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Preparation of alumina-chromium composites by reactive hot-pressing Al + Cr₂O₃ based powders

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Chromium-Alumina based composites have been obtained by reactive sintering under load and vacuum of various powder blends. The starting mixtures have been prepared from commercially available aluminium metal, chromium and aluminium oxides, and a thermally unstable titanium compound respectively. Differential thermal analysis (DTA) and differential calorimetry (DSC) as well as X-ray diffraction were used to identify chemical transformations taking place within the system. Microstructure changes were observed via scanning electron microscopy (SEM) with an energy dispersive spectroscopy system (EDS). Chemical reactions in relevant binary subsystems have been investigated qualitatively in order to understand the course of events in the more complex quaternary mixtures. The possibilities of forming intermetallic phases in both the Al-Ti and Cr-Ti systems and of dissolving some Cr₂O₃ into the product Al₂O₃ phase have been considered. The influence of such parameters as thermal schedule and initial aluminium content on those side reactions and the resulting microstructures was investigated.

1- INTRODUCTION

Since the 1950's, much attention has been devoted to the goal of combining metals to ceramics in order to generate novel materials with improved properties [1]. Several processing routes have been considered, in particular the conventional powder metallurgy process was extensively studied. For example the synthesis of ceramic metal composites by reactions between aluminium and various oxides has been achieved [2]. One of the first cermets obtained was in the alumina-chromium system [3-5]. The alumina chromium combination indeed appears quite an appealing one with respect to both microstructures and properties. Both oxides have the same crystal structure and are completely soluble into each other which maybe favorable for the achievement of good bonding between the metal and oxide phases. Alumina and chromium offer good high-temperature characteristics with respect to oxidation resistance, strength and chemical stability [6]. Unfortunately, these composites suffer from poor thermal shock resistance and inadequate fracture toughness [7].

On the other hand, recent literature reports point to the interest of reactive sintering as a promising way to produce a wide range of ceramic-ceramic or ceramic-metal composites [8-13]. Modern powders with better controlled characteristics [14], and improved processing techniques have been thought to justify revival of work on the classical alumina chromium couple. This work therefore will report on the preparation of alumina chromium composites by reactive hot-pressing Al+Cr₂O₃ based powders. The heat of reaction ($\Delta H_r = -535$ kJ/mol)[15] of the overall chemical scheme :



was found not to be so high as to create important difficulties in the control of the development of microstructure during heat treatment. In the following, attention will be focused mostly on the description of chemical changes taking place in the system and on the effect of small titanium amounts which were a priori added to the base composition as potential wetting agent [16].

2- EXPERIMENTAL MATERIALS AND PROCEDURE

The starting materials were commercially available aluminium, α -alumina and chromium oxide powders. Titanium and iron have also been used as additives. To provide metallic titanium during heating a low temperature unstable compound of titanium (α -Ti) was chosen. The powder characteristics are reported in Table 1 as provided by the suppliers. Also given in Table 1 are the two initial compositions of the reacting system which have been

investigated in this work and provided by industrial partners. These two mixtures were prepared by conventional powder metallurgy techniques. Some sintered samples of 019 and 020 composition were also provided by industrial partners. The alumina addition was made in order to increase the ceramic content in the final material up to 85 vol.%. Some iron powder addition in composition 019 was aimed at improving the mechanical properties of the chromium phase [17], it being kept in mind that iron contamination during milling amounted to about 1.18 wt % (cf 020 composition).

After drying, the powders appeared as homogeneous mixture within about 250-300 μ m granulates of rounded shape (fig1). X-ray diffraction (XRD) confirmed that no reaction had occurred during milling between the initial constituents.

Hot pressing was carried out in graphite dies on the cold compacted (20MPa) granules. Heating under vacuum was conducted up to 1500°C. For investigation, use was made of differential thermal analysis (DTA) and differential scanning calorimetry (DSC) experiments in argon atmosphere. XRD with $\text{CoK}\alpha$ radiation was used to identify composition and phase changes. The microstructures of the samples were observed with a scanning electron microscope (SEM) with an energy dispersive spectroscopy system (EDS). In some cases more quantitative chemical analyses were obtained with a CAMEBAX SX 50 microprobe on diamond polished samples.

Table 1 : powder specifications (from suppliers)

Powders	mean size (μm)	purity (%)	019 (wt %)	020 (wt %)
$\alpha\text{-Al}_2\text{O}_3$	0.6	99.99	56.42	53.91
Al	1.3	99.5	12.35	11.12
Cr_2O_3	0.5	99.0	27.96	31.30
Ti compound (u-Ti)	5.0	99.5	0.78	2.48
Fe			2.48	1.18

3- RESULTS AND DISCUSSION

3-1- Reaction sequences

In order to gain better insight into the chemical evolution taking place within the final system (cf compositions Table 1) more simple subsystems have been investigated with respect to their reactivities. The same powders and overall experimental procedures as previously mentioned have been used for this purpose. The relative proportions however were chosen in relation to anticipated behaviors within the overall mixture.

First of all, $2\text{Al}+\text{Cr}_2\text{O}_3$ mixtures (in moles) have been reacted and the corresponding DTA curve is shown on fig 2. The endothermic melting of aluminium is quite apparent at 660°C and the aluminothermic reaction is seen to initiate at 800°C and is completed at about 1200°C, in agreement with previous reports [2]. XRD analyses confirm the reaction products to consist of $\alpha\text{-Al}_2\text{O}_3$ and chromium metal with some residual unreacted Cr_2O_3 because of imperfect mixing. The XRD pattern shift revealed that the alumina phase contains some dissolved chromium and that similarly metallic chromium contains aluminium.

Secondly, both DSC and DTA were performed on the titanium compound powder and a mixture of $3\text{Al}+\text{u-Ti}$ respectively (fig 3). The titanium compound is seen to undergo a double endothermic transformation into Ti metal at 490°C and 530°C respectively. The same endotherms yet slightly shifted are observed with the Ti-Al mixture and an extra exothermic reaction is seen to initiate at 650°C (before the endothermic melting of Al at 660°C which is therefore not apparent). XRD reveal this exotherm to correspond to the formation of Al_3Ti from $3\text{Al}+\text{Ti}$. The 1400°C peak corresponds to melting of the Al_3Ti phase [18]. As could be expected the endothermic solidification of Al_3Ti at 1380°C is observed upon cooling from 1500°C to room temperature.

When u-Ti is added to Cr_2O_3 however, reduction of the oxide by titanium was found to start at 850°C to form Ti_2O_3 as revealed by XRD. DTA shows that this reaction slowly occurred with a weak exotherm extending up to 1200°C.

Finally, The behavior of the ternary mixture $23\text{wt}\%\text{Al}-58\text{wt}\%\text{Cr}_2\text{O}_3-19\text{wt}\%\text{u-Ti}$ has also been investigated up to 1500°C. The DTA recording (fig 4) again exhibits endothermic decomposition of u-Ti, the initiation of aluminium melting, the exothermic Al_3Ti formation and the larger exotherm corresponding to the reduction of Cr_2O_3 followed by endothermic melting of Al_3Ti at 1350°C. Cooling back to room temperature evidenced the exothermic solidification of Al_3Ti at 1350°C and a second exothermic reaction beginning at 1080°C. This latter peak was not previously observed and is therefore believed to be related to some chromium species, but was not further identified.

Coming now to the complete multicomponent systems, referred as 019 and 020 (Table 1), DTA experiments were performed with constant heating rate (10K/min)(fig 5-6). After burning the organics at $\approx 220^\circ\text{C}$ the previously mentioned sequences of reactions again were observed. However, the corresponding peaks appeared to be more or less overlapping with each other. It should be pointed out here that XRD on the cooled material failed to detect the Al_3Ti intermetallic phase. It is therefore concluded that Al_3Ti must have reacted at some stage during cooling, but before its anticipated solidification temperature. Presumably with chromium or a chromium containing compound to yield another phase which remains unidentified. This point will again be considered below. Similarly, neither DTA nor XRD brought any evidence of chemical or structural change which could be specifically ascribed to the presence of small amounts of iron in either 019 or 020 compositions.

3-2- Microstructure and phases compositions

A typical example of microstructure obtained at the end of the reaction hot-pressing schedule is shown in fig 7. The major phases to be noted are : α -alumina (estimated mean grain size $\approx 3 \mu\text{m}$) and the chromium rich metal phase. Minor amounts of a third phase could also be detected by XRD and were more easily visible on the microstructure of samples corresponding to composition 020. This third phase appears as dispersoids always in contact with the metallic chromium phase and was never seen within Al_2O_3 grains (fig 8). Local element EDS analyses of both the alumina and chromium phases (Table 3) proved them to have dissolved some amounts of alloying elements. More precisely, chromium and titanium are present in the corundum phase presumably as oxides whereas most of the additive is found in the chromium metal areas. It may be noted that the chromium metallic phase is alloyed with 30wt% of iron which correspond to an iron initial composition twice that anticipated from table 1. A more comprehensive electron microprobe analysis of the third minor phase provided the following typical composition (Table 4). These latter results are consistent with an assumed overall composition $5\text{Al}_2\text{O}_3\text{-}4\text{Cr}_2\text{O}_3\text{-}11\text{Ti}_2\text{O}_3$ mixed oxide. It is important to bear in mind that such is only an estimation which is not meant to imply the corresponding grain to be single phase. It is tempting to assign to this mixed ternary oxide phase the previously mentioned unidentified set of XRD peaks (fig 9). Increasing the aluminium content in the starting powder mixtures has been observed to reduce the amount of the ternary oxide in the final material. It has not been possible however to eliminate it completely. Finally, changing the rate of heating in the 800-1000°C temperature range has been observed to affect the amount of Chromium dissolved in the $\alpha\text{-Al}_2\text{O}_3$ phase. Concentrations corresponding to $\text{Al}_{1.84}\text{Cr}_{0.16}\text{O}_3$ and $\text{Al}_{1.70}\text{Cr}_{0.30}\text{O}_3$ were estimated for 5K/min and 14K/min heating rates respectively. It therefore appears that competition between the kinetics of chromium oxide reduction by aluminium and chromium dissolution into alumina is taking place during such a temperature interval, and can be influenced by the heating rate.

Table 3: elemental analysis of the major phases by EDS

sample	Al (wt %)	Ti (wt %)	Cr (wt %)	Fe (wt %)
alumina phase				
019	80.5	1.5	16.4	1.5
020	83.5	2.5	14.0	0.0
metallic phase				
019	0.1	0.3	65.2	34.4
020	0.9	0.4	60.9	35.9

Table 4: ternary oxide composition (at%)

sample	Al	Cr	O	Ti	Fe
020	10.03	8.51	59.66	21.59	0.20

4- CONCLUSION

Synthesis of alumina-chromium cermets by reactive hot-pressing has been performed with granulated mixed powders consisting of aluminium, α -alumina and chromium oxide and additions of a titanium bearing compound and iron. The following sequence of reactions has been found to take place during heating :



During cooling the Al_3Ti melt seemed to react with a chromium containing compound to form mixed oxide compound(s) with overall composition $5\text{Al}_2\text{O}_3\text{-}4\text{Cr}_2\text{O}_3\text{-}11\text{Ti}_2\text{O}_3$ (as revealed by electron microprobe analysis) which remain unindexed by XRD. Secondly, the importance of the thermal schedule evidenced especially with the heating rate between 800 and 1000°C (temperature range corresponding to reaction between Al and Cr_2O_3) has been brought out as influencing the amount of dissolved chromium in the alumina phase. So heating rates could be used to control the amount of dissolved Cr_2O_3 in Al_2O_3 which, as shown by DAVIES [19], affects the mechanical properties of the α -alumina phase.

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References

- [1] P.ETTMEYER, W.LENGAUER, *Powder metallurgy international* **21** (1989) 37-38.
- [2] J.D.WALTON, N.E.POULOS, *J of Am. ceram. soc.* **42** (1959) 40-49.
- [3] A.R.BLACKBURN, *J. Am. Ceram. Soc.* **34** (1951) 327.
- [4] A.R.BLACKBURN T.S.SHELVIN, H.R.LOWERS, *J. Am. Ceram. Soc.* **32** (1949) 81.
- [5] T.S.SHELVIN, *J. Am. ceram. Soc.* **37** [1954] 140-145.
- [6] *Cermets*, Reinhold publishing corp. new-york (1960) 239.
- [7] *Metal handbook*, American Society for Metals **2** (1990) 978-1007.
- [8] C.H.HENAGER J.L.BRIMHALL, *Scripta met.* **26** (1992) 585-89.
- [9] G.GROBETY, T.SPERISEN, A.MOCELLIN, *Sci. of ceram.* **14** (1987) 315-20.
- [10] C.NISHIMURA, C.T.LIU, *Acta met.* **41** (1993) 113-20.
- [11] R.A.CUTLER, K.M.RIGTRUP, A.V.VIRKAR, *J am. ceram. soc.* **75** (1992) 36-43.
- [12] R.A.CUTLER, A.V.VIRKAR, J.B.HOLT, *Ceram. eng. sci. proc.* **6** (1985),715-28.
- [13] S.C.CHUANG, C.T.KUO, C.S.LEE, C.T.HO, A.K.LI, *J. of mat. sci.* **27** (1992) 5844-48.
- [14] J.BINNER, *metals and materials* (1992) 534-37.
- [15] *Handbook of chemistry and physics*, CRC press inc., 68st edition (1987).
- [16] N.EUSTATOPOULOS, D.CHATAIN, L.COUDURIER, *Mat. sci. eng.* **A135** (1991) 83-88.
- [17] A.H.SULLY, E.A.BRANDES, *chromium* 2nd edition Plenum pub (1967) 573-77.
- [18] *Binary alloy phase diagram*, American Society for Metals **2** (1986).
- [19] T.J.DAVIES, H.G.EMBLEM, C.S.NWOBODO, A.A.OGWU, V.TSANTZALOU, *Bri.ceram. trans.J.* **91** (1992) 71-76.

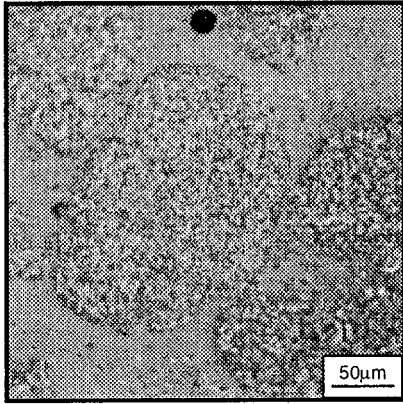


fig 1 : granulated powders (optical image).

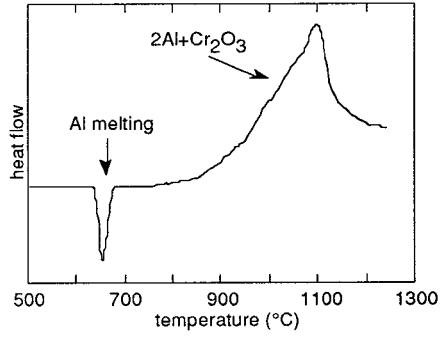


fig 2 : DTA of 2Al+Cr₂O₃ mixture (10K/min)

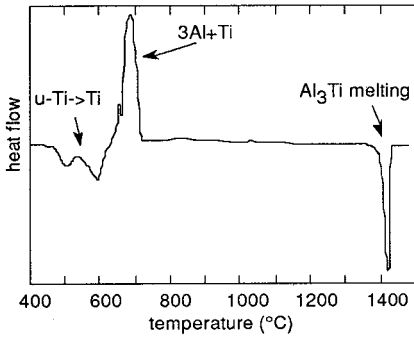


fig 3 : DTA of 3Al+u-Ti mixture (10K/min).

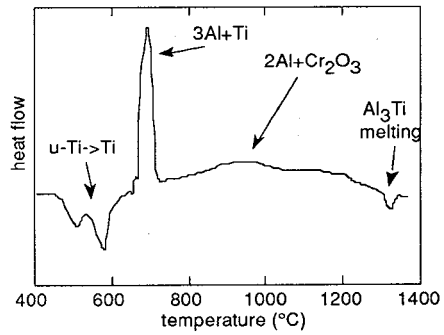


fig 4 : DTA of 23Al+58Cr₂O₃+19u-Ti(wt%) (10K/min).

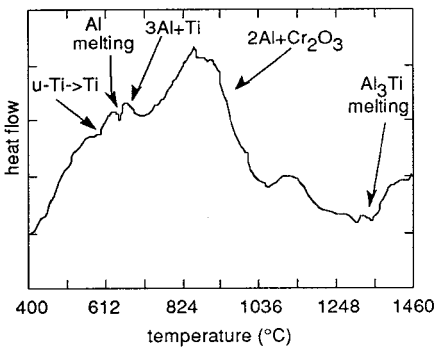


fig 5 : DTA of composition 019 (10K/min).

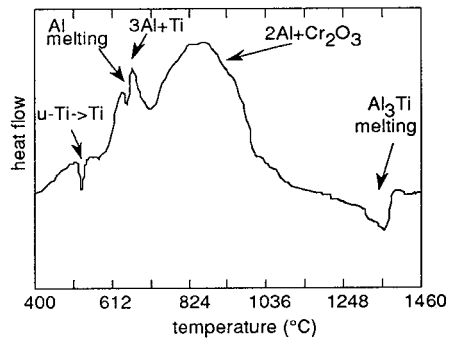


fig 6 : DTA of composition 020 (10K/min).

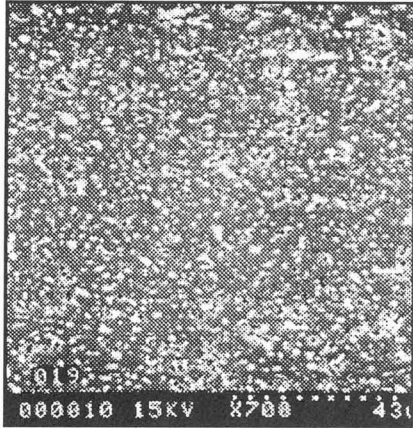


fig 7 : composition 019 (SEM image).

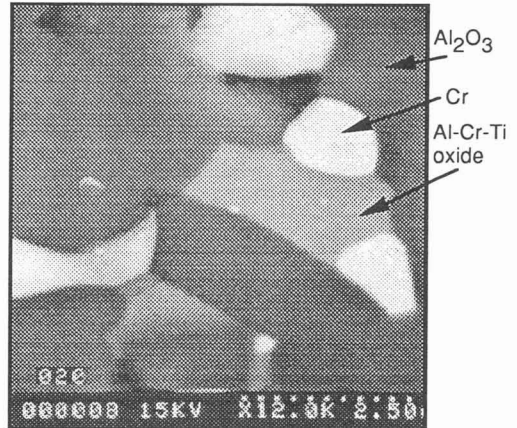


fig 8 : composition 020 (SEM image).

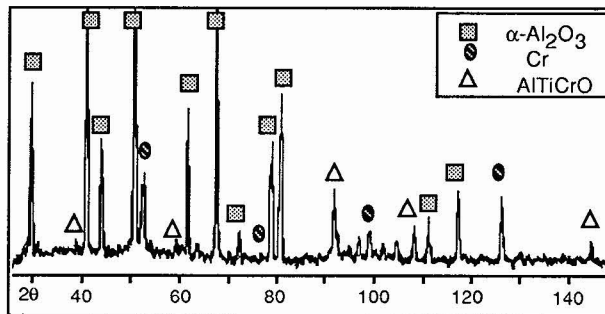


fig 9 : X-ray diffraction of composition 020 after sintering.