



Dependence of the Stabilization of α -Alumina on the Spray Process

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A phase change from α -alumina (corundum) in the feedstock powder to predominantly other alumina phases, such as γ -alumina in the coating normally takes place, as a result of the spray process. It is expected that the prevention of this phase transformation will significantly improve the mechanical, electrical, and other properties of thermally sprayed alumina coatings. The results regarding the possibility of stabilization of α -alumina through addition of chromia published in the literature are ambiguous. In this work, stabilization using different spray processes (water-stabilized plasma (WSP), gas-stabilized plasma (APS), and high-velocity oxy-fuel spray (HVOF)) was studied. Mechanical mixtures of alumina and chromia were used, as were prealloyed powders consisting of solid solutions. The investigations focused on mechanical mixtures with both APS and WSP and on prealloyed powders with WSP. The coatings were studied by x-ray diffraction, including Rietveld analysis, and analysis of the lattice parameters. Microstructures were investigated by optical microscopy using metallographic cross-sections. It was shown that in the case of the mechanically mixed powders, the stabilization predominantly depends on the applied spray process. The stabilization of the α phase by use of the WSP process starting from mechanical mixtures was confirmed. It appears that stabilization exhibits a complex dependence on the spray process, the process parameters (in particular the thermal history), the nature of the powder (mechanically mixed or prealloyed), and the chromia content.

Keywords α -Al₂O₃ stabilization, alumina, chromia, solid solution, X-ray diffraction

1. Introduction

A phase change from α -alumina (corundum) in the feedstock powder to predominantly other alumina phases, such as γ -alumina in the coating takes place, as a result of the spray process. These phases are metastable and have different properties that are normally not desired. This is a well-known, but often neglected fact in the preparation and use of alumina coatings and is of special interest, because the high usage properties of thermally sprayed

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alumina coatings are generally derived from sintered alumina ceramics consisting of corundum. It is expected that the prevention of this phase transformation will significantly improve the mechanical, electrical, and other properties of thermally sprayed alumina coatings.

The effect of formation of metastable phases was first described in the literature by Ault (Ref 1). Detailed and important investigations of the mechanism of these transformations were made by McPherson (Ref 2, 3). More recent work related to materials behavior in the inductively coupled plasma (ICP) was performed by Dzur (Ref 4, 5). In most of the published works, the γ phase is described as the predominant phase in the coatings. This is usually explained, with reference being given to the work of McPherson, through the lower nucleation energy needed for the γ phase, when the molten particles are rapidly quenched. According to Heintze and Uematsu (Ref 6) and the literature cited in this article, the structure of the so-called γ phase in the coatings differs from the γ phase derived from calcination of aluminum hydroxides. The remaining α phase content is explained most often by the appearance of unmolten particles, e.g., by Kreye (Ref 7). However, McPherson (Ref 3, 8) gave a more detailed explanation, describing the total content of the α phase in the coatings by the presence of α -Al₂O₃ nuclei introduced into the coating by incompletely fused particles.

As the newly formed phases are not stable, a heat treatment transforms them either partially or fully into the α phase (Ref 6, 9). In the experimental work of Lima et al. (Ref 9), a flame-spray process with acetylene as a fuel gas was used for specimen preparation. In this work, the complete back-transformation into the α phase occurred

between 1200 °C and 1300 °C. Therefore, a heat-treatment is not adequate for most of the technical purposes when metallic substrates are used.

Several studies have made attempts to increase the α phase content by realizing specific predetermined thermal histories for the spray-powder particles, e.g., by applying special spray processes, and the coating cooling process (Ref 5-7). In his work, Kreye (Ref 7) found a higher content of α phase for high-frequency (HF) plasma-sprayed coatings than for DC plasma- and HVOF-sprayed ones. This was described to be related to the higher substrate temperature and the larger particles used. Using the ICP spray process (similar to that used by Kreye (Ref 7)), Dzur (Ref 5) detected only α -alumina in the ICP-sprayed coatings due to defined process parameters and a low cooling rate.

Comparison of gas-stabilized plasma (APS), high-power plasma spray (HPPS), and detonation gun spray (DGS) showed minor differences in phase composition (Ref 10). The HPPS process resulted in coatings with the highest α phase content, and DGS led to coatings containing only traces of corundum.

In order to avoid the phase transformation of Al_2O_3 , as a result of the spray process, mixing or alloying with different materials can be employed. Studies with Cr_2O_3 , Fe_2O_3 , and TiO_2 additions (Ref 7, 11-12) have been published. Ilavsky et al. (Ref 13) pointed out that TiO_2 additions lead to a decrease in the formation temperature of the α phase. However, as quoted in many studies, TiO_2 additions improve the mechanical and tribological properties of Al_2O_3 coatings, but do not stabilize the desired α phase. Venkataraman et al. (Ref 14) claim stabilization of the α phase in plasma-sprayed Al_2O_3 -13 mol% TiO_2 , but not in pure Al_2O_3 . However, as also mentioned by the authors (Ref 14), the change in phase composition might be due to other reasons, such as different spray parameters.

Corundum and the isostructural eskolaite (Cr_2O_3) form solid solutions that can be designated as $(\text{Al,Cr})_2\text{O}_3$. The formation of a solid solution between α - Al_2O_3 and Cr_2O_3 is possible for a broad range of concentrations (Ref 15, 16). At high temperatures, both are fully dissolved in each other. The linear dependence of the lattice parameters on the composition is reported by Rossi and Lawrence (Ref 17), and by Watanabe et al. for a heat-treatment temperature of 1400 °C (Ref 18). As reported by Sitte (Ref 19), below 1250 °C, a miscibility gap exists from 30% to nearly 100% Al_2O_3 (see Fig. 1). The decomposition depends on diffusion kinetics and, therefore, occurs only above 1000 °C.

Figures 2 and 3 show the two basic strategies of α phase stabilization by Cr_2O_3 . Either the feedstock powder is a mechanical mixture of separated particles of Cr_2O_3 and Al_2O_3 (Fig. 2) or the feedstock powder consists of homogeneous solid solution particles (Fig. 3). The solid solution is formed by a heat treatment before or during feedstock-powder preparation.

In the literature, contradictory results on the increase in the α phase content are given for use of both mechanically mixed and prealloyed solid-solution particles. Earlier studies performed at IPP in Prague (Ref 21, 22)

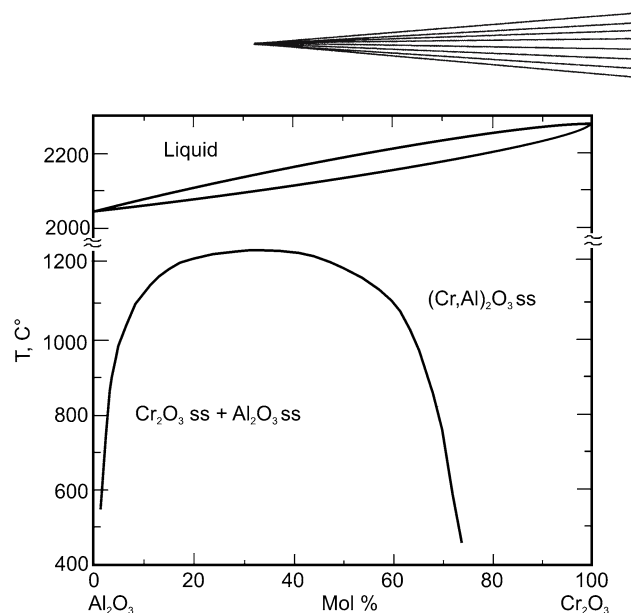


Fig. 1 Al_2O_3 - Cr_2O_3 phase diagram with miscibility gap (Ref 19, 20)

described a significant stabilization of the α phase. According to Ilavsky et al. (Ref 13), Cr_2O_3 additions lead to an increase in the formation temperature of the α phase. With the addition of more than 20 mass% of Cr_2O_3 and the use of water-stabilized plasma (WSP), only the α phase is detected (Ref 21). Verification of stabilization for various contents of Cr_2O_3 was done by Dubsy et al. (Ref 22) using the WSP process with mechanically mixed powders and with prealloyed solid-solution powders. A significant increase in the α phase content was reported with 8 mass% Cr_2O_3 . A further increase, but not complete stabilization, occurred with 33 mass% Cr_2O_3 . Prealloyed and mixed powders were described as exhibiting insignificant differences in terms of stabilization of the α phase for a lower Cr_2O_3 content. This effect was explained by the sufficient time and temperature for mass transfer to occur in the spray process (Ref 21, 23). It is supposed that the mass transport is realized by partial evaporation (Ref 22).

Contrary to this, other authors (Ref 7, 24) reported insufficient stabilization of the α phase with powders containing up to 20 mass% Cr_2O_3 and, therefore, no improvement in the results for coating properties. Voyer et al. (Ref 25) and Marple et al. (Ref 26) reported a small remaining γ phase content with use of a prealloyed powder with a spherical shape and containing 20 mol% Cr_2O_3 (corresponding to about 27 mass%). A reason for the contradictory results described in the literature might be the differences in particle behavior in the different spray processes. The spray processes applied range from high-velocity oxy-fuel spray (HVOF), APS, and HF plasma by Müller and Kreye (Ref 24) and Kreye (Ref 7), WSP by Chraska et al. and Dubsy et al. (Ref 13, 21), and high-power plasma by Voyer et al. (Ref 25) and Marple et al. (Ref 26). The spray processes used differ particularly in enthalpy, particle velocity, powder feed rate, and residence time of the particles in the flame or the torch as well as in the composition of the flame or torch-forming gas.

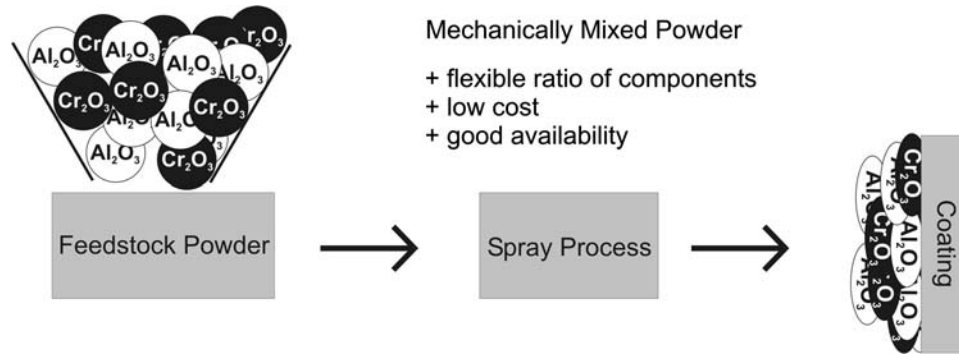


Fig. 2 Schematic drawing illustrating the preparation of coatings from mechanically mixed powders

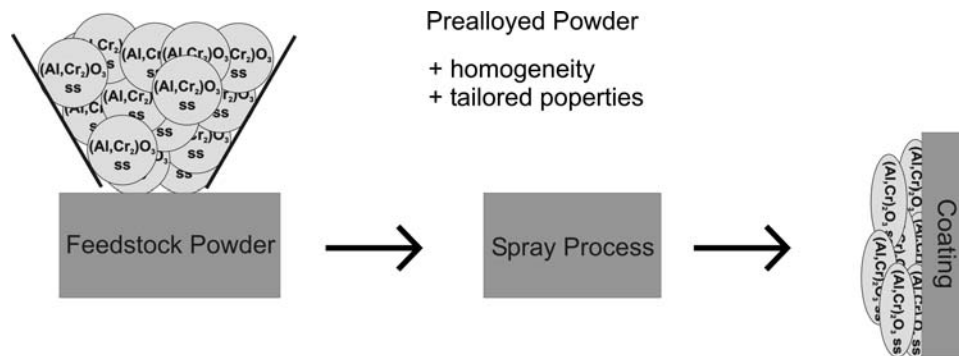


Fig. 3 Schematic drawing illustrating the preparation of coatings from prealloyed powders

The aim of this article was to investigate whether or not the stabilization of the α phase of Al_2O_3 by Cr_2O_3 is dependent on the characteristics of the spray process (WSP, APS, and HVOF). In order to clarify the ambiguous statements in the literature, mechanical mixtures of alumina and chromia, as well as prealloyed powders consisting of solid solutions were used. The investigations focused on mechanical mixtures with both APS and WSP and on prealloyed powders with WSP. All powder compositions used in this work were on the alumina-rich side of the Al_2O_3 - Cr_2O_3 binary system. Other current developments are focused on the chromia-rich side and mainly aim to avoid hexavalent chromium in the spray process, while keeping the desired properties of the chromia coatings (Ref 27, 28).

2. Experimental Procedure

Mild steel substrates (100 mm \times 60 mm \times 5 mm) were used for coating preparation. As usual, they were degreased and grit-blasted with corundum before being sprayed. Some of the samples were coated using the WSP plasma spray process (PAL 160 equipment) at the Institute of Plasma Physics of the Academy of Sciences in Prague, Czech Republic. All other samples were prepared at the Fraunhofer Institute for Material and Beam Technology in Dresden, Germany. APS coatings were sprayed

with an F6 Gun (GTV mbH, Luckenbach, Germany) and HVOF coatings were sprayed with the TopGun system (GTV mbH, Luckenbach, Germany) using ethene as a fuel. The main spray parameters are compiled in Table 1. Coating thicknesses varied from 200 to 350 μm .

Table 2 gives an overview of the powders used, including their phase compositions. Here, and in the following, the composition is given in mass% for all powders. Besides pure alumina, mechanical mixtures of Al_2O_3 and Cr_2O_3 and prealloyed $(\text{Al,Cr})_2\text{O}_3$ solid solution powders were used. The mechanical mixtures were prepared from fused and crushed pure alumina and chromia particles. The prealloyed powders were prepared by, simultaneously, melting of alumina and chromia in the desired ratio and subsequent crushing. The powder particle size was varied in dependence on the spray process. For coatings prepared by WSP, both mechanically mixed and prealloyed powders were used. With the exception of the coatings containing only Al_2O_3 , all APS coatings were prepared from mechanically mixed powders and the HVOF coating from a prealloyed powder. The choice of powder compositions mainly depended on their commercial availability. In addition, the use of prealloyed powders was limited by the availability of the required particle size fractions for the different processes. All alumina powders contained only α - Al_2O_3 , whereas the mechanical mixtures contained α - Al_2O_3 and Cr_2O_3 . For prealloyed powders with 2% Cr_2O_3 , the only peaks detected in the pattern

were those of corundum. The powder prepared with 8% Cr₂O₃ contained α -Al₂O₃ and the solid solution (Al,Cr)₂O₃. The prealloyed powder with 33% Cr₂O₃ consisted of the solid solution only.

CuK α radiation was used for determining the phase composition of the powders and coatings by x-ray diffraction (D8 Advance, Bruker AXS). The diffraction pattern was measured in the range of 2 θ from 15° to 90° with steps of 0.05°. The patterns given below in this article display only the ranges in which the strongest peaks occurred. In Table 3, the JCPDS standard cards used for identification of the phases are compiled. The lattice parameters were determined from the shifted peak positions and compared with the Al₂O₃ and Cr₂O₃ standards.

Table 1 Main spray parameters

<i>HVOF TopGun, GTV mbH</i>	
C ₂ H ₄ /O ₂ , slpm	90/240
Spray distance, mm	200
<i>APS, GTV mbH</i>	
Ar/H ₂ , slpm	35/13
Power, kW	55
Spray distance, mm	115
<i>WSP PAL 160</i>	
Power, kW	146
Spray distance, mm	350

Table 2 Spray powders and processes used for preparing the coatings investigated in this study

Composition in mass%	Identified phases	Particle size, μ m	Powder type	Spray process
Al ₂ O ₃	α -Al ₂ O ₃	-22 + 5	pure	HVOF
Al ₂ O ₃	α -Al ₂ O ₃	-40 + 10	pure	APS
Al ₂ O ₃	α -Al ₂ O ₃	-60 + 45	pure	WSP
Al ₂ O ₃ -2Cr ₂ O ₃	α -Al ₂ O ₃	-22 + 5	prealloyed	HVOF
Al ₂ O ₃ -2Cr ₂ O ₃	α -Al ₂ O ₃ , Cr ₂ O ₃ (eskolaite)	-90 + 45	mixed	WSP
Al ₂ O ₃ -2Cr ₂ O ₃	α -Al ₂ O ₃	-90 + 45	prealloyed	WSP
Al ₂ O ₃ -3Cr ₂ O ₃	α -Al ₂ O ₃ , Cr ₂ O ₃ (eskolaite)	-40 + 10	mixed	APS
Al ₂ O ₃ -8Cr ₂ O ₃	α -Al ₂ O ₃ , Cr ₂ O ₃ (eskolaite)	-40 + 10	mixed	APS
Al ₂ O ₃ -8Cr ₂ O ₃	α -Al ₂ O ₃ , Cr ₂ O ₃ (eskolaite)	-90 + 45	mixed	WSP
Al ₂ O ₃ -8Cr ₂ O ₃	α -Al ₂ O ₃ , (Al,Cr) ₂ O ₃	-90 + 45	prealloyed	WSP
Al ₂ O ₃ -30Cr ₂ O ₃	α -Al ₂ O ₃ , Cr ₂ O ₃ (eskolaite)	-40 + 10	mixed	APS
Al ₂ O ₃ -33Cr ₂ O ₃	α -Al ₂ O ₃ , Cr ₂ O ₃ (eskolaite)	-90 + 45	mixed	WSP
Al ₂ O ₃ -33Cr ₂ O ₃	(Al,Cr) ₂ O ₃	-90 + 45	prealloyed	WSP

Table 3 JCPDS standard cards used for phase identification

Crystal phase	JCPDS standard card
α -Al ₂ O ₃ (corundum)	46-1212
γ -Al ₂ O ₃	10-0425
δ -Al ₂ O ₃	16-0394
Cr ₂ O ₃ (eskolaite)	38-1479
Cr	6-694
(Cr _{0.1} ,Al _{0.9}) ₂ O ₃	51-1394

More detailed information about the quantitative phase content and phase composition can be found using Rietveld analysis (REFINE++, Seifert FPM), which was performed for the WSP-sprayed samples. For these studies, the coatings were removed mechanically from the substrate, milled, and mixed with Si as an internal standard. The diffraction patterns were measured using an XRD 7 (Seifert FPM) and CuK α radiation with 2 θ ranging from 10° to 90° (step size: 0.05°). Because the data for the transition alumina phases did not fit well enough to enable determination of the phase content, only α -Al₂O₃ and Cr₂O₃ were quantified separately. The balance is the content of transition oxide phases such as γ -Al₂O₃ and δ -Al₂O₃. In some samples, metallic Cr in small quantities was able to be quantified separately.

The coating microstructures were investigated by optical microscopy using metallographic cross-sections.

3. Results

Figure 4 shows the diffraction patterns of the coatings sprayed from pure alumina; the δ , γ , and α phases of Al₂O₃ were found in the WSP coating. The main phase is the δ phase. No significant differences between the patterns of the APS and HVOF coatings were detected. Both contained mainly the γ phase, with the α phase only occurring as a secondary phase. The α phase content was somewhat higher in the HVOF coating than in the APS coating.

Figures 5-8 present the diffraction patterns for the mechanically mixed and prealloyed powders with increasing chromia content in the different spray processes.

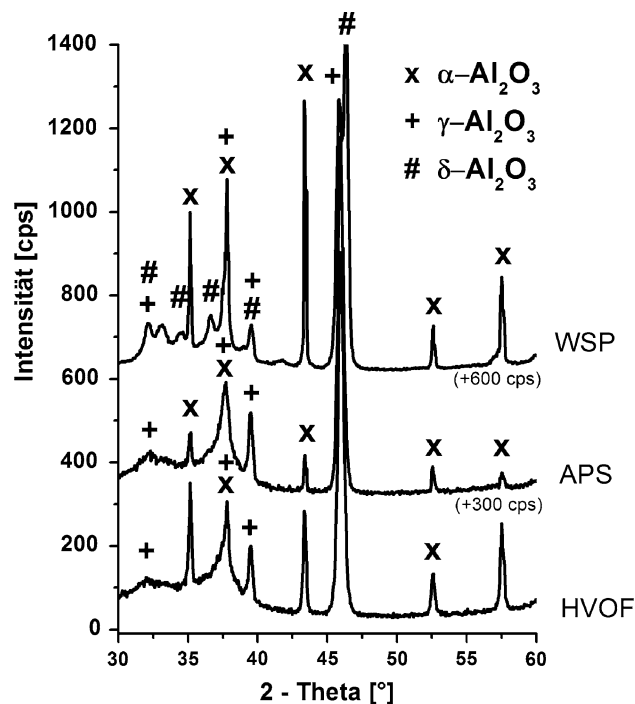


Fig. 4 Diffraction pattern of pure Al₂O₃ coatings

By alloying Al_2O_3 with 2% Cr_2O_3 , the WSP process produced a coating in which $\alpha\text{-Al}_2\text{O}_3$ is the main phase (Fig. 5). The peak intensities of the γ and δ phases were lower than in the coating produced from pure Al_2O_3 (see Fig. 4). In the coating prepared from the mechanical $\text{Al}_2\text{O}_3\text{-2% Cr}_2\text{O}_3$ mixture, no stabilization was detected (Fig. 6). The relative peak intensities were comparable to that of pure Al_2O_3 coatings. Regarding the APS coating produced from the $\text{Al}_2\text{O}_3\text{-3% Cr}_2\text{O}_3$ mixture (Fig. 7), nearly no differences compared with the pure Al_2O_3 coating were detected. Only additional peaks of eskolaite (Cr_2O_3) were detected. The diffraction pattern of the HVOF coating (Fig. 8) prepared from the prealloyed powder containing 2% chromia did not show a measurable increase in the α phase content.

When the Cr_2O_3 content was increased to 8%, the diffraction pattern for the prealloyed WSP coating (Fig. 5) showed a stabilization of the α phase. For the corresponding coating obtained from mechanically mixed powders, a significant increase in the α phase content was also detected. Contrary to the prealloyed powder, this powder exhibited additional eskolaite peaks (Fig. 6). The α phase content was significantly lower in the APS coating than in the WSP coating. For the coating sprayed from the mechanical mixture of Al_2O_3 with 8% Cr_2O_3 by APS, the γ phase was still predominant (Fig. 7).

The coating prepared from the prealloyed powder with a Cr_2O_3 content of 33% by WSP only showed an

$(\text{Al,Cr})_2\text{O}_3$ solid solution in the pattern measured on the surface of the as-sprayed coating (Fig. 5). Contrary to this, the diffraction pattern for the corresponding coating sprayed from the mechanically mixed powder (Fig. 6) showed the predominant peaks of the α phase, eskolaite, and some γ phase. The peaks of the solid solution were not detected. The most intense peaks of the APS coating containing 30% Cr_2O_3 were those of eskolaite (Fig. 7). The α phase and γ phase contents were significantly lower here than in the coatings with 8% Cr_2O_3 .

Figure 9 shows the quantitative phase content of the α -alumina phase. It is clearly shown that the α phase content increases with increasing chromia content. Using prealloyed powders instead of mixed powders always results in a higher amount of α phase in the coating. Since Rietveld analysis was performed with powdered coating materials and therefore from the whole coating volume, the α phase content of about 80 mass% was not contradictory to the measurement obtained on the coating surface (Fig. 5), where only the solid solution was detected.

Details of the changes in the lattice parameters are given in Table 4. The values for parameter a of the crystal lattice are presented in Fig. 10. The data show strong differences between the prealloyed and the mixed powders. While the lattice parameter for the coatings derived from prealloyed powders followed the Vegard's law (linear dependence on the composition), the lattice parameter

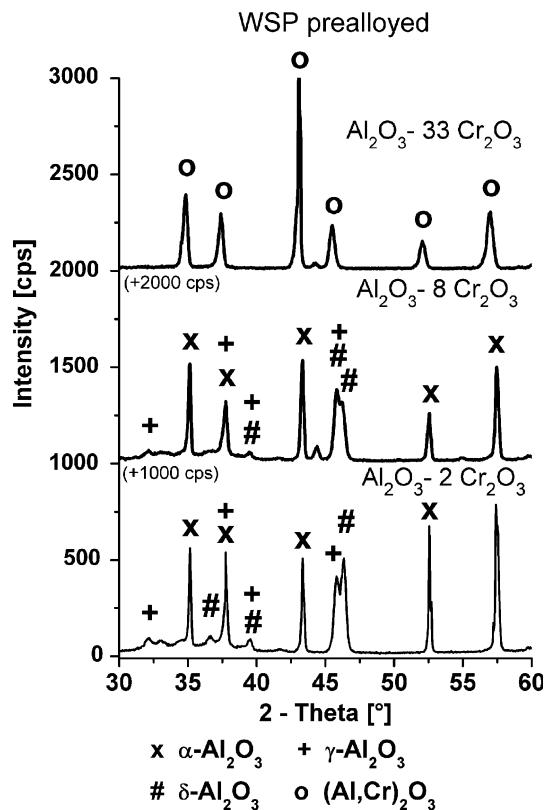


Fig. 5 Diffraction patterns of the WSP coatings prepared with prealloyed spray powders

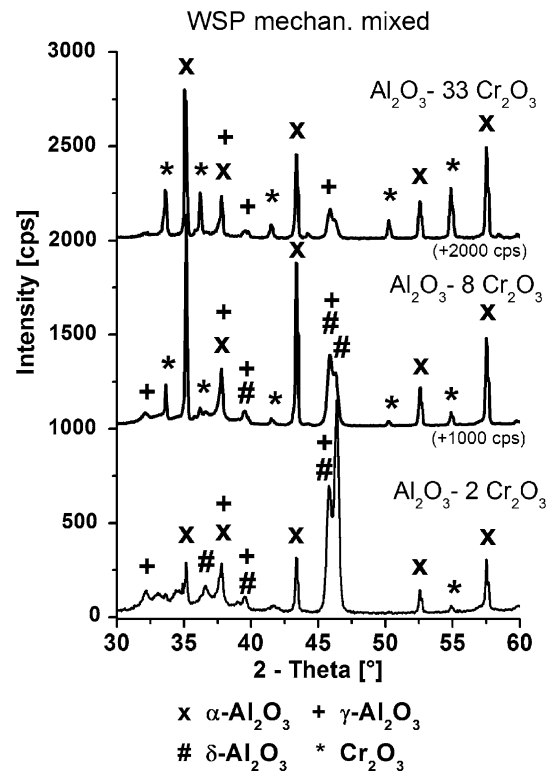


Fig. 6 Diffraction patterns of the WSP coatings prepared from mechanically mixed spray powders

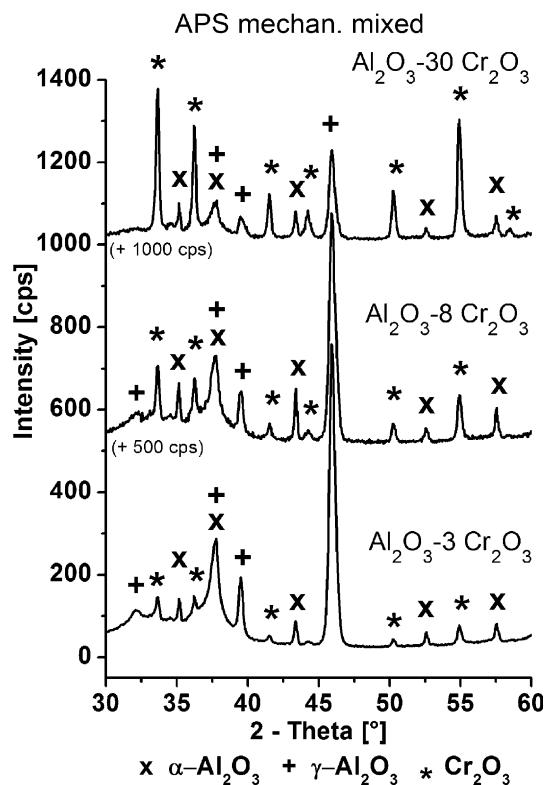


Fig. 7 Diffraction patterns of the APS coatings

of Cr_2O_3 and Al_2O_3 in the coatings derived from mechanically mixed powders did not change. This indicates that during the spray process the time was not sufficient for a solid solution to be formed from the mechanically mixed powders.

As examples of coating microstructures, Fig. 11 and 12 show the optical micrographs of Al_2O_3 -33% Cr_2O_3 coating crosssections sprayed by WSP from mechanically mixed and solid-solution powders, respectively. Coatings from mechanically mixed powders showed a more inhomogeneous structure with at least partial separation of Al_2O_3 and Cr_2O_3 .

4. Discussion

The investigations on pure Al_2O_3 coatings show the expected results. In all spray processes, corundum transforms in significant amounts to other modifications of Al_2O_3 but is detected in all coatings as a minor phase. While the APS and HVOF coatings are mixtures of the two phases $\alpha\text{-Al}_2\text{O}_3$ and $\gamma\text{-Al}_2\text{O}_3$, the WSP coating exhibits significant amounts of $\delta\text{-Al}_2\text{O}_3$. According to Damani et al. (Ref 29), the formation of $\delta\text{-Al}_2\text{O}_3$ in a WSP process occurs with a low-splat cooling rate. Attempts to increase the content of $\alpha\text{-Al}_2\text{O}_3$ in the coatings in APS by special technological measures, as performed by Heintze et al. (Ref 6), lead to a significant decrease in the effectiveness of the spray process. The presumption of

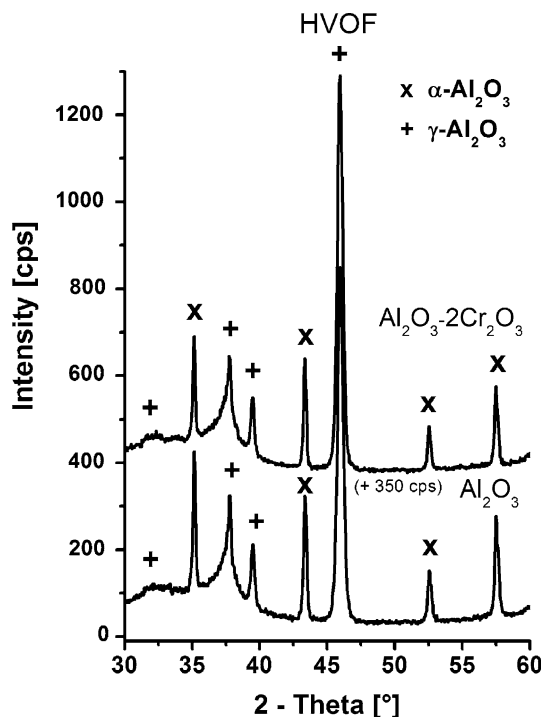


Fig. 8 Diffraction patterns of the HVOF coatings

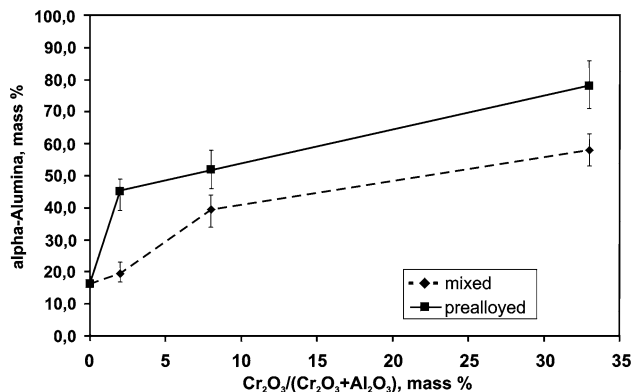


Fig. 9 Content of α alumina in WSP-sprayed $\text{Al}_2\text{O}_3/\text{Cr}_2\text{O}_3$ coatings

many authors that the remaining α phase belongs to imperfectly molten particles was not studied further. The experiments of Dzur (Ref 5) show that using ICP, $\alpha\text{-Al}_2\text{O}_3$ presumably could also be produced in the coating with full melting of the material.

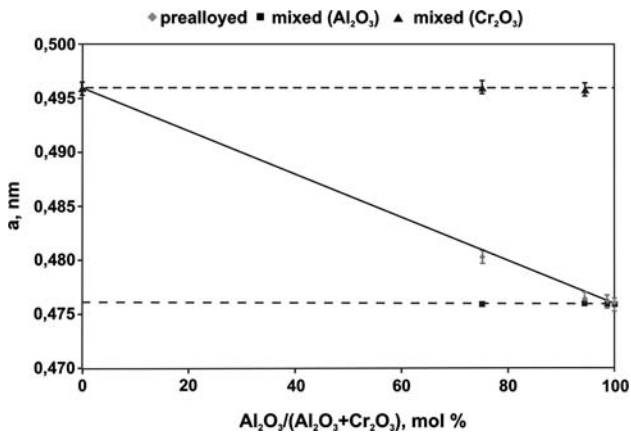
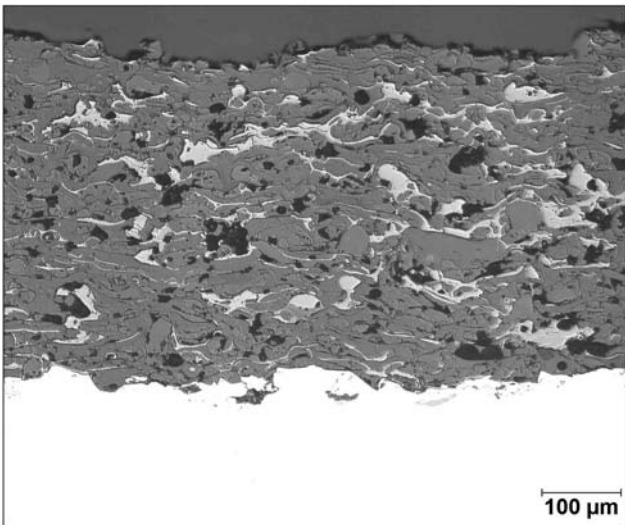
Small amounts of Cr_2O_3 (up to 3%) result in changes in the phase composition that are barely detectable by x-ray diffraction. This small amount does not seem to be sufficient to prevent the phase transformation significantly. Partial stabilization of the α phase is only detected for the WSP coatings prepared with prealloyed powders.

With a further increase in the Cr_2O_3 content, changes are clearly visible in the diffraction patterns. However, there are differences between the spray processes and the

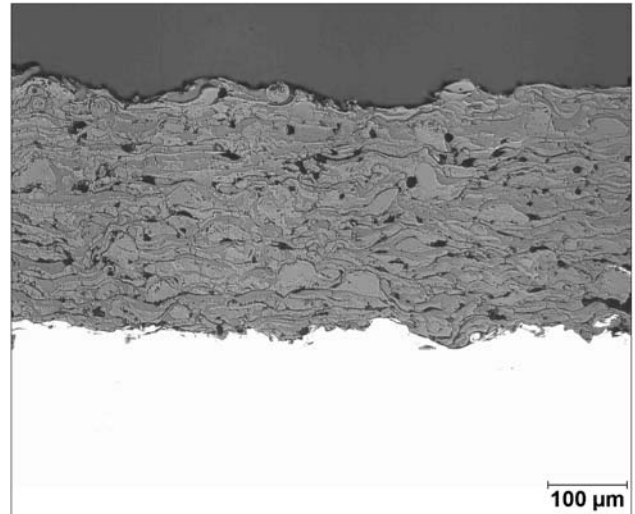
Table 4 Lattice parameters as a function of the ratio $\text{Al}_2\text{O}_3/\text{Cr}_2\text{O}_3$ and the type of starting material

$\text{Al}_2\text{O}_3/\text{Cr}_2\text{O}_3$ ratio, mass%	Starting material	$\alpha\text{-Al}_2\text{O}_3$		Cr_2O_3	
		a, nm	c, nm	a, nm	c, nm
100/0	pure	0.4760(4), 0.4759 (a)	1.2992(3), 1.2993 (a)
98/2	prealloyed	0.4762(4)	1.2997(4)
98/2	mixed	0.4760(7)	1.2990(4)
92/8	prealloyed	0.4764(4)	1.3011(3)
92/8	mixed	0.4759(4)	1.2993(4)	0.4958(18)	1.3592(76)
67/33	prealloyed	0.4803(4)	1.3110(2)
67/33	mixed	0.4759(2)	1.2995(3)	0.4960(4)	1.3587(17)
0/100	pure	0.4960(3), 0.4959 (a)	1.3588(07), 1.3594 (a)

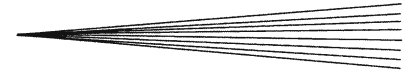
(a) indicates the values of the JCPDS standard

**Fig. 10** Change in the lattice parameter *a* of $\alpha\text{-Al}_2\text{O}_3$ and Cr_2O_3 in coatings derived from mixed and prealloyed powders**Fig. 11** Crosssection of WSP-sprayed Al_2O_3 -33% Cr_2O_3 coating prepared with the mechanically mixed powder

powder types used. Coatings produced by WSP from prealloyed powders show an increasing α phase content with increasing Cr_2O_3 content. Use of 33% Cr_2O_3 solely results in detection of the solid solution $(\text{Al,Cr})_2\text{O}_3$. Peaks of Cr_2O_3 are not detected. The values of the lattice

**Fig. 12** Crosssection of WSP-sprayed Al_2O_3 -33% Cr_2O_3 coating prepared with prealloyed solid solution powder

parameters and their linear dependence on the composition of the coatings derived from prealloyed powders are in good agreement with the results of Rossi and Lawrence (Ref 17) and those of Watanabe et al. (Ref 18). This is also in agreement with the investigations performed by Sitte (Ref 19). Even at temperatures and Cr_2O_3 contents for which the miscibility gap exists, the time in the flame or in the torch is too short for phase separation to occur. The constant lattice parameters of the phases in the coatings prepared from the mixed powders (see Fig. 10) indicate that during the spray process the solid solution is not formed. However, for the WSP process, the combination of time and temperature seems to be sufficient to suppress the phase transformation effectively by the presence of Cr_2O_3 even if the formation of the solid solution does not take place. A possible stabilization mechanism could be the growth of $\alpha\text{-Al}_2\text{O}_3$ on the surface of Cr_2O_3 nuclei. This would be in good agreement with the explanation given by McPherson (Ref 30), who suggested that unmolten Al_2O_3 particles act as nuclei for growth, resulting in a higher α -alumina content. For all Cr_2O_3 contents, the degree of stabilization is higher for the prealloyed powders than for the mixed ones. For APS



coatings, a high amount of Cr_2O_3 is necessary for changes to be detected in the diffraction pattern. Unlike for WSP, for APS, the lower energy in combination with the time and temperature in the plasma torch does not seem to be sufficient for effective stabilization of $\alpha\text{-Al}_2\text{O}_3$ by Cr_2O_3 to be realized.

Important factors seem to be the time and temperature in the flame or plasma torch, as well as the type of gases, and, therefore, the heat flux. It should also be taken into account that the powder feed rate for the WSP process is about ten times higher than that for APS. Another point, which has not yet been studied in enough detail, is the influence of the atmosphere of the torch or flame.

The contradiction to earlier reports on successful stabilization (Ref 21, 22, 25, 26) suggested by Müller and Kreye (Ref 24) does in fact not exist. When prealloyed powders are used, regardless of the spray process, the full absence of phases other than the α phase seems to require addition of about 30 mass% chromia. This can be derived from the compositions used in this work and various references (Ref 7, 21, 22-26).

It appears that stabilization exhibits a complex dependence on the spray process, the process parameters (in particular the thermal history), the nature of the powder (mechanically mixed or prealloyed), and the chromia content.

5. Summary and Conclusions

It was the main task of this work to clarify the recent contradictory opinions in the literature regarding the stabilization of $\alpha\text{-Al}_2\text{O}_3$ by additions of Cr_2O_3 . Therefore, in this work, stabilization using different spray processes (WSP, APS, and HVOF) was studied. Mechanical mixtures of alumina and chromia, as well as prealloyed powders consisting of solid solutions were used. The investigations focused on mechanical mixtures with both APS and WSP and on prealloyed powders with WSP. The studies in this work led to the conclusion that the phase content of the coatings depends both on the spray process and on the powder composition. Stabilization of the α phase using the WSP process starting from mechanical mixtures was confirmed. For the WSP process, the positive effect of an increase in the α phase with increasing Cr_2O_3 content in the coating was clearly shown. Contrary to this, in the APS process starting from mechanical mixtures, no stabilization effect was found when mechanically mixed powders are sprayed.

For both the mechanically mixed and the prealloyed powders sprayed by WSP, phase quantification by Rietveld analysis was performed. The study of the lattice parameters showed that there is no solid solution formation.

A large number of open questions regarding the behavior of Al_2O_3 in thermal-spray processes and the possibility of stabilizing the thermodynamically stable corundum still exist. In order to complete the investigations, further work with additional powder compositions will be carried out. The question of whether or not the

existence of an $(\text{Al,Cr})_2\text{O}_3$ solid solution is a precondition for preparation of coatings with a high degree of α modification in dependence on the spray process must be studied. Also, the influence of the atmosphere of the torch or flame and the thermal history of the particles and the coatings has to be investigated. These experiments will be a further step toward a full understanding of the mechanism of stabilization.

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