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# Binary and Ternary Ceramics

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## SYNTHESIS AND PHASE DEVELOPMENT IN THE Cr-Al-N SYSTEM

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### ABSTRACT

The ternary nitride system Cr-Al-N has been investigated by sintering different powder compositions. The powder compositions belong to four groups, AlN- + Cr-powder (5 compositions between 20-90 molar% AlN), Al- + Cr<sub>2</sub>N-powder (5 compositions between 15-80 molar% Cr<sub>2</sub>N), AlN- + Cr<sub>2</sub>N-powder (50- and 90 molar% Cr<sub>2</sub>N) and Al- + Cr-powder. The powders were dry mixed and pressed into pellets by uniaxial pressing followed by cold isostatic pressing (CIP). Sintering took place in a graphite lined reaction bonding furnace under nitrogen atmosphere at three different temperatures, 1350°C, 1500°C and 1800°C and in an alumina tube furnace in order to avoid access to carbon. Holding times were varied, from 2 hours up to 72 hours.

The phase development was evaluated by thermal analysis and XRD. CrAlN was formed at 1350°C but decomposed at higher temperatures. Both pure Al and Cr-powder were prone to react with carbon in the graphite furnace. Thermal analysis showed a sublimation of Cr<sub>2</sub>N at temperatures around 1050°C and nitridation of pure Al-powder between 680-750°C and of pure Cr-powder between 610-1080°C. Samples with pure Al-powder showed a very large expansion due to melting of aluminium in combination with nitridation. AlN was found to be more stable than Cr<sub>2</sub>N at higher temperatures and longer holding times. The mixtures of Al- + Cr-powder produced an intermediate Al-Cr-phase.

### INTRODUCTION

Chromium aluminium nitride has shown promising properties for cutting and wear applications, such as high hardness, wear- and oxidation resistance<sup>1,2</sup>. Increasing the amount of aluminium in Cr-N coatings increases the oxidation resistance of the film by formation of an aluminium oxide layer on the surface<sup>3</sup>. There are many reports on thin film production of CrAlN-films<sup>4,5,6</sup>, but the material is much less studied in bulk form.

CrAlN crystallizes in two different ways depending on the AlN content. The crystal structure is cubic B1 NaCl-structure CrN for lower amount of AlN and hexagonal B4 wurtzite-structure AlN (w-AlN) for higher amount of AlN<sup>7</sup>.

Little work has been reported on bulk preparation of CrAlN. The aim of this work is to investigate the phase development in the Cr-Al-N system during sintering in different temperatures.

### MATERIAL

The material in this study consisted of aluminium nitride and pure chromium powder from Alfa Aesar (Johnson Matthey, Karlsruhe, Germany), chromium(III)nitride and aluminium powder from Sigma-Aldrich (Munich, Germany). The particle sizes of the powders were around 40 microns. The chromium(III)nitride powder consists of 85% Cr<sub>2</sub>N and 15% CrN. Four different groups of compositions were made, as shown in figure 1.

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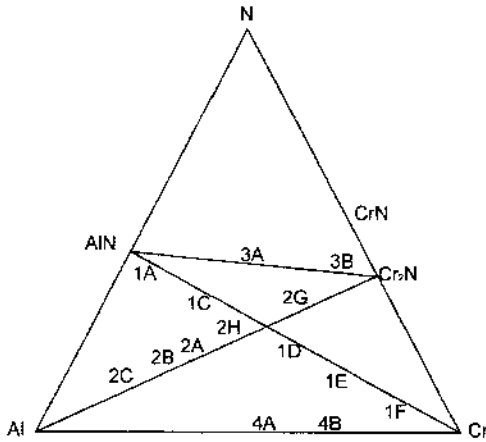


Figure 1. Compositional distribution of the tested samples.

Group 1 consists of 5 compositions of a mixture of AlN-powder and pure Cr-powder. Group 2 consists of 5 compositions of a Al- and Cr<sub>3</sub>N -powder mixture. Group 3 is two different mixtures of AlN and Cr<sub>3</sub>N -powders. Group 4 consists of two different compositions of Al- and Cr-powders. Table I shows the molar compositions of the different samples.

Table I. Compositions of all samples, in molar fractions.

| Sample ID | AlN  | Cr   | Sample ID | Cr <sub>3</sub> N | Al   |
|-----------|------|------|-----------|-------------------|------|
| 1A        | 0.87 | 0.13 | 2A        | 0.49              | 0.51 |
| 1C        | 0.65 | 0.35 | 2B        | 0.36              | 0.64 |
| 1D        | 0.50 | 0.50 | 2C        | 0.25              | 0.75 |
| 1E        | 0.37 | 0.63 | 2G        | 0.79              | 0.21 |
| 1F        | 0.20 | 0.80 | 2H        | 0.64              | 0.36 |
|           |      |      |           |                   |      |
| 3A        | 0.26 |      |           | 0.74              |      |
| 3B        | 0.04 |      |           | 0.96              |      |
|           |      |      |           |                   |      |
| 4A        |      | 0.5  |           |                   | 0.5  |
| 4B        |      | 0.67 |           |                   | 0.33 |

### EXPERIMENTAL

The powders were dry mixed and milled in a mortar and then compacted into pellets with a diameter of 10 mm by uniaxial pressing (MFL Systemc Prüf und Mess, UPD6, Mannheim, Germany) at 10 MPa, followed by cold isostatic pressing (Autoclave Engineers: STD, Erie, PA, USA) at 200 MPa. The samples were sintered in an alumina lined tube furnace (Hereaus, Hanau, Germany) at 1350°C under flowing nitrogen atmosphere with a holding time of 2 hours and in a reaction sintering furnace with graphite heating elements (Conrad Engelke Technik, Hannover, Germany) at 1350, 1500 and

1800°C in a nitrogen atmosphere during 4 hours. In the graphite lined furnace the samples were embedded in boron nitride. Some of the samples were sintered at lower temperatures in the alumina lined furnace, at 750 and 850°C respectively.

Heat treated samples were investigated with X-ray diffraction (XRD) (Philips:MRD, CuK $\alpha$  radiation and proportional detector, Almelo, The Netherlands). The X-ray diffractograms were recorded between 10 and 100° 2 $\theta$ . The phase fractions were determined by fitting a Gaussian function to the three main XRD peaks of each phase present. The relative intensity ratio,  $I_x/I_t$ , where  $I_x$  is the sum of the intensity of the three main peaks of phase  $x$  and  $I_t$  is the total intensity, i.e. the sum of the intensity of the three main peaks of all the constituent phases, is then a measure of the phase fraction of phase  $x$ .

Thermal analyses were performed in a dilatometer (Netzsch: DIL 402 C, Selb, Germany) and in a differential scanning calorimeter (DSC Netzsch: STA 449 C Jupiter, Selb, Germany) under flowing nitrogen atmosphere up to 1550°C with a heating rate of 10°C/min and cooling rate 20°C/min.

## RESULTS AND DISCUSSION

Sintering at 1350°C for 2 hours gave the largest amount of chromium aluminium nitride. Almost all samples contained the phases AlN, Cr<sub>2</sub>N and Cr<sub>x</sub>Al<sub>y</sub>N at different amounts. Group 2 contained more Cr<sub>x</sub>Al<sub>y</sub>N than group 1, suggesting that pure aluminium more easily reacts with Cr<sub>2</sub>N, than chromium does with AlN. The compositions 2A and 2H contain the largest amount of Cr<sub>x</sub>Al<sub>y</sub>N, around 40 vol%. Resulting XRD graphs for the compositions in group 2 sintered at 1350°C are shown in figure 2.

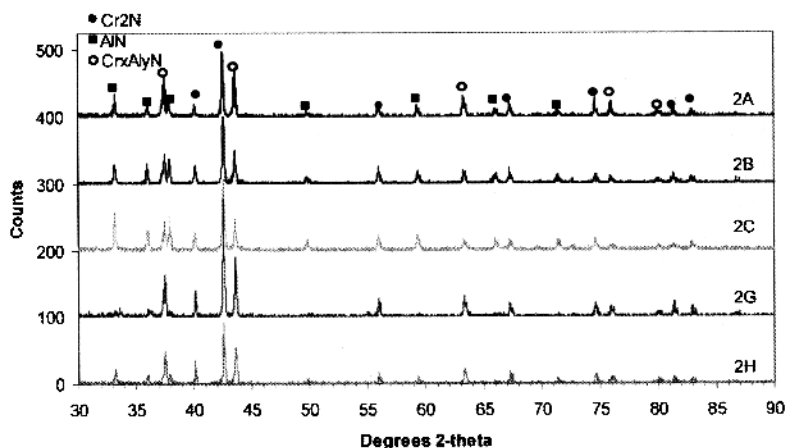


Figure 2. The samples of group 2 sintered at 1350°C.

Sample 2A was also sintered at 750° and 850°C, and a comparison of the result for three different sintering temperatures is shown in figure 3. It can be seen that there is more AlN at higher temperatures. The fact that AlN is visible only at higher sintering temperatures even though nitridation of aluminium starts below 700°C, indicates that it is a decomposition phase of the Cr<sub>x</sub>Al<sub>y</sub>N -phase rather than a

nitridation of pure aluminium powder. There is probably a maximum in  $Cr_xAl_yN$  content at a temperature lower than  $1350^\circ C$  but higher than  $850^\circ C$  and this will be investigated further.

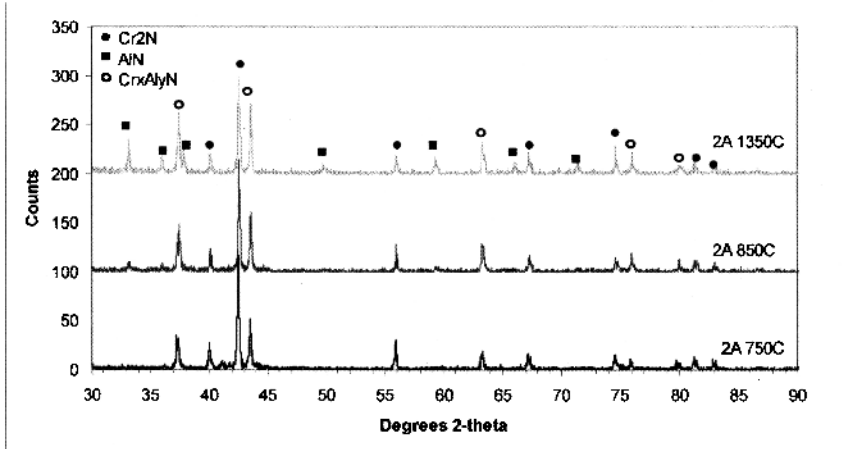


Figure 3. Sample 2A sintered at three different temperatures, 750, 850 and  $1350^\circ C$ .

Group 1 consisted generally of less  $Cr_xAl_yN$  -phase than group 2. The  $Cr_xAl_yN$  phase also developed at a higher temperature in group 1. As shown for sample 2A in figure 3 above, there is  $Cr_xAl_yN$  already at  $750^\circ C$ , but for sample 1D, there is only AlN and pure Cr even at  $850^\circ C$ , at a holding time of 2 hours, see figure 4 below.

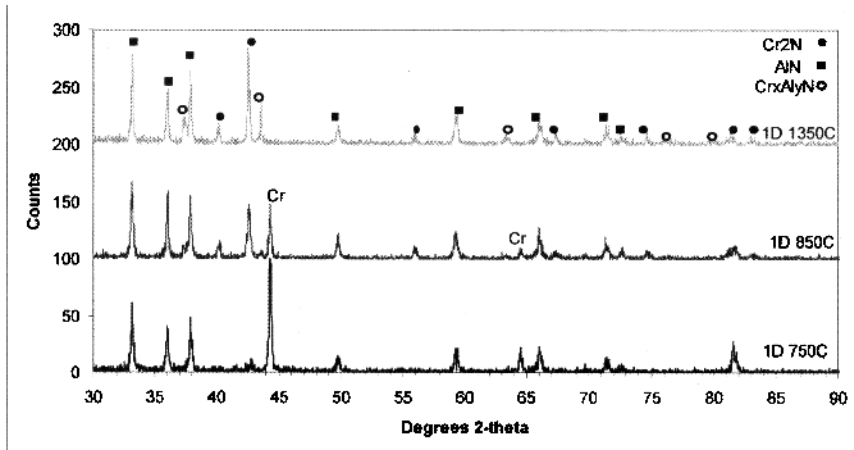


Figure 4. Sample 1D sintered at different temperatures.

The samples of group 4, i.e. a mixture of chromium and aluminium, were sintered in 1350°C, 850°C and 750°C and no  $\text{Cr}_x\text{Al}_y\text{N}$  phase was detected. Group 4 samples showed an intermediate Al-Cr phase for all temperatures. However, exact phase composition could not be determined. The resulting XRD-results of sample 4B sintered at 750°C, 850°C and 1350°C are shown in figure 5, with the intermediate Al-Cr phase denoted  $\delta$ . At 750 and 850°C the sample contains only the Al-Cr-phase and pure Cr. At 1350°C the chromium has been nitridated into  $\text{Cr}_2\text{N}$  and AlN is now visible as a decomposition phase of the Al-Cr-phase. The Al-Cr-phase could not be nitridated into a  $\text{Cr}_x\text{Al}_y\text{N}$ -phase even at 1350°C. The same behaviour was detected for sample 4A.

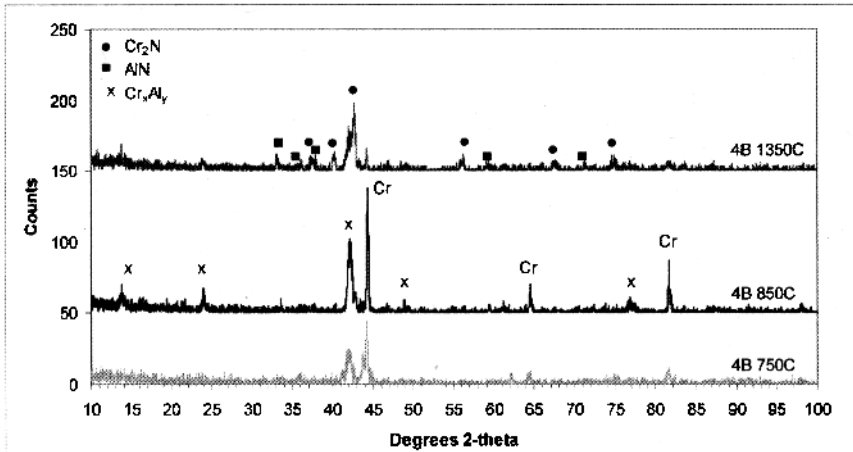
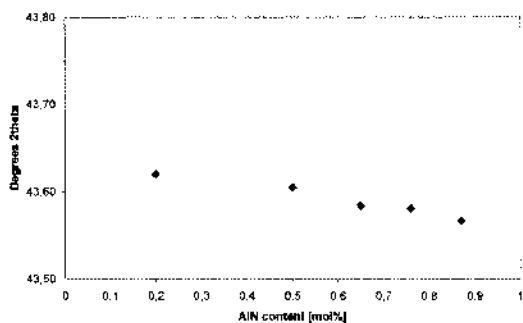


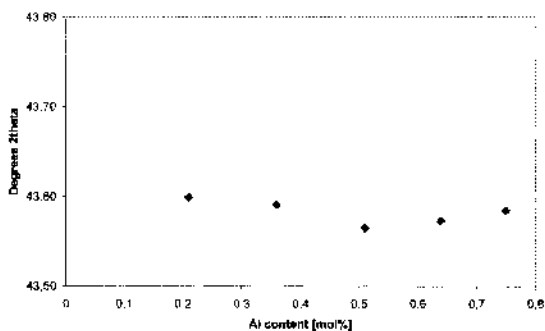
Figure 5. X-ray diffractograms of sample 4B sintered at different temperatures.

The results of the curve fitting showed that there is no shift in the  $\text{Cr}_2\text{N}$  peaks with respect to aluminium content, which indicates that there is no solid solution between Al and  $\text{Cr}_2\text{N}$ . Figure 6 shows the influence of the total amount of aluminium in the sample, i.e. aluminium- and aluminium nitride on the 200 peak position of the  $\text{Cr}_x\text{Al}_y\text{N}$  phase. The amount of each phase in the samples sintered at 1350°C in the alumina lined furnace and calculated from the intensity relationship is shown in table II and visualised in figure 7.

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a) Group 1



b) Group 2

Figure 6. Peak position of main peak of  $Cr_xAl_yN$  phase as a function of total aluminium content (molar%) in the sample for (a) group 1 and (b) group 2.

Table II. Amount of phases in vol% based on intensity relationships of 3 main peaks.

| Sample | $Cr_xAl_yN$ (vol%) | $Cr_2N$ (vol%) | AlN (vol%) |
|--------|--------------------|----------------|------------|
| 1A     | 7                  | 10             | 83         |
| 1C     | 15                 | 21             | 64         |
| 1D     | 15                 | 32             | 53         |
| 1E     | 10                 | 47             | 43         |
| 1F     | 16                 | 67             | 17         |
| 2A     | 41                 | 38             | 21         |
| 2B     | 31                 | 44             | 25         |
| 2C     | 25                 | 40             | 36         |
| 2G     | 37                 | 49             | 14         |
| 2H     | 42                 | 43             | 15         |
| 3A     | 21                 | 43             | 36         |
| 3B     | 0                  | 100            | 0          |

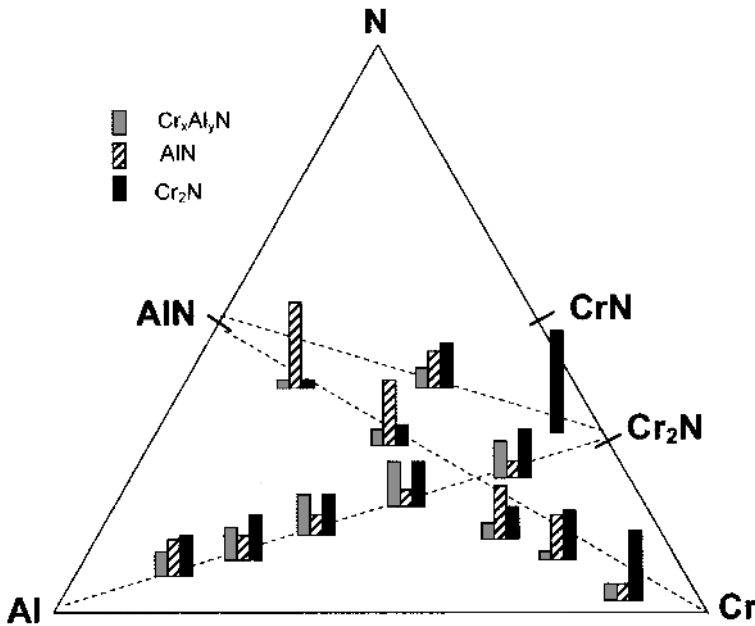


Figure 7. Amount of  $Cr_xAl_yN$  -phase in the Cr-Al-N system at 1350°C.

Of the temperatures tested in this study, 1350°C was the temperature that gave the largest amount of  $Cr_xAl_yN$ . Longer holding time at 1350°C or sintering at 1500°C and 1800°C lead to a decomposition of the  $Cr_xAl_yN$  phase into AlN and  $Cr_2N$ . In addition, a reaction occurred between the boron nitride powder that was used for embedding samples in the graphite lined furnace and pure chromium powder starting at a temperature of 1500°C, depending strongly on temperature and holding time. After 72 hours at 1500°C the only phase present was Cr(Al)B, i.e. a CrB phase with Al as a substitutional solid solution. The reaction with BN was naturally more prominent in group 1, consisting of pure Cr as a contrast to group 2 that contains  $Cr_2N$  from the start. Chromium was also easily reacting with carbon in the graphite lined furnace. The higher the temperature the more AlN and less  $Cr_2N$ , indicating that AlN is a more stable phase at higher temperatures.

The results of the dilatometer runs for sample 1D, 2A and 3A are shown in figure 8. They are representative for all the samples in the different groups. For sample 2A there is a sudden and large increase in length at 670°C which is due to the melting and nitridation of aluminium. Samples 1D and 3A has a much smaller expansion and over a larger temperature range.

The results of the DSC/TG runs for sample 1D and 2A are shown in figure 9. Also here the samples in the same group follow the same trend in behaviour. For group 1 there is a large mass increase between 610-1080°C due to nitridation of chromium. Between 1080 and 1150°C there is a decrease in mass, due to sublimation of chromium nitride. Group 2 shows a similar behaviour as group 1. Sample 2A shows a large mass increase between 680°C and 750°C and in the same temperature

interval the DSC curve shows an exothermic reaction. This is probably due to nitridation of pure aluminium. The nitridation can start at slightly different temperatures depending on the nitrogen pressure<sup>8</sup>. Aluminium is melting due to the heat of reaction generated during nitridation. A nitride layer grows on the surface of the pellet. This nitride layer prevents the nitrogen from getting in contact with the inner part of the pellet. The temperature of the surrounding nitrogen atmosphere is lower than the melting point of aluminium and the molten aluminium will solidify and crack the nitride layer on the surface, letting the nitrogen into the inner parts of the pellet and the process of melting will start again<sup>8</sup>. Between 1070 and 1170°C there is a mass loss for all samples in group 2. The mass loss is larger the more Cr<sub>2</sub>N the sample contains together with an endothermic reaction indicates a sublimation of chromium nitride.

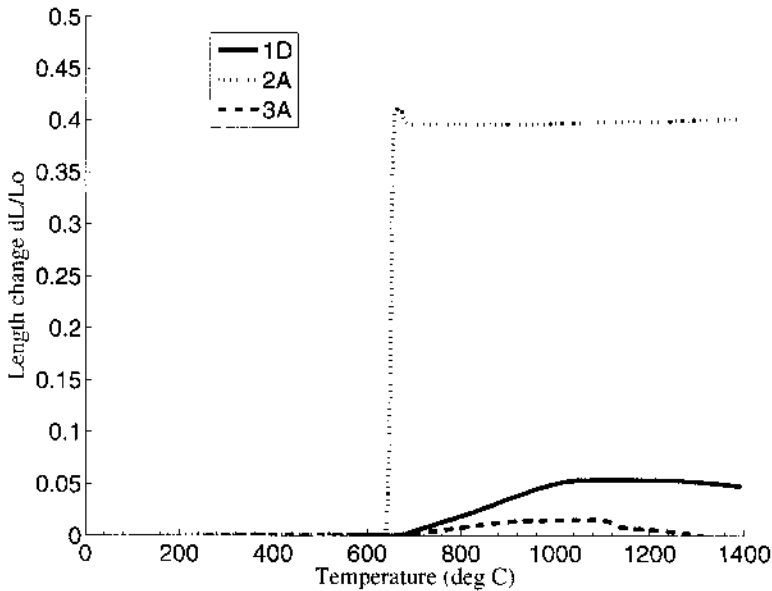
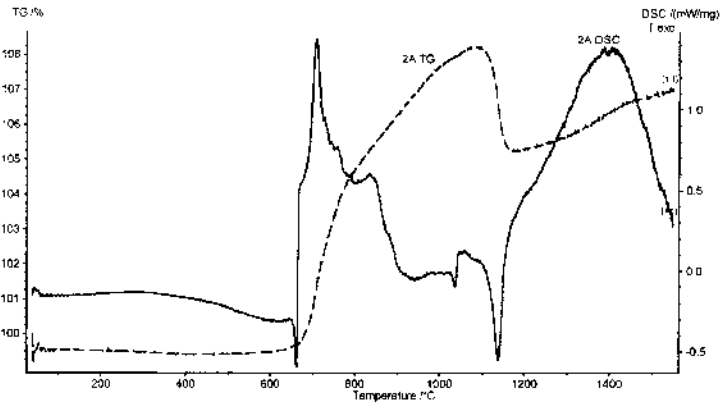
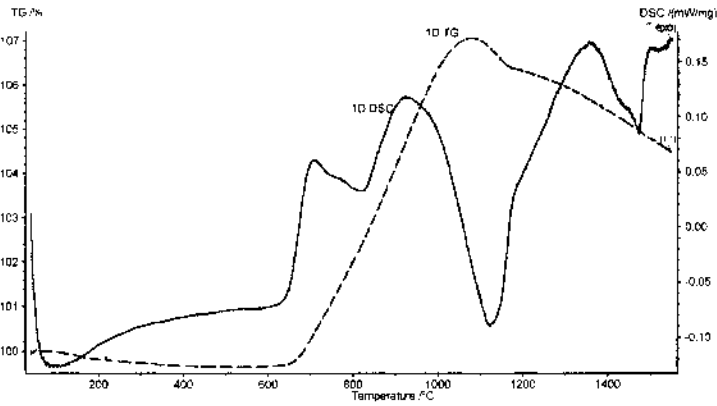


Figure 8. Dilatometer results for samples 1D, 2A and 3A.

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a) Sample 2A



b) Sample 1D

Figure 9. DSC/TG results for samples 1D and 2A.

### CONCLUSIONS

- The largest amount of  $\text{Cr}_x\text{Al}_y\text{N}$  -phase was found at a temperature of 1350°C and 2 hours holding time in this study.
- The  $\text{Cr}_x\text{Al}_y\text{N}$  -phase and the Al-Cr-phase have started to decompose at 1350°C into AlN and  $\text{Cr}_2\text{N}$  indicating that there is an optimum temperature for  $\text{Cr}_x\text{Al}_y\text{N}$  reaction below 1350°C.
- In group 4 (i.e. a powder mixture of Al + Cr) there is an intermediate phase of Al-Cr instead of  $\text{Cr}_x\text{Al}_y\text{N}$  -phase.
- The Al-Cr-phase has not been nitrated even at 1350°C.

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- AlN is more stable than Cr<sub>2</sub>N at higher temperatures and longer holding times.
- The largest amount of Cr<sub>x</sub>Al<sub>y</sub>N –phase was found in group 2 (i.e. a powder mixture of Al + Cr<sub>2</sub>N)

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