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Alumina-Base Plasma-Sprayed Materials— Part II: Phase Transformations in Aluminas*

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Aluminum oxide is widely used for plasma spraying. Alumina deposits consist of a number of metastable crystallographic modifications, which at elevated temperatures, transform to the stable a phase. It was shown that additions of various oxides changed the phase composition and shift phase transformation temperatures. This paper addresses the variation of phase compositions and temperatures of the phase changes for plasma-sprayed alumina deposits manufactured with alumina-base materials containing Cr_2O_3 and TiO_2.

This study combines the results obtained from energy dispersive analyzer of X-rays **(EDAX)** and scanning electron microscopy (SEM) chemical **analysis, differential** thermal analysis (DTA), and X-ray powder diffraction (XRD) quantitative phase analysis of as-sprayed and annealed samples of alumina deposits and shows how the two additives change the phase composition and the a-phase formation temperature. This transformation temperature varied by nearly 200 **°C.** The metastable alumina sequences were also influenced by the chemical composition; for example, the content of θ alumina varied between 0 and 55 wt%.

Keywords alumina, oxide ceramics, phase composition, phase stability, plasma spray

1. Introduction

The extensive application of aluminum oxide in the thermal spray (TS) industry is due to its important mechanical and dielectric properties, wide availability, and low cost. It was, however, recognized early that these deposits are composed of metastable phases (Ref 1), which on heating transform into the stable a-phase. This transformation can be quite complex (Ref 2, 3). The lamellar structure of these deposits is formed by impact, flow, and rapid solidification of molten or semimolten particles (Ref 4). Different regions of impacting particles can cool at different rates, which results in variations of phase content within individual splats (Ref 5, 6). Depending on the feedstock characteristics, spray conditions, cooling conditions, and a number of other variables (Ref 7), the microstructures vary widely in phase content and porosity.

The crystallographic phase composition of alumina TS deposits is strongly related to the cooling rate. Generally, higher cooling rates result in the formation of high levels of γ alumina, lower cooling rates cause formation of δ alumina (Ref 8, 9), and a further reduction in cooling rates can result in deposits comprised of a alumina (Ref 10).

Manufacturing of high-temperature ceramics is a costly process requiring high temperatures, and therefore, considerable effort has been directed toward controlling the structure of bulk alumina by chemical additives of other oxides or other phases of alumina (Ref 11-14). The transformation temperature can be modified by addition of cations of chromium and iron (Ref 13). Bonder et al. (Ref 15) found that addition of chromium significantly increased the y-a transformation temperature.

This paper describes the study of the influence of Cr_2O_3 and TiO_2 additions on the phase sequences and transformation temperatures of plasma-sprayed alumina deposits.

2. Experiment

2.1 Materials

Table 1 gives the feedstock materials chemistry, particle sizes, phase compositions, and production methods.

2.2 Spray Manufacturing

Deposits were produced using the water-stabilized plasma-spray system PAL 160 (IPP, 182 00 Prague, Czech Republic), at

Table 1 Feedstock chemistry, particle sizes, phase compositions, and production methods

Powder identification	Chemistry Al_2O_3+, wt%	Particle sizes, µm	Phase composition	Manufacturing method
AB5	0.15% Fe_2O_3	63 to 90	a, trace β	Fused and crushed
AH5	4.7% TiO_2 1.3% Fe_2O_3	50 to 90	a	Fused and crushed
ACO	1.3% Cr_2O_3 0.9% Fe_2O_3	63 to 90	a, trace β	Fused and crushed
A4T	17% TiO_2 <0.1% Fe_2O_3	40 to 80	α, trace β anatase form of TiO_2	Agglomeration of TiO_2 onto ABS powder

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*Part I of this article was printed in the September issue of JTST Vol 6 (No. 3), September 1997, p 320-326 the Institute of Plasma Physics, Czech Academy of Sciences, Czech Republic. The system was operated at 154 kW (480 A and 320 V) power. The mild steel substrates, coupons of 20 mm diameter and 5 mm thickness, were positioned on a sample holder 290 mm from the gun nozzle. The substrates were grit blasted prior to spraying. The gun was vertically traversed with the samples passing slowly through the flame horizontally. The powder feed rate was 16 kg/h. Deposits of approximately 0.5 mm thickness were formed after three substrate passes in front of the gun. The substrates were not cooled.

2.3 *Annealing*

The samples were annealed in nitrogen using two types of furnaces. One furnace was a vertical, manually controlled furnace, which offered no means of controlling the heating rate other than the speed of inserting the sample in the hot zone of the furnace. This inserting (and removing) process was rapid; the samples reached any temperature in about' 10 min. Cooling of the samples was controlled by natural cooling in a nitrogen atmosphere after removing the samples from the hot zone of the furnace. The second furnace was a box furnace, where the heating and cooling rates were controlled at 400 °C/h. The similarity of the results from these two different types of furnaces was verified by comparing phase compositions of samples annealed for 1100 °C/0.5 h and 1200 °C/0.5 h in both furnaces. The measured variations in phase compositions for samples in the same condition were from -6 wt% to +9 wt% with no systematic dependence on the type of furnace.

2.4 *Experimental Techniques*

2.4.1 X-Ray Diffraction

Quantitative x-ray diffraction (XRD) phase analysis was performed using nickel filtered copper Kα radiation. Details of the reference intensity ratio method can be found in Ref 16-19. The method is based on the measurement of integral intensities of selected peaks of the phases and relating their ratios to the weight content of a phase using a set of constants. The procedure is calibrated using samples prepared with known phase compositions. In the present experiment, these samples were powdered deposits mixed with feedstock (Ref 20).

Table 2 Chemical compositions of the feedstock materials and deposits after plasma spraying

	Chemical composition	
	Feedstock	Deposit
Sample	Al_2O_3+, wt%	Al_2O_3+, wt%
AB5	0.15% Fe_2O_3	0.9% Fe_2O_3
AH5	4.7% TiO_2	3.6% TiO_2
	1.3% Fe_2O_3	2.4% Fe_2O_3
ACO	1.3% Cr_2O_3	0.7% Cr_2O_3
	0.9% Fe_2O_3	1.4% Fe_2O_3
A4T	17% TiO_2	11.5% TiO_2
	<0.1% Fe_2O_3	0.4% Fe_2O_3

Averaged as-sprayed and two annealed conditions for each sample. Balance to 100% is alumina

2.4.2 Differential Thermal Analysis

Differential thermal analysis (DTA) in an argon atmosphere was used to study powdered deposit samples. The temperature range was 200 to 1300 °C (1450 °C for sample A4T) with a heating rate of 10 °C/min.

2.4.3 Chemical Analysis

Polished cross sections of selected samples were studied using a scanning electron microscope (SEM) equipped with an energy dispersive analyzer of X-rays (EDAX). Three samples of each chemistry were selected: as-sprayed, annealed at 1050 °C (samples AH5 and A4T) or 1100 °C (samples AB5 and ACO), and annealed at 1200 °C (sample A4T) or 1250 °C (samples AB5, ACO, and AH5). The EDAX results for the three measurements were averaged to yield the chemical composition of the deposits.

3. Results

3.1 *Chemical Changes*

The EDAX studies showed that the chemical composition of the materials changes significantly with plasma spraying. The results given in Table 2 show a significant increase in the Fe_2O_3 content after spraying. This can be related to the spraying technique, where Fe_2O_3 inclusions can be formed due to wear of the external rotational iron anode (a necessary part of the high-powered water-stabilized plasma [WSP] system). There was no systematic difference in the chemical composition of deposits between as-sprayed and annealed samples. The increase was between 0.4 and 1.1% of Fe_2O_3; the large variations between samples were probably due to an inhomogeneous distribution of Fe_2O_3 inclusions.

Some oxides decreased in content due to selective evaporation of chemical components (Ref 6). A large decrease of titania in the A4T samples can be related to the feedstock powder. Due to the powder processing method, which is an agglomeration of fine titania powder onto alumina grains, the titania grains can break loose during the feeding and spraying processes.

3.2 *Phase Changes*

Figures 1 and 2 present results of the annealing experiments. Each chemistry was studied using two sets of times and temperatures: an isochronal sequence with a constant time of 1 h at temperatures between 900 and 1400 °C and an isothermal sequence with a constant temperature of 1100 °C with times between 0.125 and 5 h. Variations of phase compositions in Fig. 1 and 2 were approximated by smooth curves to visualize the dependencies. The phase analysis results for the samples are given below.

3.2.1 AB5

The as-sprayed deposit of the AB5 material was approximately 87% of 8-phase, with the remainder being α-phase. The isochronal sequence (Fig. 1a) of the phases showed a large amount (–54%) of the θ-phase formed between 1000 and 1200

°C. The isothermal sequence (Fig. 2a) showed a maximum for the **θ-phase** content at 1 h. The **δ-phase** content leveled after about 1 h, while the a-phase increased with time.

3.2.2 AH5

The as-sprayed AH5 deposit consisted of approximately 77% y-phase and 23% a-phase. This y-phase transformed for even the lowest (900 **°C**) annealing temperature into the 6-phase. No **θ-phase** was found in this material under any conditions. During the isochronal sequence at approximately 1050 **°C,** the **δ-phase** transformed directly into the a-phase. In the isothermal sequence (Fig. **2d),** the phase composition changed during the shortest annealing time (0.125 h) into a 50:50 ratio of a and 6 phases. The deposits fully transformed into the a-phase within 1 h.

3.2.3 ACO

The as-sprayed ACO deposit consisted of approximately 89% **δ-phase** and approximately 11% **α-phase.** The isochronal sequence (Fig. 1b) showed the presence of the **θ-phase** with a

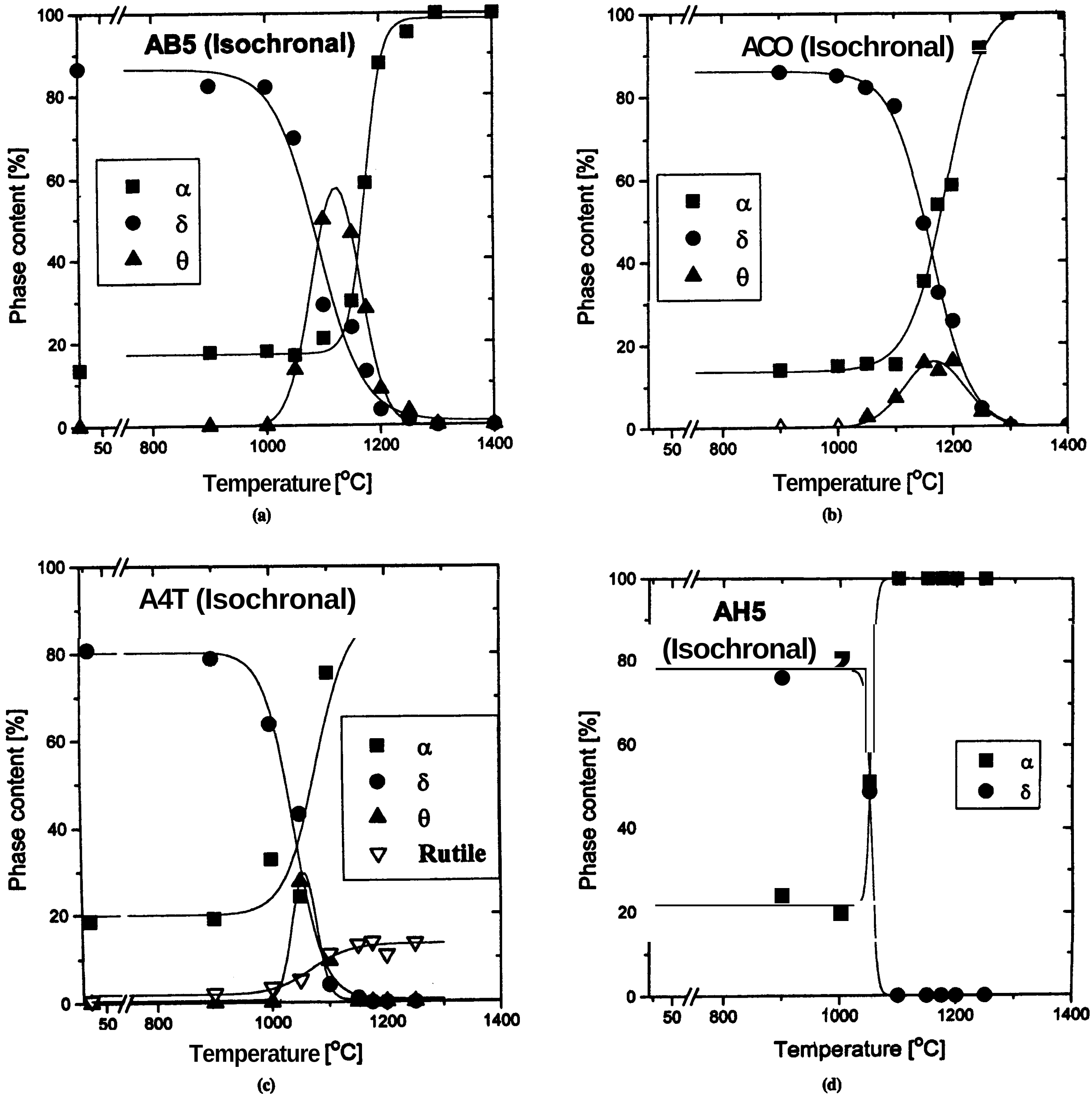

Fig. 1 Results of the isochronal experiment. Samples heat treated for 1 h at different temperatures. (a) Sample AB5. (b) Sample ACO. (c) Sample A4T. (d) Sample AH5. Dependencies are approximated by smooth curves for readability.

maximum of approximately 16% at about 1170 °C. The isothermal sequence (Fig. 2b) showed slow changes with a continuing decrease of the **δ-phase** and an increase of the α and θ phases.

3.2.4 A4T

The as-sprayed A4T deposit consisted of approximately 80% y-phase, 19% **α-phase,** and **<1%** rutile. The isochronal sequence (Fig. 1c) exhibited approximately 30% **θ-phase** at 1060 °C. Most of the rutile was formed at this temperature. The rutile content leveled at higher temperatures (above 1150 °C), which suggests that all or most of the **titania** was precipitated from the alumina. The isothermal sequence (Fig. **2c)** showed complex changes in phase content. The phase composition changed rapidly within the first hour and then remained stable.

3.2.5 All Samples

Figure 3 best illustrates the effect of chemical additives on the **α-phase** formation. The addition of Cr_2O_3 caused a shift of

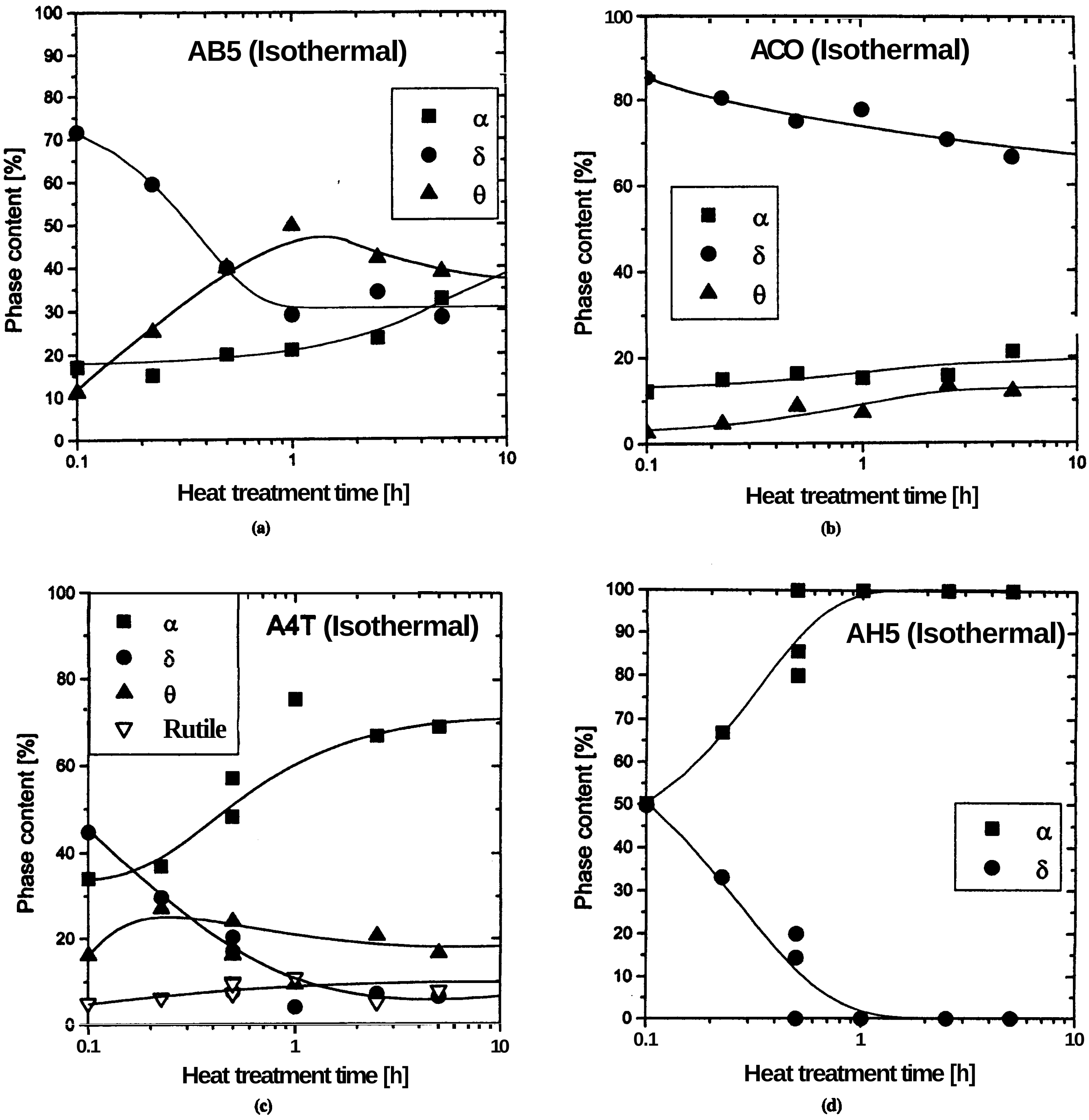

Fig. 2 Results of the isothermal experiment. Samples heat treated at 1100 °C for up to 5 h. (a) Sample AB5. (b) Sample ACO. (c) Sample A4T. (d) Sample AH5. Dependencies are approximated by smooth curves, or points are connected for better readability.

the a-phase formation **temperature** to higher values. The decrease in the slope of the graph for this sample indicates that the **transformation** occurred in a wider range of temperatures. Additions of TiO_2 caused a decrease in the a-phase transformation temperature.

3.3 *DTA*

Figure 4 shows the results of the DTA measurements. Previous measurements (Ref 21) reported a weak response of the DTA for most of the phase transformations in alumina. The only phase transformation reported in Ref 21 that can be reliably recognized in the DTA **spectrum** is the a-phase formation, which is represented as an exothermic peak between **1100** and **1300** °C. This was also verified in this study. The enthalpies of transformations between y-6 and 6-a phases **are** approximately –2.7 kcal mol^{-1} (Ref **22),** while data for the δ-θ transformation are not available. Different kinetics of these phase transformations **are** the likely reasons for difficulties in recognizing the y-6 **transformation** as compared to the 6-a **transformation.** Sample A4T exhibited another (endothermic) peak at approximately 1350 **°C,** which was identified by XRD analysis to be part of the Al_2TiO_5 phase.

Temperatures of the DTA peaks for the 6-a phase **transformation** varied with the chemical composition. The results generally agree with the findings from the annealing experiments regarding the dependence on the chemical composition. For **AB5,** ACO, and **AH5,** the DTA results were approximately **100** to 150 **°C** higher than the heat treatment results from the isochronal sequence. This effect can be related to the different kinetics for these experiments. For **A4T,** the temperature variation is approximately 50 **°C.** This variation is probably related to the precipitation of rutile from alumina.

4. Discussion

The phase transformations in TS alumina exhibited a strong dependence on the chemical composition. The a-phase **transformation** temperature increased with the addition of Cr_2O_3 and decreased with the addition of TiO_2. **This** temperature varied by **nearly 200 °C.** The chemical inhomogeneities in the **A4T sample** (precipitation of TiO_2 in the **as-sprayed** and in the annealed conditions) cause the more complex behavior as **compared** to the AH5 **samples.** In the current experiment, no influence of the Fe_2O_3 on the phase transformations could be recognized.

The as-sprayed samples containing TiO_2 consisted mainly of y-phase, while the samples without TiO_2 were **mainly** 6-phase. The lowest annealing temperature of **900 °C** led to a transformation of all deposits into **δ-phase.** This suggests that the TiO_2 causes a shift in y-6 transformation to higher temperatures, and therefore, the deposits can **retain** a **γ** structure under the same **plasma-spraying** conditions.

The amount of **θ-phase varied** between approximately 56% for the **AB5** deposit and 0% for the AH5 deposit. The range of temperatures for which the 8-phase existed started above 1000 °C for all samples where this phase could be found. It existed up to **temperatures** where the deposits were fully transformed into the stable **α-phase.**

Less than 1% rutile was found in the A4T sample in the as-sprayed state. At approximately 1**100 °C,** the amount of rutile increased to about 13%. This was also the temperature for **α-phase** formation, suggesting that the majority of **titania** was dissolved in metastable phases of alumina and was precipitated during the formation of the stable a-phase. The DTA spectra for A4T showed that at approximately 1350 **°C,** the TiO_2 reacts with alumina and forms Al_2TiO_5. No precipitation of TiO_2 **and** Al_2TiO_5 was observed for the AH5 sample, suggesting that the limited TiO_2 content in this sample can be dissolved even in a alumina under these conditions.

5. Conclusions

The phase compositions and phase transformation temperatures in **plasma-sprayed** alumina samples were varied widely by changing the chemical composition of the feedstock material. The addition of Cr_2O_3 increased the a-phase formation temperature, while the addition of TiO_2 caused a temperature de-

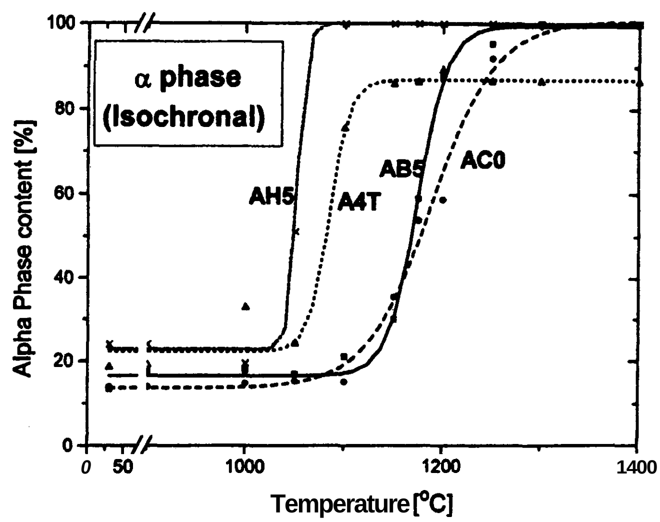

Fig. 3 **Comparison df results obtained for all samples in isochronal experiment for a-phase**

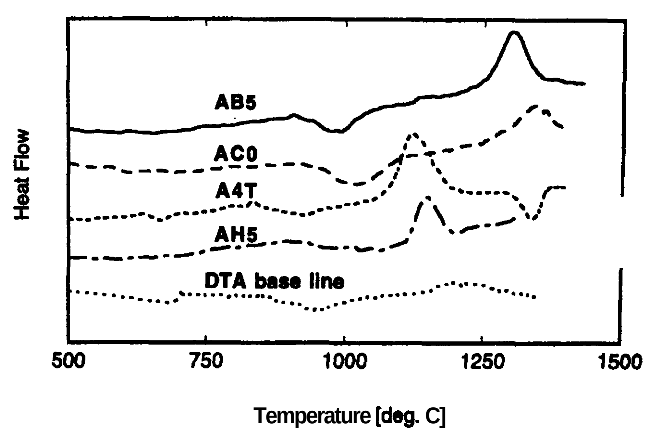

Fig. 4 **Results of the differential thermal analysis (DTA) measurements**

crease. The range within which the α-phase formation temperature was varied was –200 °C. The precise influence of the Fe_2O_3 was not established from this experiment and will require future studies.

The content of the metastable phases was varied significantly. For example, the θ-phase content varied between 0 and approximately 56%. The major metastable phase in the as-sprayed deposits was γ for deposits containing TiO_2 and δ for other deposits.

The results obtained from samples with high chemical inhomogeneities indicated an influence on the phase sequences and transformation temperatures.

Applications of plasma-sprayed alumina deposits can be optimized for phase composition and phase stability in a wide range of temperatures by relatively small variations of chemical compositions. Homogeneity of the deposits may be necessary for good control and may require suitable powder manufacturing methods.

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