Real Time X-Ray Diffraction Study of the Formation by SHS of the Phases γ' and H in the Ternary System Al Ni Ti

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Abstract. The formation of two compositions ($\text{Al}_{0.20}\text{Ni}_{0.75}\text{Ti}_{0.05}$ (γ') and $\text{Al}_{0.27}\text{Ni}_{0.50}\text{Ti}_{0.23}$ (H)) in the ternary system Al Ni Ti by solid-state high temperature synthesis (SHS) was investigated. In addition Time-Resolved X-Ray Diffraction (TRXRD) studies were carried out using a synchrotron X-ray beam and a fast detection system to monitor the phase transformations. With a time resolution of 30 ms, it was possible to observe intermediate phases by scattering of the intense X-ray beam irradiating the sample surface during the passage of the combustion front. For the two reactions Ni(Al) was observed before the appearance of the final product. These experiments have been completed by Electron-Probe MicroAnalysis (EPMA) of sample in which the reaction had been stopped. They showed concentration gradients and transitory states. Moreover, we noted for the γ' formation a steady combustion propagation with a great speed while propagation of the combustion front for the H formation was pulsating. Associating these two techniques led to a better understanding of the different phenomena which exist during liquid-solid or solid-solid combustion reaction.

1. INTRODUCTION

Since many years, our laboratory uses the self-propagating high temperature synthesis (SHS) to determine enthalpies of formation of intermetallics [1]. Recently we began to study the structural transformations induced by SHS [2]. This process consists in syntheses of compounds with negative enthalpies of formation from the compacted elemental powders which are heated by an external source. This heating ignites the reaction which becomes self sustaining and propagates through the specimen. As the combustion wave advances, the reactants are converted into the product. The process is characterized by a fast-moving combustion front (1-100 mm/s) and a temperature which may reach several thousand K [3].

In our case, we decided to study the formation of two ternary phases in the system Al Ni Ti, γ' and H. Nickel and titanium aluminides have already been under scrutiny because of their attractive mechanical properties at high temperature which could make them substitutes for superalloys. SHS requires small energy quantities and leads to cleaner products because of the combustion front high temperature which is responsible for volatilization of many impurities and the absence of contamination due to melt-crucible interface reactions during the routine melt processing [4]. We want to determine the reaction steps and their kinetics. It is possible by scattering of an intense X-ray beam irradiating the specimen surface during the reaction and by collecting and storing the patterns with a very fast detector. We used a X-ray beam (D43) produced by the LURE synchrotron in Orsay (France) and a detector capable of recording a full scan every 30 ms during 1 minute (2048 scans).

2. EXPERIMENTAL DESCRIPTION

The combustion chamber is represented in figure 1. Elemental powders were hand-mixed with a pestle and a mortar inside a glove-box under a purified argon atmosphere and pressed within a steel mould into the form of a small pellet ($20 \times 10 \times (2-3)$ mm³). Powders of aluminium (< 400 μm) obtained from Prolabo (> 99% pure), of nickel (4 to 7 μm) obtained from Goodfellow (99.8% pure) and of titanium (< 44 μm) obtained from Ventron (99.7% pure) were used during this investigation. After compaction, samples had a green density in the range of 65-75% of their theoretical bulk density. They were placed in an alumina sample-holder which was positioned at the center of the chamber. An electrical-heater made of a tungsten

coil inserted into a alumina support was placed near one end of the sample. When a sufficient intensity passed through the wire, the reaction initiated. As soon as ignition was detected the energy source was turned off. The temperature measurements were made by a chromel-alumel thermocouple. The thermocouple junction was placed under the sample at about 3 mm of the electrical-heater and its e.m.f was recorded. Before ignition, the reaction chamber was pumped down to avoid oxidation of the metal particles during combustion and to minimise X-ray absorption by air. A Mylar (polyester) sheet (thickness 23 μm) separated the reaction chamber from the atmosphere.

During our experiments we used a X-ray detector designed by J.F. Berar et al. for rapid acquisition [5]. Its beryllium window has an aperture of 120 $\times$ 6 mm². It has been constructed to be located at a distance of 400 mm from the diffracting center and in these conditions it has an equivalent angular aperture of 17° in 2 θ but we used it at shorter distance (170 mm) in order to widen the angular window and to minimize the X-ray beam. In this case the angular aperture represents 32° (2 θ) and the resolution is 0.15° for 214 channels. The parallax error due to the distance of 170 mm instead of 400 mm was not a problem for our experiments as this was verified. The wavelength of the X-rays was 0.159 nm.

We studied two ternary nickel (aluminium + titanium) alloys : $\text{Al}_{0.20}\text{Ni}_{0.75}\text{Ti}_{0.05}$ (γ') and $\text{Al}_{0.27}\text{Ni}_{0.50}\text{Ti}_{0.23}$ (H) (cf. figure 2).

Figure 1: A schematic diagram showing the reaction chamber.

Figure 2: The Al Ni Ti ternary diagram [6] with the selected compositions

3. RESULTS

3.1 Synthesis of γ'

To monitor the formation of γ' , the $32^\circ 2\Theta$ angular window was chosen to include the strongest diffraction peaks of Ni, Ti and γ' . The detector center was at $2\Theta = 55^\circ$. The peaks which were recorded were Ni(111) and (200), γ' (111) and (200) and Ti(101). The strongest peak of aluminium (Al(111)) is out of the window. For this reaction, 2048 scans were realized, each one of 30 ms, so the time of recording was about 61 s. The choice of 30 ms gave the best combination of speed and resolution. It was determined experimentally. The reaction front velocity of this combustion is very high and is estimated to be around 10 to 40 mm/s [7]. Figure 3 represents a 3-dimensional plot of the Time-Resolved X-Ray Diffraction (TRXRD) patterns for the combustion reaction : 20at% Al + 75at% Ni + 5at% Ti $\longrightarrow$ γ' . Only a part of the 3-D plot is shown and we can observe the evolution of the combustion reaction during the passage of the front. The time scale began at $t=0$ second when the detector started to record the first pattern, i.e. several seconds before sample ignition. The start of reaction or ignition cannot be timed very accurately and this explains the delay (here 48 s) between the beginning of the TRXRD recording ($t=0$) and the propagation of the reaction front into the irradiated zone. One hundred diffractograms are represented, each one being the average of 5 successive 30 ms patterns. At $t = 45.00$ s we observe only the Ni (111) and (200) peaks since the Al (111) is out of the angular window and the Ti(101) is too weak because of the small quantity (5at%) in comparison with Ni. After about 48 s of recording we note the abrupt disappearance of nickel peaks and the rise of the two γ' peaks. For a best examination of phase transformations during combustion we have selected 6 diffractograms which are plotted each one being an average of five 30 ms diagrams as in figure 4. After 48.30 s Ni (111) and (200) peaks are always present but 0.15 s later we note a shoulder on the side of Ni (200) and at $t = 48.60$ s we observe a new phase. We think that it is a solid solution of Al in Ni, γ' (111) peak is already present (44.54° in 2Θ) and after 48.75 s γ' (111) increases and becomes predominant. After about 48.60 seconds Ni has completely disappeared. Checks made in our laboratory with classical X-ray devices and by electron-probe microanalysis (EPMA) showed that the final state of the sample was pure γ' . These results have been reproduced with five samples of identical compositions.

3.2 Synthesis of H

Small pellets containing 80wt% (27at% Al + 50at% Ni + 23at% Ti) and 20wt% of H with composition $\text{Al}_{0.27}\text{Ni}_{0.50}\text{Ti}_{0.23}$ were prepared. The addition of the final product (H) to the elements as an heat sink reduced the reaction front temperature and thus avoided the sample deformation to preserve the diffraction conditions, but it induced a pulsed mode of combustion propagation.

The recording of the experiment was carried out as before. The angular window was centered at $2\Theta = 55^\circ$ and the time resolution was 30 ms. In these conditions H(220) and (400) are collected by the detector.

The front velocity for this combustion was unknown but the fact that we observed a pulsating regime showed us that it was lower than that of γ' .

Figure 5 shows a 3-D plot of the interesting part of the recording. As for γ' we have selected 6 diffractograms which reveal all stages of the phase transformations (cf. figure 6). At $t = 30.90$ s we note the presence of Ni, Ti and H original phases. 0.30 s later we observe a new Ni(Al) phase. At this time the remaining pure Al is liquid. A temperature measurement at the center of the specimen gave a temperature of 1230°C . At $t = 31.35$ s the H peaks increase while pure Ni(Al) disappears.

Figure 3: A 3-D plot of the TRXRD patterns for γ' formation by combustion reaction

Figure 5: A 3-D plot of the TRXRD patterns for H formation by combustion reaction

Figure 4: Selected TRXRD patterns showing events in the course of γ' reaction

Figure 6: Selected TRXRD patterns showing events in the course of H reaction

4. ELECTRON PROBE MICRO ANALYSIS (EPMA) COMPLEMENTARY STUDIES

In addition to the results obtained by the TRXRD we have studied by EPMA pellets of the same size and composition in which the reaction propagation was interrupted by placing an heat sink on the second half of the sample in order to freeze the reaction front after its propagation through the first half. Figures 7, 8 and 9 show the state of a γ' specimen i) just beyond the combustion wave, ii) during the passage and iii) after the passage respectively. These pictures have been obtained from back-scattered electrons on an electron microprobe. Figure 10 gives an optical overview of one sample.

As we can see on figure 7 there is a concentration of different grains at the center white are pure Ni, grey pure Ti, black pure Al, the largest black zones being some cavities. At this point beyond the reaction front aluminium has already been affected by the temperature rise, it has begun to melt and to encapsulate Ti and Ni grains.

Figure 8 represents a subsequent state. The temperature was higher and all aluminium at this point of the specimen was melted.

Figure 9 shows that the reaction is nearly completed but still unachieved. The whitest areas are Ni-rich while the others are Al- and Ti-rich. EPMA allowed us to identify only $\gamma' \text{ Ni}_3(\text{Al,Ti})$ and $\gamma \text{ Ni}(\text{Al,Ti})$ both with non homogenous compositions.

The same kind of observations has been made on H samples and the results are comparable.

Figure 7: EPMA sample beyond the combustion front.

Figure 8: EPMA γ' during the passage of the combustion wave.

Figure 9: EPMA γ' behind the combustion front.

Figure 10: Optical macrography, interrupted reaction.
i) fig. 7, ii) fig. 8, iii) fig. 9
Real size of the pellet: $2 \times 1 \text{ cm}^2$.

5. CONCLUSION

Time-Resolved X-Ray Diffraction (TRXRD) studies of Solid-state High temperature Synthesis (SHS) become possible with the help of a synchrotron X-ray beam and a fast detection system. Here is presented a short survey of experiments which were realized with the LURE synchrotron in Orsay (France). The synthesis of ternary phases γ' ($\text{Al}_{0.20}\text{Ni}_{0.75}\text{Ti}_{0.05}$) and H ($\text{Al}_{0.27}\text{Ni}_{0.50}\text{Ti}_{0.23}$) have been monitored and recorded. These experiments have been completed by Electron-Probe MicroAnalysis (EPMA) of frozen samples which showed concentration gradients and transitory phases. The combustion of both techniques may help to get a better insight of SHS.

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