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Mechanical–Thermal Synthesis of Al₂O₃–Cr Composite Powders

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Abstract

Three different approaches have been investigated to synthesize alumina–chromium composites by displacement reactions between aluminium and chromia. The reactions have been performed either by pure mechanosynthesis or pure thermal ignition or also by a combined mechanical and thermal activation process. Differential thermal analysis, dilatometry and high temperature X-ray diffraction have been used to show the various reaction mechanisms and chemical transformations. High-energy milling of the powder modifies the reactivity of the system. A partial pre-milling treatment not only reduces the reaction temperature but can also induce a different reaction path. It has been shown that an appropriate mechanical–thermal treatment leads to the synthesis of an alumina–chromia composite by a pure solid-state process: intermediate reaction stages exhibit little if any liquid phases.

1 Introduction

Solid-state displacement reactions proceed generally by diffusional transformations whereby two or more reactants form new product phases.[1] Such reactions are of considerable interest for producing ceramic/ceramic or metal/ceramic composites *in situ* with novel microstructures and possibly improved properties.[1-6] Depending upon the thermodynamic and kinetic parameters of the reacting system, several types of product morphology can be obtained: from interwoven to more or less connected and dispersed microstructures.[7] The control of such morphologies during synthesis is a critical aspect of these processes. Their detailed mechanisms and kinetics have been investigated in several typical cases and found to be strongly related to the diffusion paths and rates of individual

species within the corresponding multicomponent system.[8-9]

In a conventional, thermally activated system, the diffusion processes are strongly related to temperature and the microstructure then depends on the thermal schedule. Nevertheless, for the case of some thermite reactions or self-propagating high temperature synthesis reactions (SHS), the prediction and control of the product morphology are less straightforward. In this type of reaction, involving for example the reduction of metallic oxides with aluminium to yield alumina and metals, a large quantity of heat is released,[10] which may be sufficient to heat some of the phases present above their melting points, thus making the control of microstructure difficult. Fine interwoven or dispersed homogeneous microstructures, favourable *a priori* for reaching high composite strength and toughness for example, require that displacement reactions be effected in carefully optimized conditions.

To this aim, a mechanical initiation of the reaction, referred to as 'mechanosynthesis', has been proposed as an alternative to the more classical thermal initiation. This mechanical process consists of repeated welding, fracturing and rewelding of powder particles in a high-energy ball charge. Reactive powder surfaces are brought into intimate contact and chemical reactions may take place gradually by short-range interdiffusion across welded interfaces. Then, after an appropriate milling time, the powders consist of finely divided, nanometre-sized crystallites with a high defect density and interface content. The exchange reaction occurs during this room temperature process. Sometimes the heat released during the reaction may initiate an unstable combustion effect which leads to a partial melting of the product and/or a phase separation as previously described, but in such a case a chemically inert substance[11] or a less reactive milling[10] can be used to keep the process under control. Although mechanosynthesis appears a simple and promising technique to

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yield homogeneous composite powders with nano-type characteristics, the benefits due to the displacement reaction approach may not be fully achieved as subsequent firing, necessary for consolidation into solid pieces, usually brings about coarsening and perhaps side reactions. Moreover, contamination from the milling environment is difficult to avoid.

To gain better understanding of the specific features, mechanisms and kinetics of reaction as influenced by thermal and mechanical activations respectively, the present experimental programme was devised so that sound comparisons could be made between either approach. It is conceivable that the results of such an investigation may subsequently find practical applications in composites processing via an optimized sequence of partial milling in order to bring the degree of reaction advancement to some appropriate level, followed by more conventional thermal activation up to completion. Three sets of experiments were consequently performed with a simple model system. The first one, consisting of pure thermal activation, was carried out with a blend of chromia and aluminium powders. The second, consisting of pure mechanical activation, was conducted by high-energy milling up to completion of the reaction. Finally, a combined mechanical and thermal activation was performed by short milling times followed by thermal treatment. These short milling times do not exceed the incubation time for the reaction when performed by grinding at room temperature.

2 Experimental Procedures

The starting high purity (> 99·9%) powder materials were metallic aluminium and chromium oxide (Cr_2O_3). Average particle sizes of both these powders were in the micrometre range: 1·3 and 0·5 μm, respectively. The as-received atomized aluminium powders were oxidized on their surface and their typical alumina content was 0·5–1 wt%.[12]

Powder blends of aluminium and chromia were prepared in proportions corresponding to the reaction scheme:

$$Cr_2O_3 + 2Al \rightarrow Al_2O_3 + 2Cr \qquad (1)$$
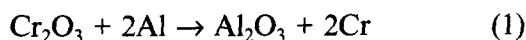
Milling was carried out in a planetary ball-mill (Fritsch Pulverisette 7) under argon atmosphere. Grinding utensils (seven balls of 15 mm diameter and vials) were either hardened chromium steel or tungsten carbide.

Thermal differential analyses were performed with a Setaram HTC-1800K equipment under argon flux. Heating rate was 10 K min^{-1} and alu-

mina was used as reference. Dilatometry experiments used an Adamel-Lhomargy DI 24 dilatometer under argon flux from 20 to 1500°C at a rate of 10 K min^{-1}. Samples (5 × 5 × 15 mm) were obtained by cold pressing the powders.

The resulting products were characterized at room temperature by X-ray diffraction (XRD) using CoK_α radiation. The mean crystallite size was estimated from the full-width at half-maximum of X-ray peaks.[13]

In addition, high temperature X-ray diffraction (HT-XRD) was used to follow directly the progress of reaction in samples pre-milled for different times with hardened steel tools. The XRD unit was a Philips powder diffractometer with a vertical goniometer PW 1050/25, graphite monochromator PW 1752/00, proportional counter for reflected beam PW 1711/10 and PW 1730/10 generator. The XRD was controlled by a PW 1710 diffractometer control system. The raw data were collected, processed and analysed with APD 1700 software supplied by Philips. The high temperature unit is based on an Anton-PAAR HTK-10 high temperature chamber. This standard equipment was re-engineered to increase the maximum working temperature to 2300 K. In designing the high temperature attachment, much attention was paid to the heating element. The platinum strip which is used as heater in the standard HTK-10 equipment was replaced by a graphite furnace.[14] The generator settings were 50 kV and 30 mA with a Cu-target tube. The temperature of the samples was measured with a Pt–13% Rh/Pt thermocouple. The runs were conducted with a quasi-constant heating rate of 7°C min^{-1} in a static helium atmosphere of 0·11 MPa. All scans were performed over a 2Θ range of 20–60°.

3 Results and Discussion

3.1 Thermal displacement reaction

Uncompacted $2Al/Cr_2O_3$ powder mixtures were heated to 1500°C in argon. These mixtures reacted, the chromium oxide being reduced by aluminium. The corresponding DTA is shown in Fig. 1. The endothermic melting of aluminium is quite apparent at 660°C, and the aluminothermic reaction is seen to initiate at 800°C and be completed at about 1200°C. The XRD analyses confirmed that the reaction products consisted of α-Al_2O_3 and chromium metal. HT-XRD revealed an amorphous liquid phase around 650°C, corresponding to the melting of aluminium (Fig. 2). No other intermediate transient phases were detected. Chromia is reduced in the simple direct but progressive way according to the following reaction as expected:
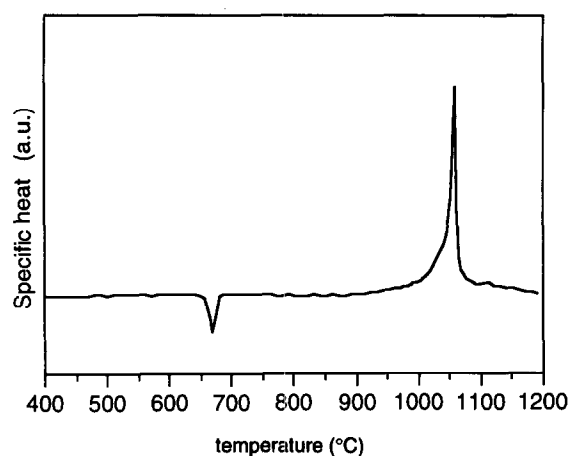
Fig. 1. DTA of 2Al + Cr₂O₃ powders (dT/dt = 10 K min⁻¹).

$$Cr_2O_3 + 2Al_{(liq)} \rightarrow \alpha\text{-}Al_2O_3 + 2Cr \qquad (1)$$

Dilatometry experiments confirmed the melting of aluminium and showed a sudden expansion of the sample (Fig. 3). The slight shrinkage observed just before aluminium melting can be explained by particle rearrangements favoured by the increasing ductility of the Al phase. The slope discontinuity at 850°C has not yet been unambiguously rationalized. It does not result from the overall molar volume change which is negative for reaction (1). Neither can it be ascribed to an effective thermal expansion coefficient which would be higher after
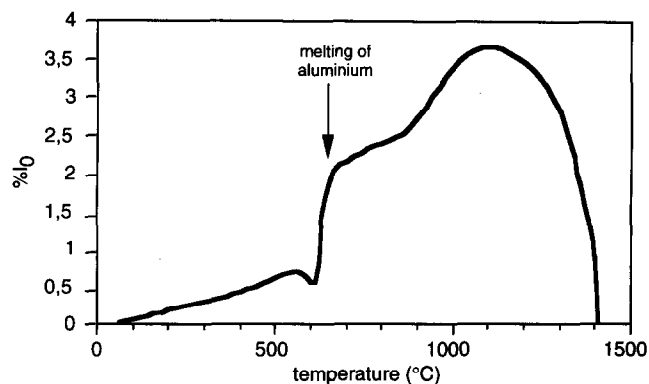

Fig. 2. HT-XRD patterns of 2Al + Cr₂O₃ powders: (a) as a function of temperature; (b) T = 650°C.

Fig. 3. Dilatometry of 2Al + Cr₂O₃ powders (dT/dt = 10 K min⁻¹).

the system has reacted than before, because re-heating the same sample after cool-down yields a different and smaller slope than upon this first heat-up. Bloating due to some gas evolution can also be ruled out since thermogravimetric experiments showed that, if anything, the sample mass tended to increase very slightly (presumably due to oxidation by residual oxygen present in the system). It may nonetheless be worth pointing out that 850°C coincides with the temperature at which Al₂O₃ characteristic lines are first detected on the HT-XRD patterns.

3.2 Mechanosynthesis

The synthesis of nanocomposite powders of alumina-Cr has been investigated by reactive milling with either hardened steel or tungsten carbide tools. In the former case, only a partial reaction was obtained. Even milling for 48 h was not enough to reach a complete transformation of the initial mixtures. In the latter case, the reaction starts suddenly after ~15 min incubation milling time (Fig. 4), then the reaction needs 1 h to be completed. Beyond that time, the XRD patterns show peaks of α-alumina and chromium, neither chromia nor aluminium could be detected by XRD.
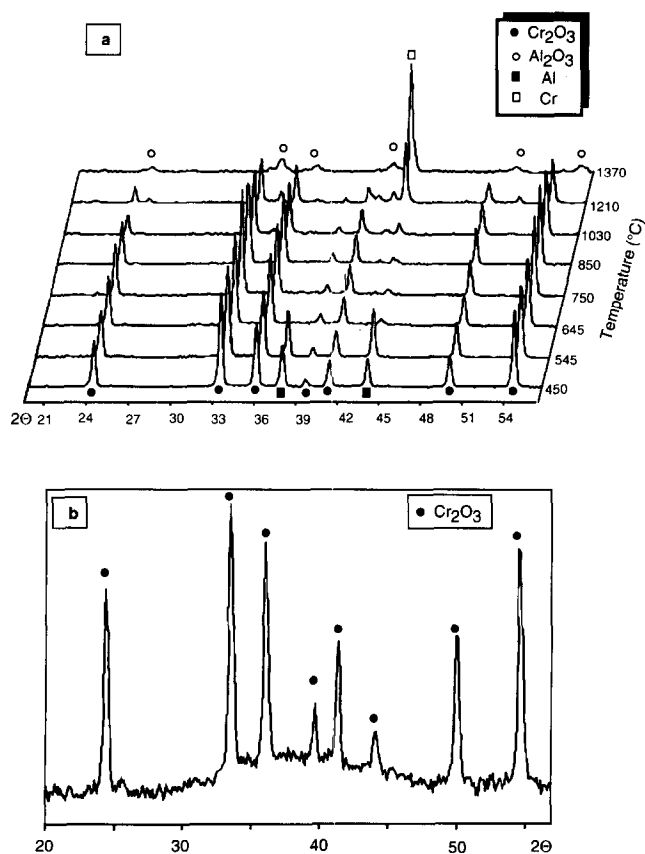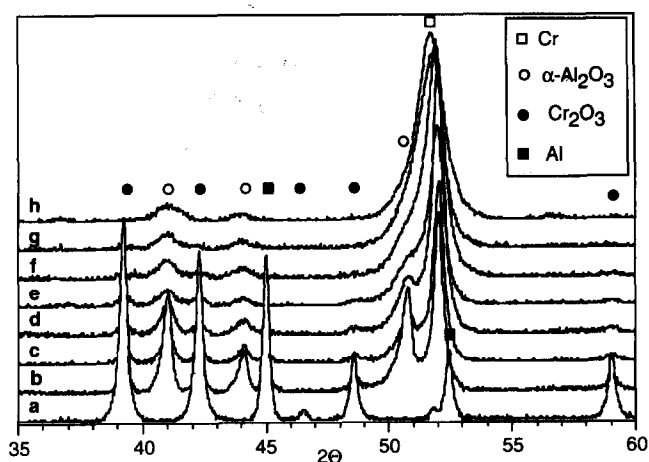

Fig. 4. X-ray diffraction patterns of Al₂O₃-Cr powders mechanically alloyed in carbide tools after various times: (a) 8 min; (b) 15 min; (c) 23 min; (d) 30 min; (e) 45 min; (f) 60 min; (g) 90 min; (h) 180 min.

After 1 h, nanometre-sized crystallites are produced from micrometre-sized powders (Fig. 5). And after a milling time of 3 h, for example, the mean crystallite size lies around 10 nm for both Al_2O_3 and Cr. The corresponding particles show homogeneous sub-micrometre microstructure of α-Al_2O_3 and chromium (Fig. 5).

No major changes were detected by differential thermal analysis on the powders milled for 3 h except for a large variation of the baseline up to 800°C. The diffraction patterns of samples before thermal treatment are identical to those of the original milled powders, except for the line width. Such variation of the DTA baseline and X-ray peak profiles with decreasing width reflect crystal-

lite growth. Significant crystallite growth occurred only after reaching 900°C.[15]

3.3 Combined mechanical–thermal synthesis

The above experiments have shown the existence of an 'incubation time' during mechanosynthesis. A certain level of mixing, particle refinement and accumulation of lattice defects are thought to be needed for ignition, and then the combustion reaction may be completed rather quickly. The pre-ignition time depends on the experimental conditions and the start of the reaction is a direct consequence of the so enhanced chemical reactivity.[16]

To gain a better understanding of the effect of short milling on the subsequent course of events, two-stage experiments were carried out. The powders were mechanically alloyed with steel utensils using different grinding times within the incubation period, and the resulting powders then were thermally treated. The choice of steel grinding tools was made so that the kinetics of mechanosynthesis be slower and the incubation time longer than with the carbide utensils.[10] The reduction was studied by DTA (Fig. 6), dilatometry (Fig. 7) and high temperature X-ray diffraction (Fig. 8).

For the powders milled for 5 min, these different experiments revealed no large differences compared with the unmilled powders, i.e. the melting of aluminium and the occurrence of the displacement reaction were still observed in the range 650–750°C and 800–1200°C, respectively. Thus the first 5 min can be viewed as a time of mixing and of homogeneization at the particle size scale. No significant energy due to grinding is present in the
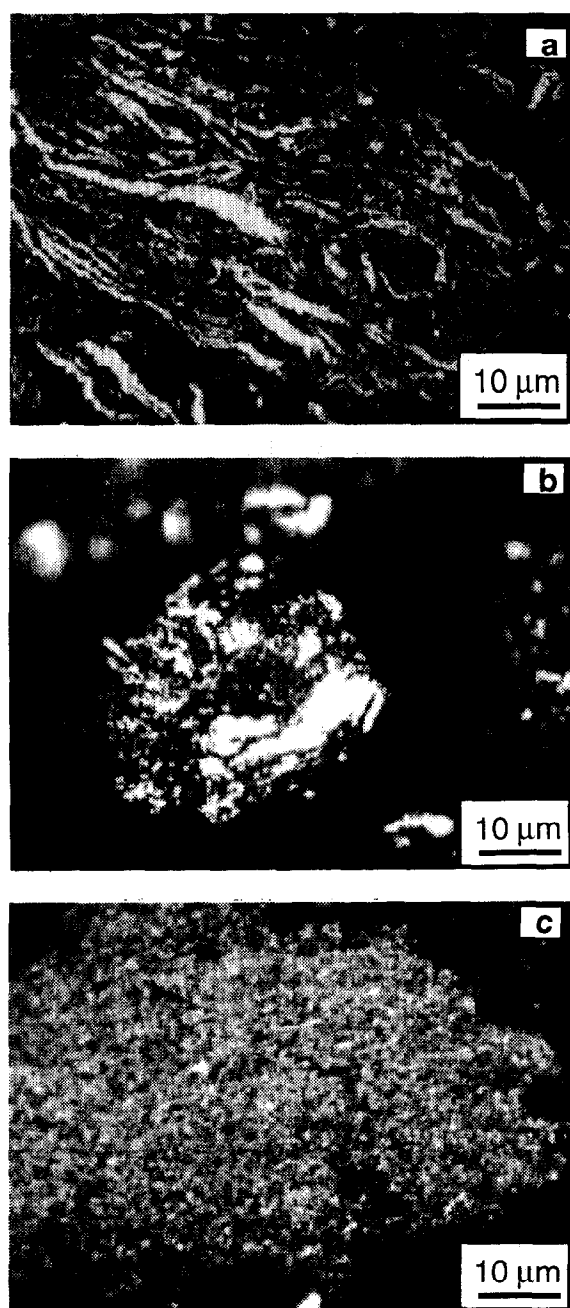

Fig. 5. Optical micrographs of Al_2O_3–Cr powders prepared by mechanosynthesis $2Al + Cr_2O_3$ powders after various milling times: (a) 20 min; (b) 60 min; (c) 180 min. Light phase: chromium, dark phase: alumina.

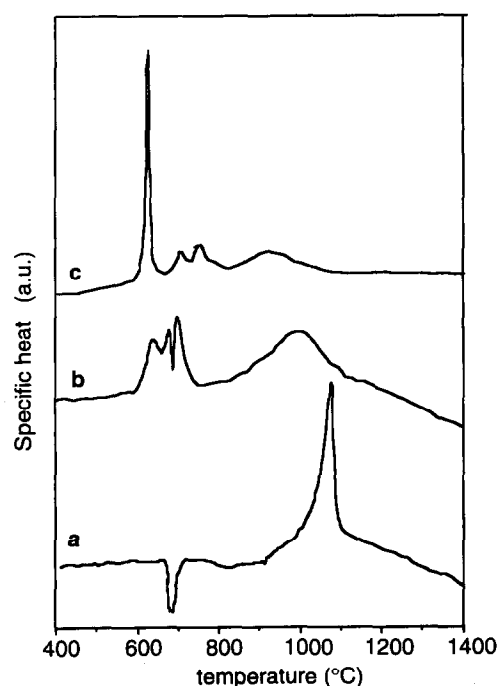**Fig. 6.** DTA of milled $2Al + Cr_2O_3$ powders (dT/dt = 10 K min^{-1}) after (a) 5 min, (b) 15 min and (c) 30 min.

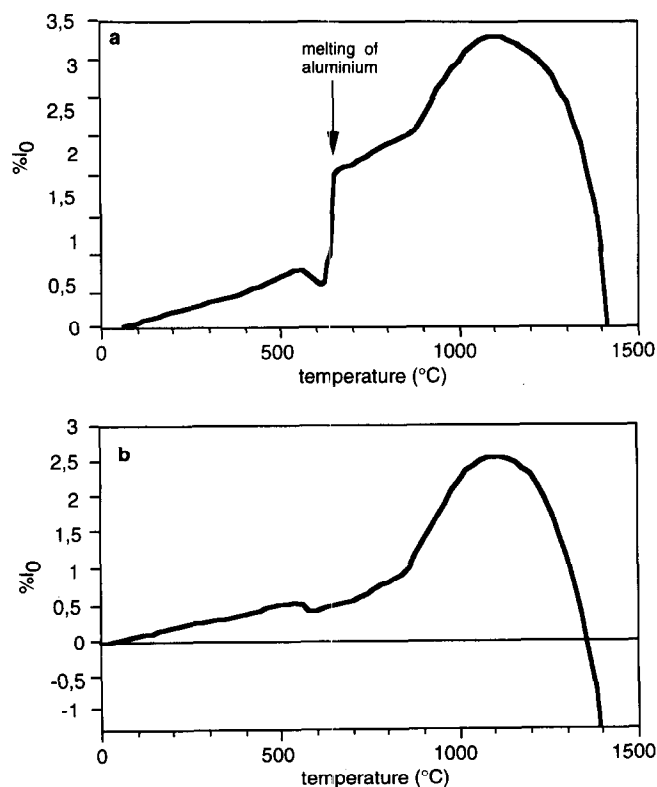Fig. 7. Dilatometry of 2Al + Cr₂O₃ powders mechanically alloyed for (a) 15 min and (b) 30 min ($dT/dt=10$ K min⁻¹).

Fig. 8. HT-XRD patterns of 2Al + Cr₂O₃ powders mechanically alloyed for (a) 15 min and (b) 30 min.

crystallite, except possibly for a small amount of extra surface energy arising from a small reduction of average particle sizes.

For longer milling times (15 and 30 min), the experiments showed drastic differences. Concerning the melting of aluminium, we observed near 660°C a progressive decrease both of the endotherm in the DTA curves and of the expansion effect in the dilatometry curves. With the 30 min milled powders it was not possible to detect any aluminium melting. Parallel to this phenomenon, the large exotherms in the DTA curves due to the displacement reaction were modified. New exotherms appeared in the range 550–700°C, while the large exotherm centred near 1100°C progressively decreased in intensity with milling time and was shifted to lower temperatures. For the 30 min milled powders, only a weak thermal effect was observed between 800 and 1000°C, but a large exotherm was observed at 620°C. On the other hand, except for the modification of the aluminium melting, the dilatometry recordings were similar to those obtained with the unmilled thermally reacting system (Fig. 3).

The HT-XRD patterns help clarify the reaction path. First of all an amorphous liquid phase is observed around 650°C with the powders milled for short times. But this phase could not be observed for the 30 min powders. For this milling time, a solid-state reaction was obtained without any intermediate liquid phase.
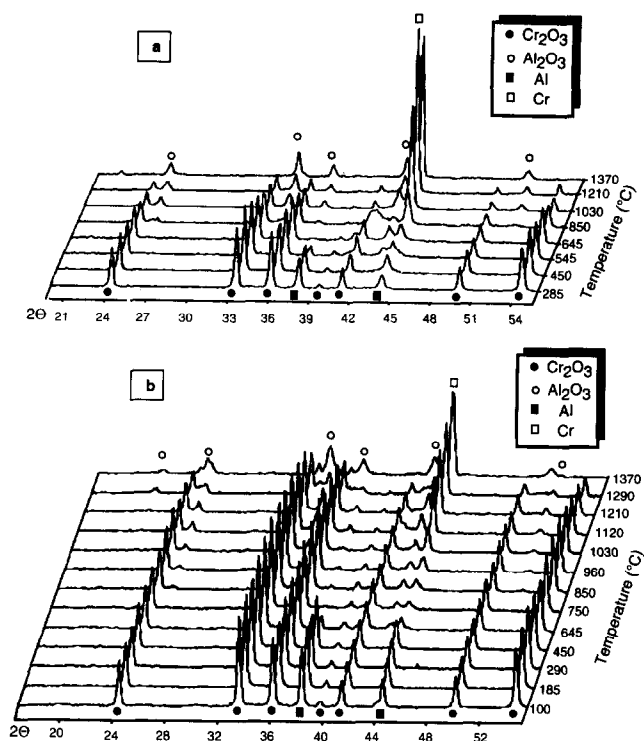
For the 5 min milled powders, the (110)Cr peak was observed above 850°C and the converted fraction of chromia strongly increased above 1000°C. For the 30 min milled powders, however, a small amount of metallic chromium was detected at room temperature and the converted fraction of chromia was seen to increase above 600°C. The 15 min sample appeared to exhibit an intermediate behaviour and two steps may be identified. A first formation of chromium is observed in the range 650–800°C and a second formation appears above 1000°C. The temperature intervals of both chromium formation steps appear to correspond to exotherms observed on the DTA curves. Each exotherm, either between 600 and 650°C or 850 and 1200°C, thus corresponds to the heat released by the reduction of chromia by aluminium. It is interesting to note the presence of an intermediate second low temperature exotherm (650–750°C). This one is thought to be related to the transient formation of Al₇Cr and/or Al₆Cr compounds[17] observed by HT-XRD on the 15 and 30 min samples. The X-ray peaks were too few and too weak to allow for their compositions to be more precisely established but it is thought that formation of these phases is due to the reaction between the already formed chromium and the not yet reacted aluminium.

In summary, the present experiments revealed two different chemical reaction paths: a classical 'non-milled reaction' path (near 1000°C) between Cr₂O₃ and liquid aluminium, and a modified 'milled reaction' path (near 600°C) which is a pure solid-state reaction.

4 Conclusions

The present experiments show that, depending on activation mode and milling time, a displacement reaction path can be modified by an appropriate choice of experimental conditions. The onset of a reaction is essentially determined by its activation energy, i.e. the difference in energy between the activated and the initial states. Repeated milling enhances the reactivity of powder particles via the development of large amounts of interfaces and defects. During an 'incubation period', chemical characteristics are modified and energy is being stored in the powders, thereby reducing the activation barrier compared with that of the classical reaction route. If the thermal treatment provides an energy to overcome the activation barrier, due to the modification of the reaction path, the reaction may initiate at lower temperature and could result in different final microstructures.

Some monitoring of this residual activation barrier is then possible by the way of choosing the grinding conditions. Then, by appropriate choices of the chemical status of the reactants and the operating conditions (grinding and heating), the systems are allowed a greater freedom in selecting reaction paths than with temperature as the only activation parameter. The ability to control the size and morphology of the composite particles, while not demonstrated here, gives thermal–mechanical displacement reaction processing important advantages over other routes of synthesis. By avoiding the formation of liquid phase, such oriented reaction paths could bring novel solutions to the development of a whole range of composite microstructures.

References

1. Henager, C. H., Brimhalland, J. L. & Hirth, J. P., Synthesis of a MoSi$_2$/SiC composite *in situ* using a solid state displacement reaction between Mo$_2$C and Si. *Scripta Met.*, **26** (1992) 585–604.
2. Grobety, G., Sperisen, T. & Mocellin, A., Influence of powder processing on mechanical properties of TiN/Al$_2$O$_3$ particulate composite prepared by reaction hot-pressing of AlN/TiO$_2$. *Sci. of Ceram.*, **14** (1987) 315–20.
3. Nishimura, C. & Liu, C. T., Reactive sintering of Ni$_3$Al under compression. *Acta Met.*, **41** (1993) 113–20.
4. Cutler, R. A., Rigtrup, K. M. & Virkar, A. V., Synthesis, sintering microstructure and mechanical properties of ceramics made by exothermic reactions. *J. Am. Ceram. Soc.*, **75** (1992) 36–43.
5. Cutler, R. A., Virkar, A. V. & Holt, J. B., Synthesis and densification of oxide–carbide composites. *Ceram. Eng. Sci. Proc.*, **6** (1985) 715–28.
6. Chaung, S. C., Kuo, C. T., Lee, C. S., Ho, C. T. & Li, A. K., Alumina–chromium carbide composite through an internal synthesis method. *J. Mater. Sci.*, **27** (1992) 5844–8.
7. Rapp, R. A., Ezis, A. & Yurek, G. J., Displacement reactions in the solid state. *Metall. Trans.*, **4** (1973) 1283–92.
8. Shatynski, S. R., Hirth, J. P. & Rapp, R. A., Solid-state displacement reactions between selected metals and sulfides. *Metall. Trans.*, **10A** (1979) 591–8.
9. Wang, L. L., Munir, Z. A. & Maximov, Y. M., Review thermite reactions: their utilization in the synthesis and processing of materials. *J. Mater. Sci.*, **28** (1993) 3693–708.
10. Osso, D., Tillement, O., Le Caer, G., Mocellin, A. and Matteazzi, P., Alumina–metal nanocermets by mechanosynthesis. In *8th CIMTECH, Proceedings of World Ceramics Congress and Forum on New Materials.* Techna srl, Faenza, Italy, 1994.
11. Schaffer, G. B. & McCormick, P. G., Displacement reactions during mechanical alloying. *Metall Trans.*, **21A** (1990) 2789–94.
12. Eckart-Werke, Technische information, F 385 (1992)1.
13. Matteazi, P. & Le Caer G., Synthesis of nanocrystalline alumina–metal composites by room temperature ball milling of metal oxide and aluminium. *J. Am. Ceram. Soc.*, **75** (1992) 2749–53.
14. Babushkin, O., Harrysson, R., Lindbäck, T. & Tegman, R., A high temperature graphite furnace for X-ray powder diffraction, *J. Meas. Sci. Technol.*, **4** (1993) 816–19.15. Osso, D., Elaboration de nanocomposites alumine-métal par mécanosynthése. Thesis, Institut National Polytechnique de Lorraine, Nancy, France, 1995.
16. Boldyrev, V. V., Mechanochemistry and mechanical activation of solids. *Solid State Ionics*, **63–65** (1993) 537–43.
17. Reference patterns 39-1276, Powder diffraction file. JCPDS, USA.