PHASE FORMATION CONTROL IN PLASMA SPRAYED ALUMINA–CHROMIA COATINGS

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Alumina is an inexpensive material often used as feedstock for plasma spraying. Hard corundum (α-Al_2O_3) is desirable in coatings, but other phases, unstable at elevated temperatures, also form as result of the complexity of the spraying processes. When chromia (Cr_2O_3) is added to Al_2O_3 a complex corundum type α-$(Al,Cr)_2O_3$ phase forms in the deposits. Two types of Al_2O_3/Cr_2O_3 powder feedstock with 2%, 8%, 33% and 50% Cr_2O_3 were sprayed: fused materials and mixtures of Al_2O_3 and Cr_2O_3 powders. Coatings were made by the water-stabilized plasma (WSP®) system and by commercial atmospheric plasma spraying (APS) and compared by various characterization techniques, including X-ray diffraction, scanning electron microscopy and microanalysis. Coatings made from fused feedstock by both spraying methods contain the corundum phase with its fraction increasing with increasing Cr_2O_3 content. In case of mixed feedstock the stabilization effect was observed for WSP® spraying only. Explanation of this finding is offered on basis of differences in the spraying technologies, in particular the spraying temperature.

INTRODUCTION

Plasma spraying is a technology that can be applied in many industrial fields. It can be used for production of various protective coatings on one hand or to manufacture special self-supporting structures of ceramics or composites, difficult to prepare by other techniques, on the other. A principle of this technology has been described in detail many times in the literature. However, the fact that the physical processes occurring during spraying are quite complex has been mentioned in the literature less frequently. Powder injected into the plasma jet undergoes at least two and often more phase transformations, including melting, solidification and solid-state transformations. In addition, plasma itself can stimulate plasma-chemical processes in the injected feedstock. Both, the dynamic loading accompanying impact of the molten droplets onto the substrate, and the cooling rates of the order of 10^6 Ks^{-1}, may affect the final structure and properties. Deposited structures are mostly in non-equilibrium and non-stoichiometric states rather different from the original state and properties of the feedstock.

A typical example is plasma spraying of Al_2O_3. It is well known that the a phase of Al_2O_3 - i.e. corundum - is very stable, exhibits excellent mechanical properties, and it is resistant to many chemicals. However, when corundum powder is used as the feedstock for plasma spraying, the deposited material consists mostly of the metastable γ-Al_2O_3 [1] phase, exhibiting less attractive properties. This is due to the lower nucleation energy of the γ phase, as it has been pointed out by McPherson [2]. To produce α-Al_2O_3 deposits directly, substrate and deposited coatings would have to be kept during spraying above the α-Al_2O_3 nucleation temperature, i.e. about 1700 °C. This method therefore can be hardly used with metallic substrates due to the associated oxidation, but high stress evolution and a loss of adhesion would come out in any case.

Several other techniques how to prepare corundum type deposits were suggested:

a) Deposited coatings are transformed to a by their subsequent annealing above the γ-to-a transformation temperature. This process is technically easier than direct deposition at elevated temperatures but produces similar results (substrate oxidation, etc.).

b) To use unmelted particles of α-Al_2O_3 feedstock in deposits as nuclei for α-Al_2O_3 formation [3] - this is a theoretically elegant suggestion but very complicated to realize. Varying feedstock particle sizes and trajectories in the plasma jet make it very difficult to produce the needed amount of unmelted corundum cores in deposits from injected feedstock particles.

c) To stabilize corundum type phase in deposits by addition of another oxide into feedstock, analogous to the stabilization of zirconia by yttria as described first in the work of Garvie [4].

Papers by. Kuroda et al. [5], Dubský et al. [6] and Chráska et al. [7] reported formation of a corundum-type phase in deposits through alloying the alumina feedstock with chromia (Cr_2O_3). Chromia has been used because it has the same crystal lattice as α-Al_2O_3 and both components exhibit full solubility in the equilibrium state above 1250°C. Below this temperature, however, the solubility is only partial (miscibility gap) and two solid solutions with different compositions and lattice parameters form. Consequently, further results were published [8, 9] to describe various aspects of this stabilization. It has been pointed out that during spraying with the water-stabilized plasma gun (WSP®), a mechanical mixture of the two oxides is sufficient to enhance the fraction of the corundum phase in the deposits. However, Müller and Kreye [10] repeated these experiments with gas-stabilized atmospheric plasma spraying (APS) and observed no stabilization. As suggested by Stahr et al. [11], the cause of this disagreement could be found in the spraying method itself. This paper extends Stahr's suggestion and directly compares results of spraying done by WSP® and by APS. In addition, the experiments were designed to provide further insight into processes involved in formation of various phases in alumina-chromia coatings.

EXPERIMENTAL

Substrate and feedstock

Plain steel strips with dimensions 2.5×25×120 mm were grit-blasted and then used as substrates in all spraying experiments. Pure alumina, alumina with 2 wt.%, 8 wt.%, 33 wt.% and - in a limited extent - 50 % of chromia and finally pure chromia powders were used for spraying. Two types of alumina-chromia feedstock were prepared:

a) fused solid solutions of both oxides crushed into powders of the desired particle size (furthermore called "fused");

b) pure α-alumina and pure chromia powder mechanically mixed to desired composition (furthermore "mixed").

Commercial powders (Industriekeramik Hochrhein, Germany) were used as primary components for the mixtures. In general, for WSP® spraying larger particle size is used - usually 45-90 μm while for APS it is smaller: 20-70 μm. However, in order to determine the influence of powder size on evaporation rates of chromia admixture during interaction with very hot WSP® plasma jet, two additional smaller particle sizes of chromia (5-25 μm, 10-45 μm) were used for preparing the mixed feedstock, labeled A8D, A33D, A8E and A33E in Table 1. All feedstock with compositions, particle sizes, types and used spraying processes are listed in Table 1.

Spraying

WSP® spraying was done at IPP Prague by WSP® PAL 160 unit with the feeding rate around 25 kg h^{-1}. APS coatings were made using Metco 7MB system (H_2/N_2 gas) at the State University of New York, Stony Brook, U.S.A. The average feeding rate was around 1.8 kg h^{-1}.

Table 1. Summary of the experiments.

Feedstock powder	Composition (wt.%)	Particle size (μm)	Powder type	Applied spraying process
A	100 Al_2O_3	45-90	Pure	WSP®
B	100 Al_2O_3	20-70	Pure	APS
C	100 Cr_2O_3	45-90	Pure	WSP®
D	100 Cr_2O_3	10-45	Pure	WSP®
E	100 Cr_2O_3	5-25	Pure	WSP®
F	100 Cr_2O_3	16-53	Pure	APS
G	$98Al_2O_3/2Cr_2O_3$	45-90	Fused	WSP®
H	$92Al_2O_3/8Cr_2O_3$	45-90	Fused	WSP®
I	$67Al_2O_3/33Cr_2O_3$	45-90	Fused	WSP®
A2C	$98Al_2O_3/2Cr_2O_3$		Mixed	WSP®
A8C	$92Al_2O_3/8Cr_2O_3$		Mixed	WSP®
A33C	$67Al_2O_3/33Cr_2O_3$		Mixed	WSP®
B2F	$98Al_2O_3/2Cr_2O_3$		Mixed	APS
B8F	$92Al_2O_3/8Cr_2O_3$		Mixed	APS
B33F	$67Al_2O_3/33Cr_2O_3$		Mixed	APS
B50F	50Al2O3/50Cr2O3		Mixed	APS
A8D	$92Al_2O_3/8Cr_2O_3$		Mixed	WSP®
A33D	$67Al_2O_3/33Cr_2O_3$		Mixed	WSP®
A8E	$92Al_2O_3/8Cr_2O_3$		Mixed	WSP®
A33E	$67Al_2O_3/33Cr_2O_3$		Mixed	WSP®

Note: Label "A2C" denotes mechanical mixture of powder "A" with 2 wt.% of powder "C", and so on.

Besides spraying of coatings additional experiments helping to understand the processes “in-flight” were also done. In these experiments the same feedstock was used as for coatings but instead of impacting on a substrate, the flying droplets were caught in air stream. This technique preserves the state of droplets in flight as so called “free flight particles” (FFP) which are then used for the process characterization.

The DPV 2000 measurement system (TECNAR, St-Bruno, Canada) was employed to monitor and analyze the spraying processes for both, the APS and WSP® systems; the average temperature, average velocity, and average size of particles in flight were evaluated.

Materials characterization

Two main techniques were used for the feedstock, FFPs and coatings characterization:

1) *X-ray diffraction (XRD)*. XRD was used for the phase analysis and was carried out by D 500 diffractometer (Siemens, Germany) with filtered copper radiation over “2θ” range of 30° to 50°. Existing phases were identified using PDF 2 ICDD database. The following integral intensities were selected for calculation of phase fractions: diffraction peaks (104) and (113) for the complex α-$(AlCr)_2O_3$ phase and diffraction peaks (400) and (0012) for the sum of γ- and δ-Al_2O_3 metastable phases. The sum was used because of the full coincidence of the (400) peak for γ- and δ-Al_2O_3 phases, making it difficult to separate both fractions easily - for the purpose of the work the sum is sufficient.
2) *Scanning electron microscopy* (SEM). CamScan 4DV, equipped for chemical microanalysis (XMA) with Link AN1000, was used for visualization and monitoring of the coatings structure, its morphology and chemical analysis. Mostly the Secondary electron (SE) or the Backscattered electron (BSE) modes were used. Since BSE detects contrast between areas with different chemical compositions the heavier Chromium appear brighter than regions rich on Aluminum. XMA was then employed for detailed quantitative studies of the chemical compositions of individual splats at the coatings cross-sections. Samples for SEM/XMA were sputtered by carbon before analysis.

RESULTS

Figure 1 shows typical cross-sections of samples sprayed by WSP® where: 1a) represents structure made of fused feedstock, such as “I” (Table 1) and 1b the structure for mixed feedstock with the same composition (“A33C”). Both structures are shown in BSE modes revealing Cr containing particles. Figure 2 then presents XRD patterns of WSP® coatings made from pure alumina and chromia powders and from fused and mixed feedstock “I” and “A33C” of the same composition.

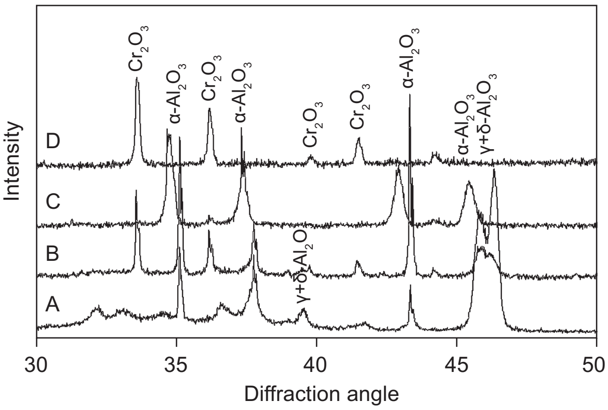
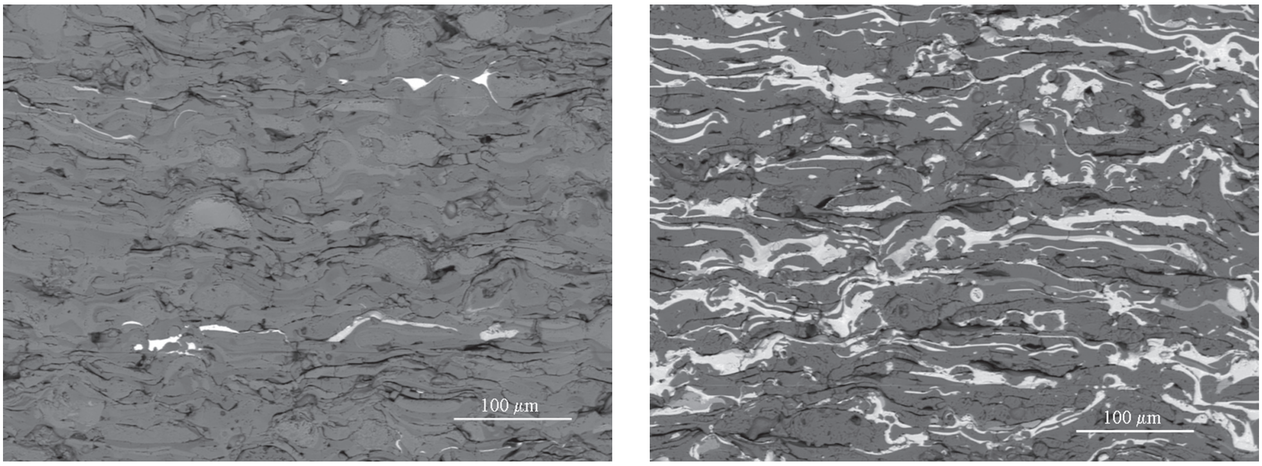


Figure 2. XRD patterns of WSP® coatings made from pure alumina and pure chromia powders and from fused and mixed feedstock of the same composition (the main peaks are labeled).



a) Cross section of WSP® coating prepared from fused feedstock “I” – BSE

b) Cross section of WSP® coating prepared from mixed feedstock “A33C” – BSE

Figure 1. Typical structures of coatings made of the same composition of feedstock.

Figure 3 illustrates the influence of the increasing chromia admixture in feedstock (0 → 33 → 50 wt.%) on XRD patterns of coatings made by APS. Both pictures clearly demonstrate the recorded shifts of positions and shape changes of XRD peaks.

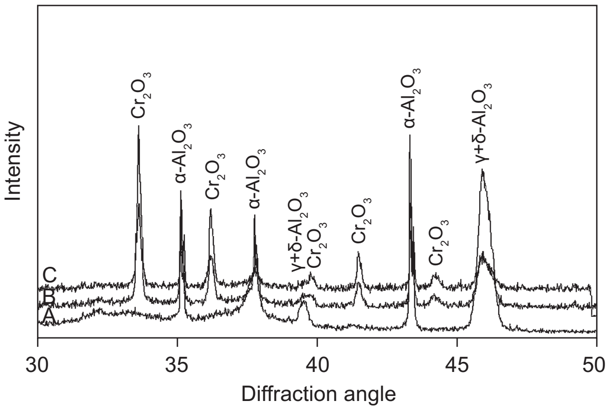


Figure 3. XRD patterns of APS coatings made from pure alumina and mixed feedstock with 33 wt.% and 50 wt.% chromia (the main peaks are labeled).

WSP® spraying

Table 2 summarizes results of the coatings phase composition for various chromia contents and for both, the fused and mixed feedstock. It is evident, that the fraction of the α-phase increases with increasing chromia content. While there is only 11 wt.% of α-Al_2O_3 for pure alumina feedstock, addition of merely 2 wt.% of chromia into feedstock increases α-Al_2O_3 content to 35 % in case of fused feedstock and to about ½ of that amount for mixed one. When 33 wt.% of chromia is added to fused feedstock, the α-phase is fully stabilized but for mixed feedstock amout of α-phase in coatings reaches only 50 %. Besides the a phase, only γ-Al_2O_3 and δ-Al_2O_3 phases were present in coatings from fused powders, while separate chromia was recorded in coatings from mixed feedstock. Detailed XMA analysis shows in coatings a number of splats made of "unreacted" original chromia particles, explaining thus the presence of separate chromia lines in the XRD patterns (white splats on Figure 1b).

Table 2. Phase composition of coatings - WSP® spraying.

Cr_2O_3 (wt.%)	α-Al_2O_3		γ+δ-Al_2O_3		Cr_2O_3	
	fused	mixed	fused	mixed	fused	mixed
0	11	11	89	89	0	0
2	35	16	65	82	0	2
8	32	43	68	52	0	5
33	100	50	0	16	0	33
100	0	0	0	0	100	100

A certain amount of vaporization of chromia powder from the mixed feedstock was registered during WSP® spraying. In order to clarify this fact, additional series of experiments was performed where "standard" size alumina powder was mixed with chromia of different powder size - feedstock "A8D", "A33D", "A8E", "A33E" in Table 1. Figure 4 clearly shows that the smaller the chromia size, the lower the content of chromia in coatings. In order to develop this finding further, mean chromia particle size was measured, approximated by spheres and then the surface-to-volume ratio for each powder was calculated and used to represent the size of the "free surface area" entering into vaporization. Figure 5 then shows the plot of this "surface-to-volume" ratio against the "evaporation ratio (e)", defined as the measured content of chromia in coatings relative to the original content of chromia in the feedstock (e = 1 – (splat Cr_2O_3/feedstock Cr_2O_3)). It is evident that the larger the "free surface area", the higher the extent of vaporization.

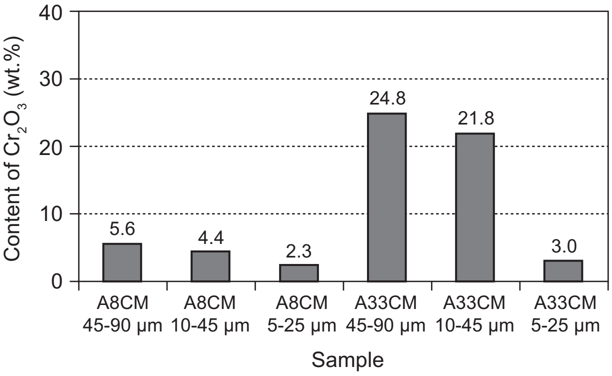


Figure 4. Dependency of the content of chromia in coatings made of mixed feedstock, using the same particle size of alumina and various particle sizes of added chromia powders.

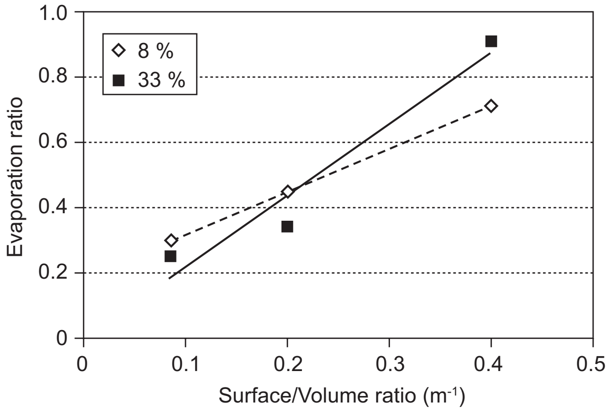


Figure 5. Dependency of chromia evaporation ratio on the surface/volume ratio ("free surface area") of chromia particles in WSP® coatings from mixed feedstock.

APS spraying

For APS spraying only mixed feedstock was used. Since no significant stabilization effect of chromia at conventional APS spraying has been reported in [10], detail analysis of APS spraying with varying parameters was done first, using DPV 2000. Two sets of spraying parameters were then selected:

1) parameters leading to the maximal temperature and velocity of the "in-flight" particles (labeled "medial");
2) parameters modified by changing the H_2/N_2 ratio to decrease the velocity of particles in the jet and thus increasing their dwell time at a higher temperature (labeled HT-LV).

Results are given in Table 3. It is evident that increasing amount of chromia at "medial" spraying mode practically does not change the amount of α phase in coatings while for HT-LV mode it does.

Table 3. Phase composition of coatings - APS spraying of mixed feedstock.

Sample	α-Al_2O_3	$\gamma+\delta$-Al_2O_3	Cr_2O_3
B	16	84	0
B2F	18	79	3
B8F	19	72	9
B33F	16	48	36
B50F	16	33	50
B HT-LV	3	97	0
B33F HT-LV	13	61	25

Diffusion in mixed feedstock

Evidently an important issue for stabilization of α-alumina in deposits from the mixed feedstock would be the ability of a fast diffusion of chromium from chromia into alumina particles during the spraying process to form the complex corundum phase in deposits.

Results of detailed analysis of the chromia content in splats after WSP® and APS spraying of the mechanically mixed feedstock are given in Figure 6. For WSP® spraying "standard" size of alumina powder with 3 different sizes of chromia was measured, for APS only comparison of chromia contents in splats made by spraying of the same mixed feedstock at two different processing parameters was done. In all measurements the amount of chromia was calculated from the chromium content measured by the XMA analysis on cross-sections of deposits, each point representing the average value for at least 25 measurements.

The data for WSP® seems to suggest that more chromia reacts with alumina and enters into splats for the larger admixture (33 %) and smaller particle size of chromia powder. That would agree well with the fact, that smaller particles have a larger "relative free surface area" allowing chromia species to diffuse out. Limited number of measurements for APS spraying seems to indicate, that the higher the dwell time of powder particles at elevated temperature (HT-LV), the slightly higher the chromia content in splats. The longer dwell time probably allows mixing of melted alumina and chromia before their solidification. For comparison purposes FFP from WSP® spraying were also analyzed. In this case, the chromia concentration in alumina was the highest recorded, reaching 2.2 wt.%, probably as result of a relatively longer dwell time for FPP at a high temperature in comparison to deposited particles. However, even for that recorded concentration of chromia in FFP no direct effect on formation of the corundum-like phase was found.

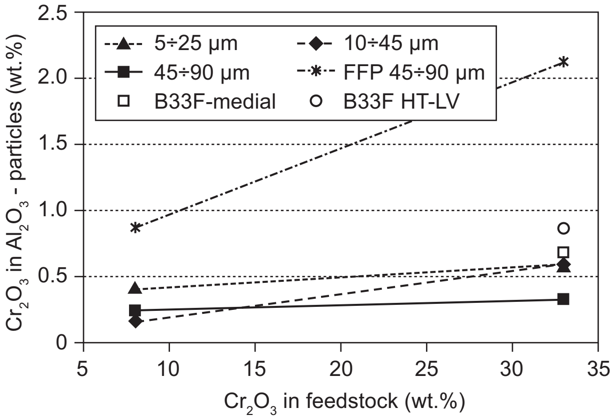


Figure 6. Comparison of Cr_2O_3 content in particles made from mixed feedstock for WSP® spraying using different Cr_2O_3 particle sizes and made by APS spraying of "B33F" feedstock with two different processing set ups.

DISCUSSION

Data presented in this paper are in agreement with other published results regarding formation of the α-type (corundum) phase in plasma-sprayed alumina-chromia coatings. Without doubt, the complex corundum like α-phase [$(Al,Cr)_2O_3$] is formed during WSP® spraying of the fused feedstock. Stabilization of the corundum-type phase takes place also for WSP® spraying of the mixed feedstock - in that case, however, other mechanisms of stabilization must operate because the resulting phase is not the complex one [$(Al,Cr)_2O_3$], but a plain α-alumina. In the case of the APS technology, when for the fused feedstock increased content of the complex α-phase was observed by Stahr [11], no stabilization for the mixed feedstock was found in this work.

The stabilization is attributed to the substitution of Al ions in alumina by Cr. Recent experimental results, ours including, however suggest that there might be other operating mechanisms as well, when diffusion has not been proven and stabilization nevertheless occurred. Clearly some differences - especially between results of WSP® and APS spraying - might be explained by the used technology, as suggested by Stahr et al. [11].

Table 4, taken from Hrabovský et al. [12] and our DPV results (Figure 7) clearly show the main differences between WSP® and APS spraying. The available enthalpy for plasma spraying with the WSP® system is almost an order of magnitude higher than for any APS unit. It is evident that the average particle diameter is substantially larger for WSP®, that the temperature of droplets in flight is in all cases well above the melting point of alumina (2072°C), and that APS droplets have much higher velocities. In addition to these differences it is important to note that the feed rate for WSP® spraying is roughly an order of magnitude higher and the plasma jet affects much larger coated area than for APS. As it can be seen from Figure 7, increasing amount of chromia admixture to alumina practically doesn't affect the recorded values of velocities, temperatures and diameters of particles compared to that of pure alumina.

Taking into account all these facts it is likely that at WSP® spraying, compared to APS, molten particles of fused feedstock impact at a very hot coatings surface with temperature well above the nucleation temperature for α phase, and that, in general, the coating is at a higher temperature for a longer time, thus enabling possible needed redistribution of species and nucleation of the complex α-$(Al,Cr)_2O_3$ phase. A longer dwell time of the deposited coatings at higher temperatures during WSP® spraying also explains formation of δ-Al_2O_3 at the expense of γ-Al_2O_3, since it is well known that δ-phase forms by annealing of γ-phase. On the contrary, γ-Al_2O_3 is predominant in coatings done by the APS process which are less "annealed" by impacting droplets and by the plasma jet itself. Practically no δ-phase has been observed in APS coatings.

Another case is the stabilization recorded for WSP® spraying of mixed feedstock. In general, reported results show that chromia doesn't enter much into reaction with alumina. However, certain vaporization of chromia was demonstrated in the present experiments (Figure 5) and traces of solid solution $(Al,Cr)_2O_3$ were detected in splats. Evaporated Cr evidently diffuses during the flight into alumina and later - during cooling - it can substitute Al ions and the solid solution then forms. Extension of the dwell time at a higher temperature in the jet and use of finer chromia powder increased the amount of chromia at the coatings cross-sections as measured by quantitative microscopy. However, the determined content of chromia in alumina (Figure 6) even for FFPs was still too low to enhance a massive development of α-phase - the limiting value lies somewhere between 3 and 8 wt.% of Cr_2O_3 [6,11]. Therefore, there must evidently operate other mechanism helping to promote formation of the increasing amount of the corundum α phase in coatings. One of them could be possibly the epitaxial growth of the α phase on chromia or other splats having the "right corundum" type crystal lattice. This is, however, a hypothesis requiring additional experiments, including transmission electron microscopy of the cross-section through the interface between two splats. Another mechanism could stem out of the fact, that molten chromia has a higher melting point than alumina (2435 against 2072ºC) and that there is a substantial volume difference of several percent between α and γ (δ) phases of alumina. Combination of these facts could lead to a severe stress condition during crystallization supporting nucleation of "smaller" α-alumina. Again, additional experiments are needed.

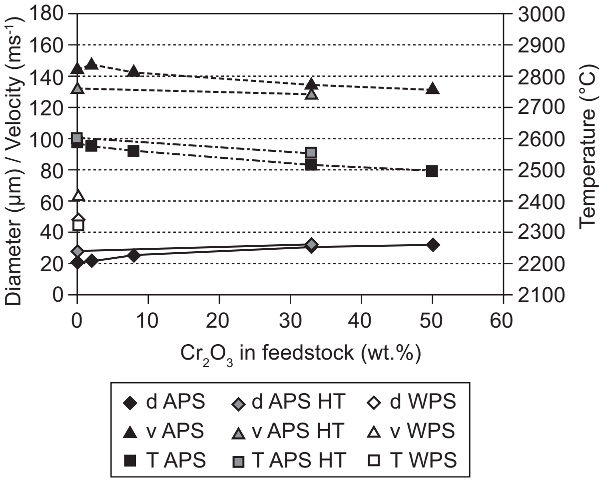


Figure 7. Dependency of the particle diameter, velocity, and temperature on Cr_2O_3 concentration in mixed feedstock sprayed by APS and by WSP® as measured by DPV 2000.

Table 4. Properties of different plasma systems (from Hrabovsky [12]).

Plasma medium	Arc current (A)	Arc power (kW)	Mass flow rate (g/s)	G/L (kg/sm)	Mean enthalpy (MJ/kg)	Mean temperature (K)
Ar/H_2 (65/3 slpm)	750	44	1.93	0.15	13.5	12100
Ar/H_2 (33/10 slpm)	500	25	0.98	0.08	15.3	10800
N_2/H_2 (235/94 slpm)	500	200	5.0	0.1	24	6200
Water	300	54	0.20	0.004	157	13750
Water	600	133	0.33	0.006	272	16200

CONCLUSIONS

The presence of chromia definitely facilitates formation of the α phase in plasma-sprayed alumina coatings. When the fused feedstock is used then the complex α-$(Al,Cr)_2O_3$ phase will form, regardless of the plasma system used. When the feedstock is made of a mechanical mixture of powders, only WSP® spraying will bring in increased formation of the corundum α phase in coatings - APS technology will not yield the needed results. There is clear evidence that during plasma spraying of mechanical mixtures of alumina and chromia, the chromia particles vaporize, some escape and some enrich the molten alumina droplets. However, the extent of this enrichment is insufficient to induce nucleation of the α phase in coatings. Since chromia doesn't enter into reaction with alumina, other mechanisms of stabilization besides ions substitution likely take place. Epitaxial growth of α-alumina has been suggested as one possible.

WSP® sprayed particles impact on the still hot splats surface well above the nucleation temperature of the α phase and the coatings stay longer at a higher temperature in general. That is probably the reason why WSP® spraying of alumina-chromia feedstock results in formation of the corundum type phase and why formation of this phase was not observed at APS spraying.

Practically no δ-phase has been observed in APS coatings where γ-Al_2O_3 is predominant. Coatings by the APS process are less "annealed" by impacting droplets and by the plasma jet than coatings by WSP®, where besides α-type phase also both, γ- and δ-phase has been found.

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