerably lower speed and under a sharp angle Φ with the substrate. The basic phenomenon is sketched in fig. 9. The secondarily adhering particles move along trajectory ABCD. Real fat rebounding particles will stick to the innerwall of the tube or will not be accelerated sufficiently from C to D to escape from the viscous forces of the spray gases. These particles are ejected along trajectory CE; the secondarily adhering particles are small in size.

Again, the same basic picture of the deposit structure holds as shown in fig. 7. However,the interlayers 1 and 3 are now due to secondarily adhering particles. The structure of the deposit shows good cohesion between the spray particles, alternating with the poor quality of the interlayers. A representative example of such deposits is given in photo 4. The coating is Mo of commercial quality. Photo 5 shows a detail of the structure. There is a fairly good coherence between the lamellae and a small interlayer of minor quality between the first deposit and the substrate. Photo 6 shows a scanning electron microscopic picture of the interlayer at a position of coarse porosity.

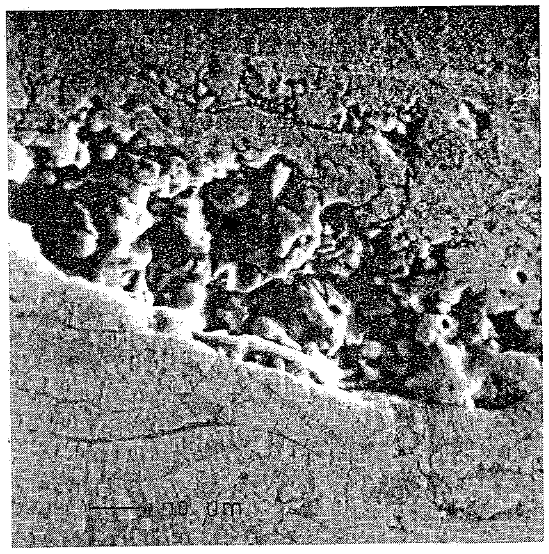


Photo 6: SEM picture of a cavity between two passes of the torch.

The pore sizes are approx. 100 μm parallel to the substrate and ∿ 30 μm perpendicular to it. The large size of the pore can not be caused by one single particle but only by the interaction of many of them. From another sample we took the SEM-photographs 7 and 8. No. 7 shows that the pores occur particularly at the interfaces; no.8 shows a detail of 7 in which the central tower

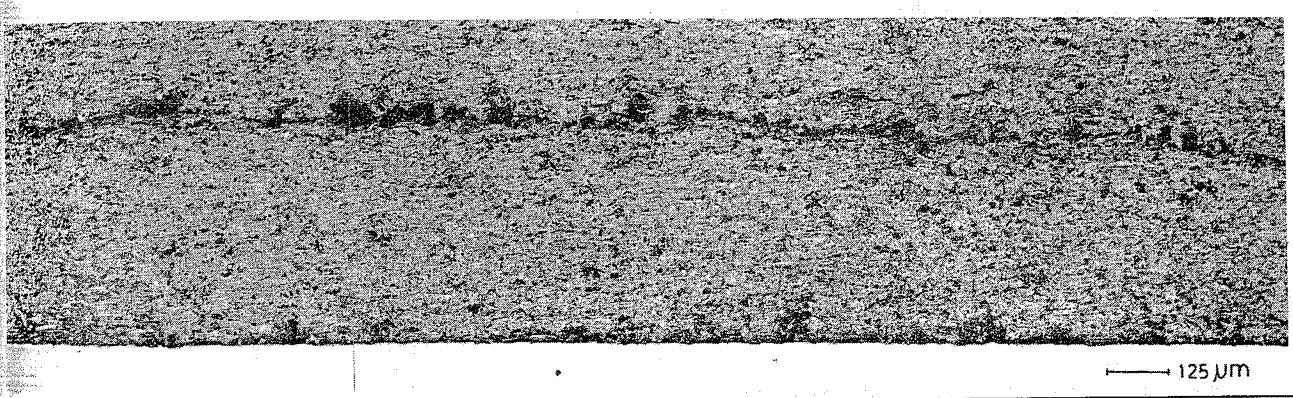


Photo 4: Fail structure of the interfaces.

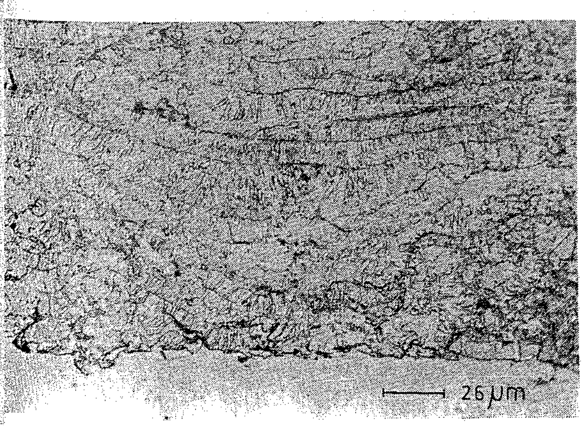


Photo 5: Detail of photo 4, good coherence between the lamellae, zone of minor quality adjacent to the substrate.

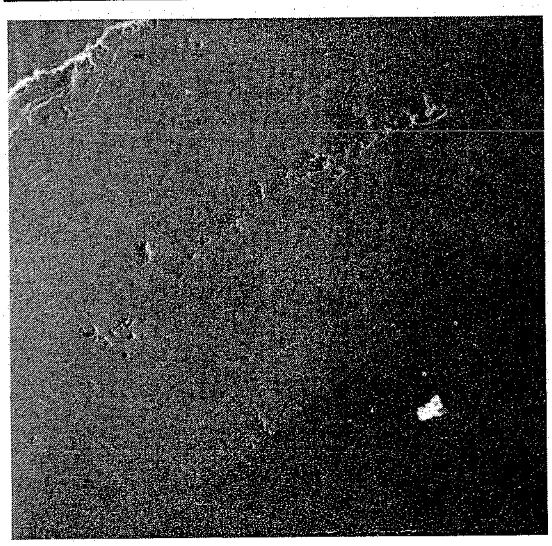


Photo 7: SEM picture of the fail structure of the interfaces.

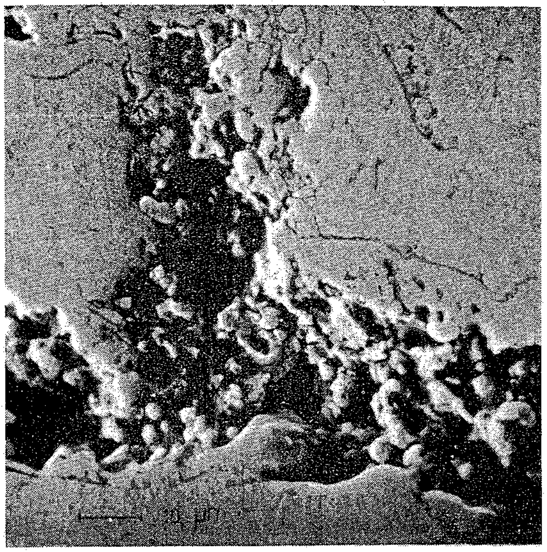


Photo 8: SEM picture of pile up porosity located in the interfaces.

of porosity and the many small, partly spherical particles within the cavity are characteristic for this kind of coarse defects. Photo 9 is intentionally taken in the border zone of a sprayed sample. It shows clearly the defective interlayer structure which can partly be repaired by the subsequently deposited central main stream of spray particles. On the left side a large cloud of piled up small particles is hanging somewhere above the substrate surface. At the right hand side of the same photograph we see that such clouds are connected with the surface under a certain angle Φ. It only depends on the direction of the specimen cross section whether we see a free hanging cloud or the piled up inclined tower based on the substrate. Further it will be clear that the space between the piled up particle tower and the substrate surface can not be filled up by the central stream of spray particles. So, the main causal relation between the coarse pores at the interfaces and the spray process, seems to be cleared up.

A further proof to this causal relation appears from photo 10. In this specimen the surface of the first deposit has been grinded to take away the polluted top. We still can see the connection line between the second and the first layer, but the coarse porosity vanished.

At last, from the SEM surface photographs 11, 12 and 13 we can see the piling up phenomenon as a cause for porosity from another view point. Photo 11 is a grinded substrate surface before spraying. Photo 12 is such a surface after one pass of the torch outside but in the vicinity of the first depot. The grinding edges picked up the secondarily adhering particles from the overflowing gasstream. Photo 13 shows, as a detail of no. 12, the accumulation of these particles. Not only grinding edges will act as a first base for the stacking particles. Also a single attached particle outside the main stream will act as such.

4. FUTURE DEVELOPMENTS OF SHIELDING TUBES.

In the foregoing report we gave evidence of two detrimental effects in relation with the use of narrow bounded spray jets and shielding tubes. Remedies to avoid the fail structure of the interlayers are:

a: prevention of excessive vapour deposition by the use of purified spray materials

b: prevention of rebounding particles. To improve the deposit efficiency we must ensure that all particles undergo more or less the same heat treatment by the plasma. In ref. 9 this problem has been discussed more specifically. It turned out that for realising proper heat treatment a relatively long plasma (compared to those in use nowadays) is required.

The combined experiences with wide body shielding tubes and the theoretical investigation of the plasma spray process have lead to a new kind of shielding tube which is under development now. Fig. 10 shows a schematic draw of such a tube which can be attached to the conventional plasma torches and which is fitted for working up coarse grains. By means of this tube the plasma of a conventional torch (20-60 kw) can be extended to a length of 125 mm and even more. The small diverging angle of $1,5^{o}$ ensures the adherence of the plasma to the inner side of the tube. There is no more a reverse stream of air, thus realising a 100 % protection of the particles against air contamination.

The elongation of the plasma by a narrow tube is primarily due to the prevention of momentum exchange between plasma and air. The tube has got a possibility to feed sheath gas merely to influence the extension of the plasma outside the tube, to control the chemical environment and the temperature of the spray gases.

Such narrow tubes only can be operated if absolutely can be assured that the particles do not contact the inside tube wall. Additional to the powder injector principle for coarse particles [8] there will be required an adjustable flow resistance for the particles during the injection. The tube is not fitted for working up low melting materials.

A characteristic example of the deposit structure that can be reached by the use of coarse

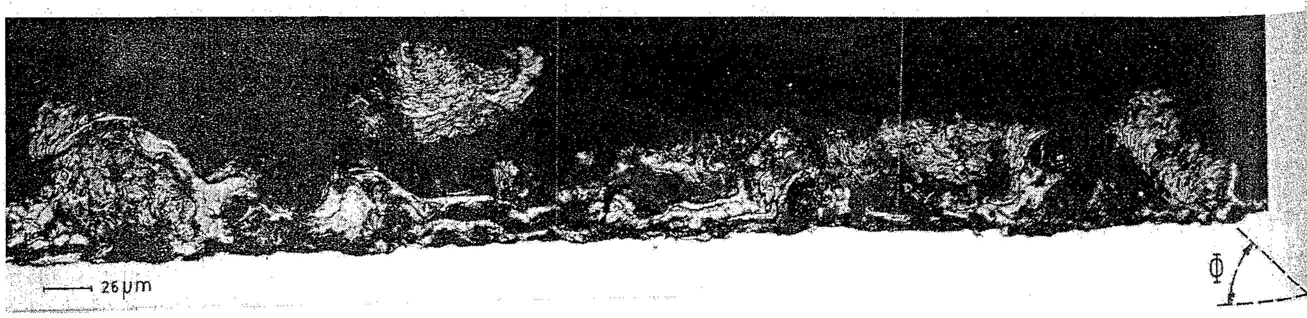


Photo 9: Defective interlayer structure in the border zone of the spray jet.

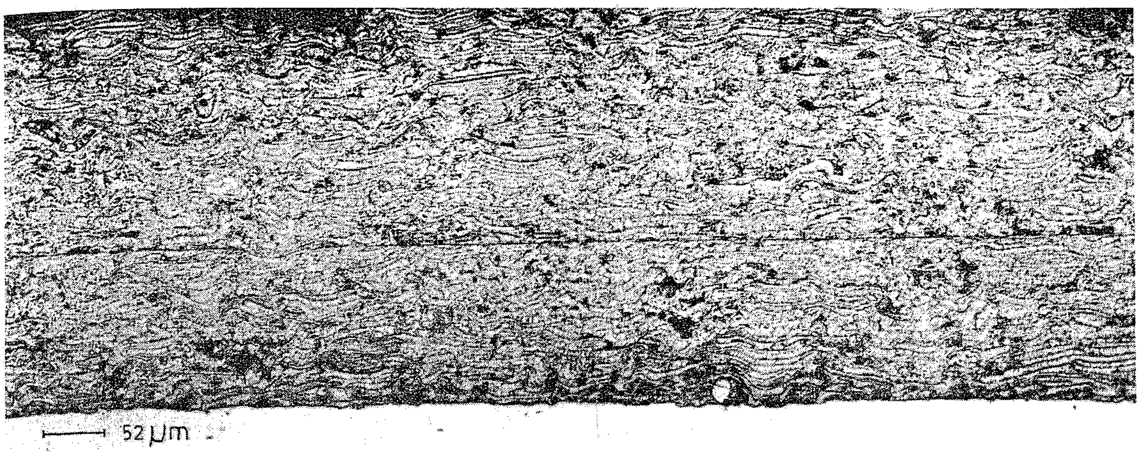


Photo 10: Structure of the interlayer after grinding of the first pass surface.

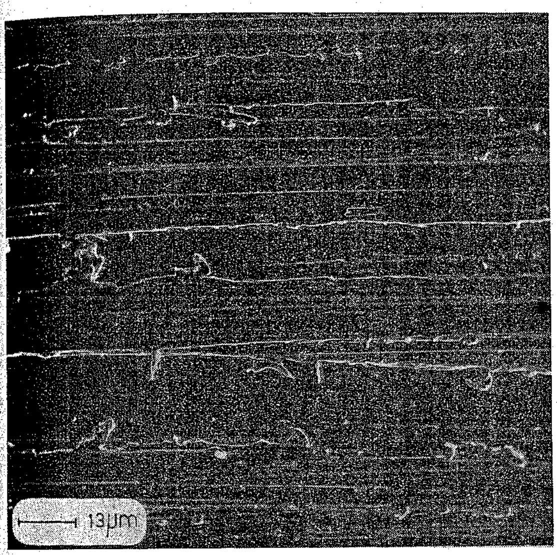


Photo 11: SEM picture of grinded substrate surface before speaying.

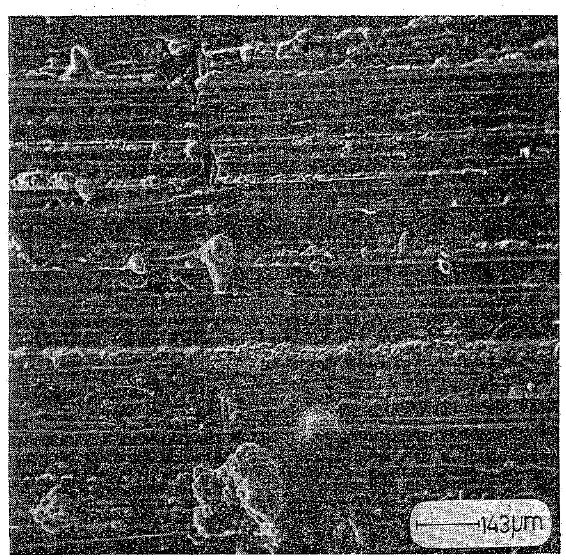


Photo 13: SEM picture of piling up of secondarily adhering particles, detail of photo 12.

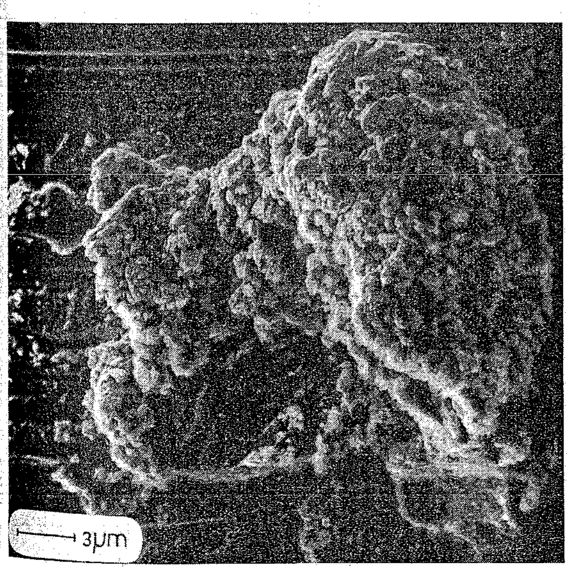


Photo 12: SEM picture of grinded substrate surface after one pass of the torch next to the main deposit.

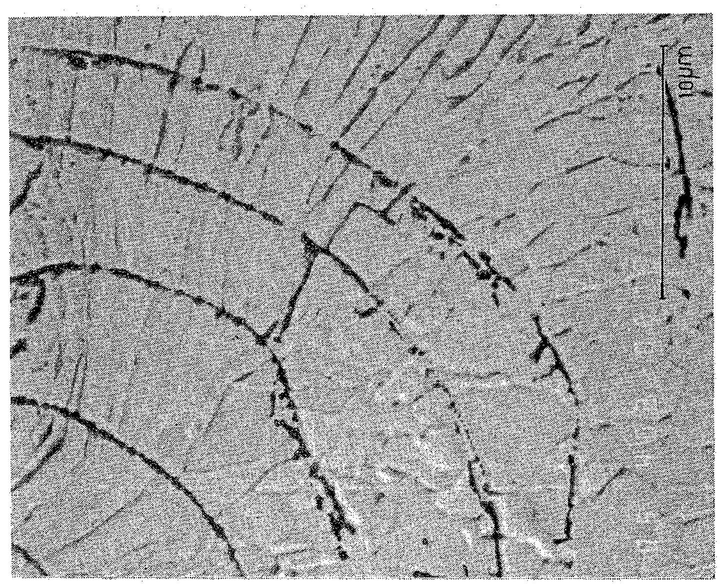


Photo 14: SEM picture of epitaxy in a Mo coating produced with narrow shielding tube and purified Mo of coarse grain size.

purified grains and a narrow shielding tube is given in SEM photograph 14. The coating is Mo, grain size 75-90 µm. The operation conditions of the torch were:
power : 500 A and 44 V over the electrodes
arcgas: 75 Nl/min argon and 16,8 Nl/min hydrogen
nozzle diameter : 8 mm.
free gap between tube and substrate: 15 mm.
The coating has been etched very heavily by Murahami's reagent. Thus, face etching of the columnar cristals took place, making visible that there is epitaxy over several lamellae (up to all thirteen of one pass). The dark grooves between the lamellae are natural effects of heavily etching. The cristal growth is not broken off at the position of these grooves.

5. CONCLUDING REMARKS.

1. The presented wide body shielding tubes offer limited possibilities for operating at low sheath gas consumption and sufficient free distance between tube exhaust plane and substrate. The high shielding gas consumption affects the economical performance. Further development efforts will be directed to the practical application of these devices.
2. Two main phenomena occur when spraying with a narrow particle jet or a shielding tube: vapour deposition and pile up porosity. Both phenomena must be suppressed to make shielding gas devices fit for practice.
3. On a laboratory scale it has been proved that narrow shielding tubes cause a considerable elongation of the plasma, thus offering the possibility for working up coarse grains of high melting point materials. The narrow tube prevents from air contamination without extra sheath gas consumption and a free distance of 15 mm between tube and surface. The operation of this tube type will be object of future research.

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