TiC–NiAl composites obtained by SHS: a time-resolved XRD study

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Abstract

Self-propagating high-temperature synthesis (SHS) has been performed in the quaternary Al–Ni–Ti–C system in order to obtain intermetallic–ceramic composites. These kind of reaction synthesis are very fast (linear velocity of the synthesis front is in the range 1–100 mm/s) and the productivity would be very high from the industrial point of view. Nevertheless, this characteristic is a negative point when synthesis mechanism and kinetics must be studied. There are only a few tools with enough time resolution in order to study these kinds of fast reactions. Synchrotron radiation (ESRF, Grenoble) has been employed to follow the reactions in situ on a time-scale of ∼100 ms. Powder diffraction patterns were recorded in this time-interval using a high-speed CCD camera coupled to an image intensifier X-ray sensitive detector with 1024×1024 pixels frames. As the reactions proceed patterns from the pre-heated, reaction front, post-heated and cooling zones of the reaction were sampled. The phases occurring during the reactions were identified and information of the reaction mechanism and the nucleation kinetics were obtained. SEM was used to characterize the final microstructure. © 2002 Published by Elsevier Science Ltd.

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1. Introduction

Self-propagating high-temperature synthesis (SHS) is an interesting method for producing a wide variety of light-weight ceramics, intermetallic compounds and composite materials.[1,2] The method is based on the use of the heat released during exothermic reactions in order to preheat raw materials and to obtain a self-sustained system. Reaction is started by the use of an electric or chemical system and after ignition the reactions proceed as a reaction front with linear speeds of 1–100 mm/s through the compacted raw materials in powder form. Temperature in the reaction front is related to the reaction synthesis, compaction of the raw materials, specific surface, and other processing parameters[2] and reach up to a few thousands of degrees. The procedure has a low energy consumption and has large potentials for industrial applications due to the high productivity and the very simple equipment involved. Also, synthesis and sintering could be made within only one step.[3] Due to the high temperatures and velocities of reactions, limited information is available on the mechanism and on the kinetics of these processes.

Although pioneering work has been performed at first and second generation synchrotron X-ray sources,[4–6] these early studies were complicated by limited counting statistics and limited volume of sample studied. The emergence of third generation synchrotron storage rings provides intense X-ray beams at high energies and it is now possible to follow these reactions in situ.

The Material Science beamline (ID 11) at the European Synchrotron Radiation Facility in Grenoble, France[7,8] has been used to study the exothermic reactions of the systems Al-Ni, Al–Ni–Ti–C and Ti–C. This paper describes time-resolved diffraction studies of these solid state reactions with a time-resolution of ms. Experimental setup and some of the results obtained studying synthesis in the quaternary system Al–Ni–Ti–C are reported. SEM images will provide complementary information in order to give further information on the

reaction kinetics and mechanisms. Obtained products, ceramic–intermetallic composites, have properties which make them very attractive for many industrial applications. Considering their low density and their high wear resistance and refractoriness, compounds of the system Al–Ni–Ti–C can be used to produce cutting tools and high temperature wear resistance components.

2. Experimental procedure

The following starting materials have been used: (1) 99.3% pure Ti metal (William Rowland Ltd. UK) with particle size smaller than 180 μm. (2) 99.5% Al metal (Alcoa, USA) with an average particle size of 16 μm. (3) 99% pure Ni metal (William Rowland Ltd. UK) with particle size smaller than 150 μm. (4) Graphite powder 99.6% (Sofacel, France) with average particle size of 10 μm.

Ti, Al, Ni, and C powders were mixed together within the molecular ratio 1:1:1:1 in a porcelain mortar and axial pressed in a 20 mm diameter stainless steel die. A pressure of 30 MPa. was applied in order to obtain approximately 55% of the theoretical density and a thickness of about 2 mm. Samples were placed between X-ray source and detector in order to record diffraction rings from the volume of the sample. The X-ray beam was centered on the middle of the sample. The experimental setup is illustrated in Fig. 1.

2.1. The X-ray source

The European Synchrotron Radiation Facility (ESRF) is a third generation X-ray synchrotron operating at an electron energy of 6 GeV with a maximum ring current of 200 mA. The beam life time (l/e) is in excess of 50 h and the beam is stable to within a few μm for extended periods of time. The ID-11 beamline is an insertion device bean-line optimized for Materials Science applications providing copious X-ray flux in the energy range 5–100 keV produced by either a 24-pole 1.25 T wiggler or a 138 pole, 23 mm period in vacuum undulator with a minimum gap of 8 mm. In this study the undulator was used at a wavelength of 0.295 Å producing a X-ray beam of $1.6 \ 10^{12}$ photons/s/O. One per cent BW over an 0.2×0.2 mm^2 area defined by slits. The X-rays were monochromatized by a double crystal Si_{111} monochromator giving an energy band pass of $\Delta E/E = 10^{-4}$. The short wavelength was chosen to allow transmission experiments with full penetration of the samples.

The reactions were started by heating one point of the lateral area of the pellets by resistive heating of a tungsten wire. Titanium powder was placed between the sample and the wire in order to further increase the local temperature.

The initiating current was fed through the wire 4 s before the starting pulse to the acquisition system composed of a Frelon CCD camera connected to an X-ray image intensifier detector.[9]

For a 1024×1024 pixels frame, the exposure time was 35 ms and total readout and data storage time was 65 ms per frame. During the experiments a total of 100 frames could be recorded consecutively at this speed. The data collection was controlled by a workstation (SUN Microsystems).

The initial, pre-reaction, reaction and post-reaction regions could thus be recorded and the exposed frames
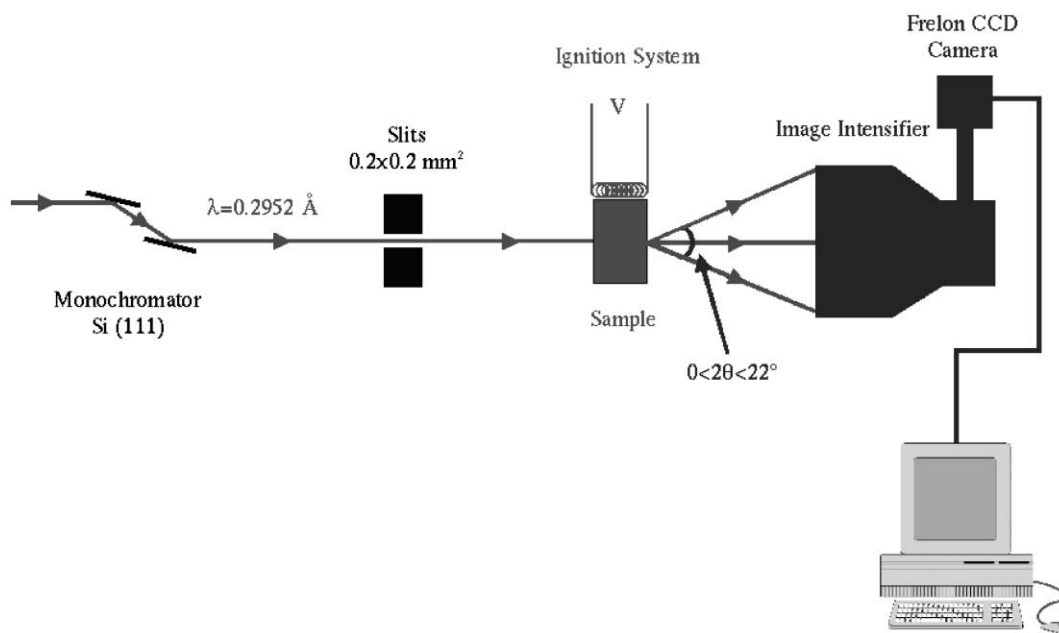

Fig. 1. Experimental setup.

were stored in the memory of the workstation. The frames were subsequently transferred to other computer storage and corrected for spatial distortion by the computer program FIT2D.[10] A powder diffraction pattern of the final product was also recorded several seconds after the end of the reaction with identical exposure conditions.

3. Results and discussion

The SHS reaction of the system Al–Ni–Ti–C was followed by time-resolved powder diffraction from the central portion of the reaction sample. Fig. 2 gives an overview of the recorded diffraction patterns as the reaction proceeds. The process was studied by six different experiments with reproducible results. The kinetic varies slightly because of small changes in the density of the different samples.

As the reaction front proceeds through the sample, the patterns recorded show the onset of the reaction, the reaction front, the subsequent reaction and the cooling down period from the center of the sample. The effective sampling period is 100 ms. It can be seen that a dramatic change in the diffraction pattern occurs after 1.3 s when the Al powder melts.

Figs. 3 and 4 show the diffraction patterns between $t = 1.3$ to $t = 5.6$ s. At the second frame in this picture a dramatic change occurs with noticeable changes in the intensities of the powder lines; some lines appear and others disappear. The first clear indication is the melting of the Al powder (see for instance the disappearance of the Al_{200} at $2\theta = 11.8°$). The melting of the Al is accompanied by a general increase in the background as the material change to the liquid state. At this time one also notices the appearance of two new sets of lines; one which remains to the end of the reaction and one which

disappears after 400 ms ($t = 1.7$ s.). The first set of lines belong to the TiC compound (TiC_{200} at $2\theta = 7.60°$). The second set of lines ($2\theta = 7.88°$) correspond to a transition phase. Since these lines do not appear in reactions of the binary systems Al–Ni, Ni–Ti, Al–Ti or Ti–C it can be deduced that it is probably not a binary phase. The identification is under way.
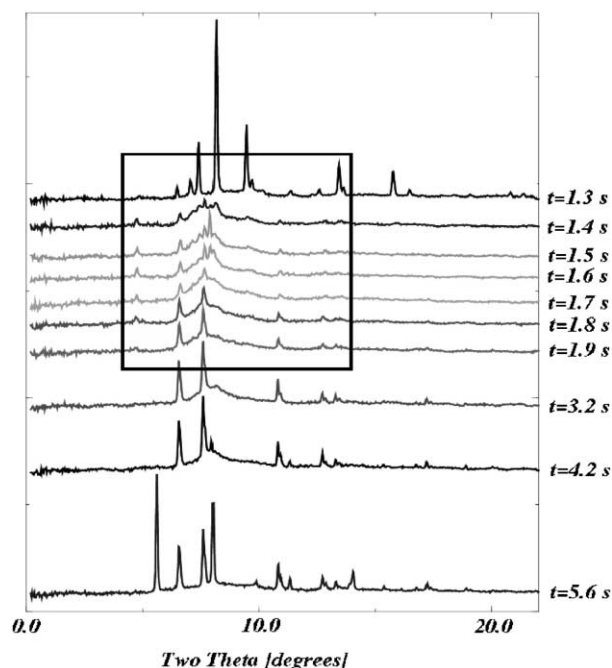

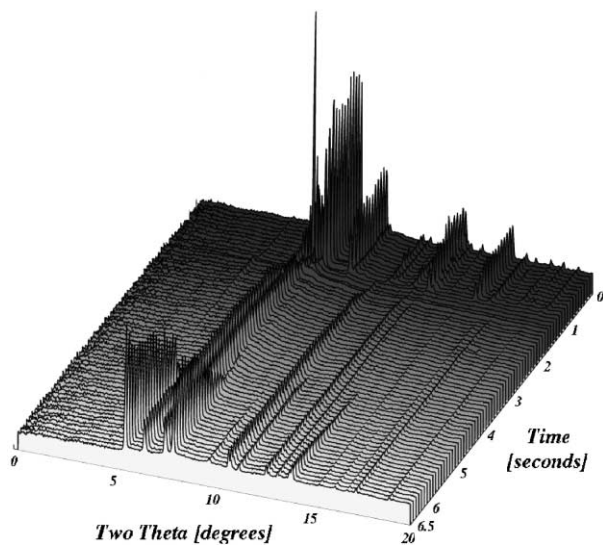Fig. 3. Evolution of the integrated diffraction patterns during synthesis.

Fig. 4. Evolution of the integrated diffraction patterns during synthesis (zoom).

Fig. 2. X-ray diffraction patterns evolution of the Al–Ni–Ti–C mixture during SHS.
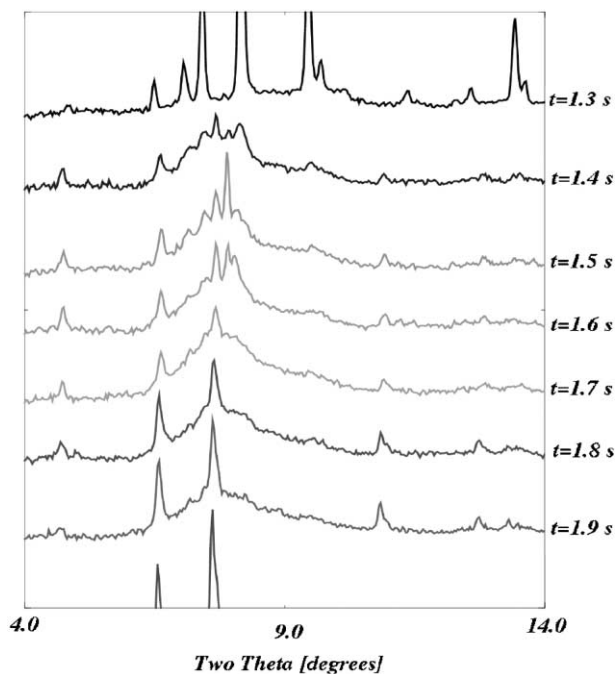
The reaction proceeds after the initial melting of Al by a subsequent melting of Ni after 200 ms ($t = 1.5$ s) as evidenced by the disappearance of the Ni_{200} at $2\theta = 9.54°$. 300 ms after the start of the reaction ($t = 1.6$ s) the Ti powder lines disappear (T_{101}, at $2\theta = 7.43°$). After 600 ms ($t = 1.9$ s) the carbon lines disappear (C at $2\theta = 4.73°$).

The formation of TiC reaches its maximum value after 1.8 s ($t = 3.1$ s) whereas the NiAl compound appears quite late at $t = 4.2$ s (2.9 s after the start of the reactions) accompanied by a general decrease in the background. Some discontinuities in the intensities can be observed caused by the formation of large single grains with different orientation. These changes can be observed in Fig. 5 where evolution of intensities of the mentioned diffraction lines are shown. From this it can be deduced that TiC synthesis starts at the same time as the melting of Al and Ni and the disappearance of Ti. It
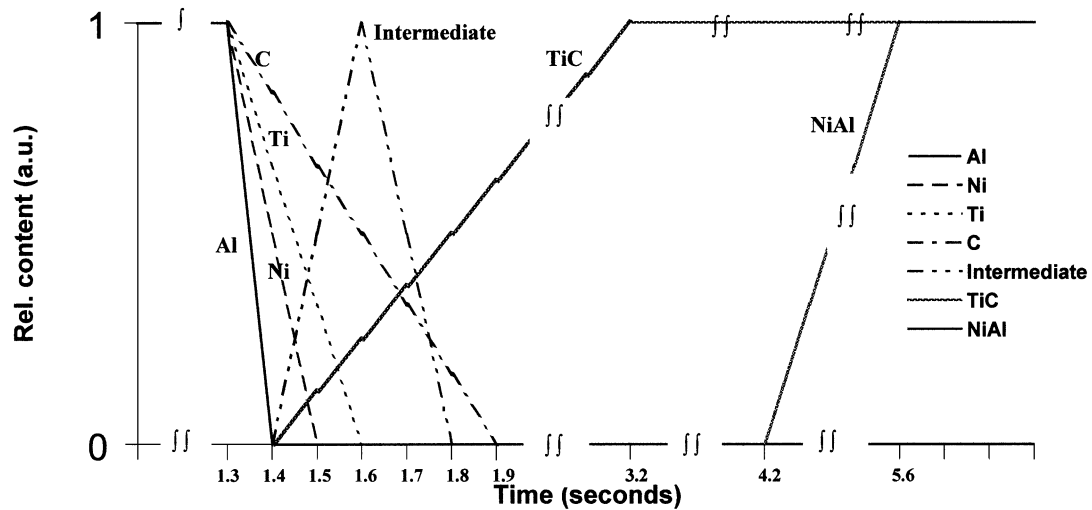

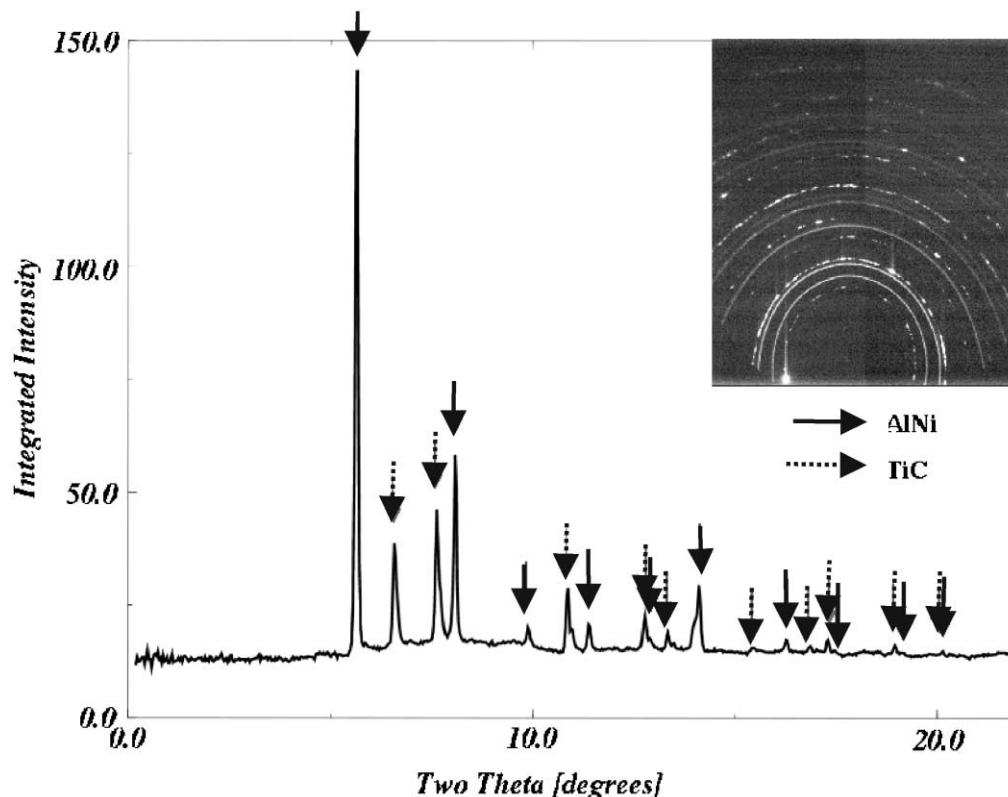Fig. 5. Evolution of peak intensities during SHS.

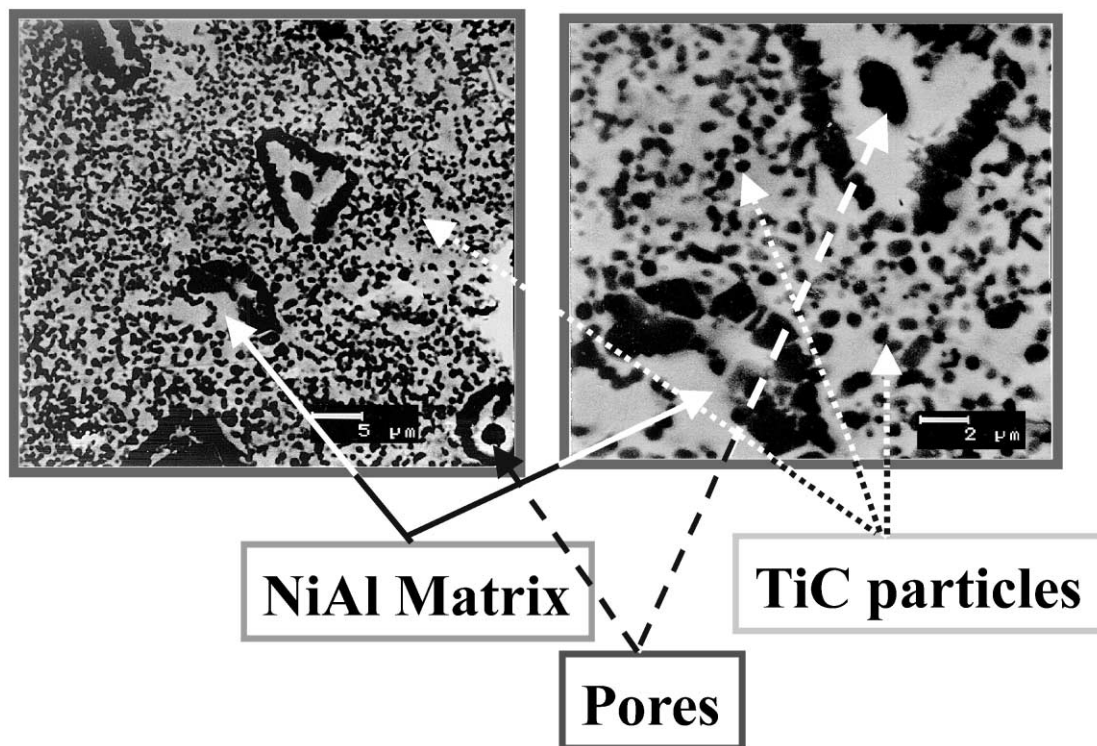Fig. 6. Final diffraction pattern after synthesis.

Fig. 7. Scanning electron micrograph of material obtained after synthesis.

means that TiC synthesis is the responsible of most of the physicochemical changes in the sample produced by the high temperatures reached due to the high value of enthalpy of this reaction. The synthesis of TiC might begin by a solid state reaction and the heat released produces the melting of Al and Ni. Thus, Ti disappears partly because of the TiC formation and partly because of the formation of a metastable phase (probably a ternary phase) which, during cooling, disappears giving TiC and Al, Ni melts. This point is supported by the fact that Ti disappears completely at the same time that this phase reaches the maximum concentration. After this phase disappears the rest of C is consumed giving the maximum content of TiC. NiAl precipitates later from the melt.

Fig. 6 gives the final diffraction pattern after the system has reached its thermal equilibrium. It can be noted that the TiC patterns are regular whereas the NiAl lines are quite ragged. This suggests that the TiC compound is under the form of small grains and the NiAl compound of large grains. This is being confirmed by electron microscopy studies of the final products.

This mechanism is fully compatible with microstructure shown in Fig. 7. Fine and well distributed round particles of TiC (particle size ~1 µm) can be observed in a continuous matrix of NiAl.

4. Conclusions

- The SHS reaction of the quaternary system Al–Ni–Ti–C has been followed by time-resolved powder diffraction, using a third generation X-ray synchrotron source, with a time-scale of 100 ms allowing a detailed study of the reaction mechanism. The intense X-ray source allowed full diffraction rings to be recorded with very good counting statistics.
- The reaction starts with the synthesis of TiC followed by melting of Al and Ni and a subsequent rather slow formation of NiAl during cooling. The TiC formation begin through a solid state reaction. An intermediate transition phase is observed during the synthesis. Further studies are under way to identify the transition phase.
- The final product is composed of small, round TiC particles embedded in a continuous matrix of NiAl. No more phases are present.

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