| ESRF | **Experiment title:**<br>**"X-Ray microtomography of Ni-Al droplets and subsequent leached Raney-type powders"** | **Experiment number**:<br>MA-636 |
|---|---|---|
| **Beamline**:<br>ID19 | **Date of experiment**:<br>from: 26 August 2008 to: 27 August 2008 | **Date of report**:<br>-- -------- 2009 |
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## Report:

### Aim of the experiment and scientific background

The main scientific objective of the IMPRESS Integrated Project within the EU 6th Framework Program is to gain a better understanding of the links between material processing routes, structures and final properties of intermetallic alloys [1]. One aim of the project is to explore new routes of producing Raney-type Ni-Al catalytic powder for use in hydrogen fuel cell electrodes and hydrogenation reactions.
The traditional production of Raney-type Ni-Al catalytic powders involves two steps: *(i)* casting-and-crushing of a solidified ingot and *(ii)* subsequent leaching with NaOH solution to remove most of the aluminium and activate the catalyst [2]. Atomisation is another powder production process which is currently being investigated. In the spray-atomisation process, a melt stream is disrupted by inert gas to produce fine

liquid droplets which are rapidly solidified. Such rapid solidification leads to spherical powders with a much finer microstructure, avoids segregation and gives a greater pore volume after leaching, as well as enhancing mechanical and rheological properties. Impulse Atomisation (IA) is another approach to generate spherical powders with rapid solidification features. IA is considered a single fluid method where a stream of metal is rendered unstable by the application of a mechanical disturbance. The atomised droplets fall and solidify in a stagnant gas.
Recent investigations have shown that the activity of the catalysts is sensitively dependent not only on the production technique but on both the particle size and composition of the original as-solidified grains.
Previous studies used the powder diffraction technique on the HRPT diffractometer at the neutron spallation source SINQ in Switzerland. This data indicated a variation of phase content with particle size in gas-atomised Ni-Al alloys. Additional measurements were recently performed at ILL in order to obtain a considerably better resolution than that available on HRPT and to identify unknown peaks in some of the neutron diffraction patterns [3]. However, investigations at the grain scale are necessary in order to further improve the understanding of the links between solidification processes and characteristics of the powders before and after leaching.

Nb. This experiment forms part of a general work-plan for the IMPRESS Integrated Project, as stated in a Memorandum of Understanding between ESRF, ILL and ESA in January 2008.

## Experimental details

Microtomography experiments were carried out on powders produced by the casting-and-crushing, spray atomised and impulse atomised processes, before and after leaching. Powders after leaching were passivated producing a thin oxide layer because they are extremely pyrophoric and are usually stored in a solvent like water, which is not feasible during the acquisition of data due to the formation of bubbles when exposed to X-rays. Particles were encapsulated into capillaries of 350 µm inner diameter. This corresponds to the chosen field of view, using a 2048x2048 FReLoN camera and an optic allowing a pixel resolution of 0.17 micron/pixels. The energy was set to 20.5 keV in order to optimise the X-ray flux in 16-bunch mode and the contrast between the different phases present in the grains.

16 samples with different compositions, production routes and sizes were succefully scanned during the allocated beamtime. Their characterisitics are summarised in tables 1 and 2.

| Initial composition (at%Al) | Size range (microns) | Production route |
|---|---|---|
| **68.5** | **90-180** | **Cast-and-Crush** |
| **68.5** | **75-106** | **Spray Atomisation** |
| **68.5** | **<355** | **Impulse Atomisation** |
| **68.5** | **425-500** | **Impulse Atomisation** |
| **75.0** | **106-150** | **Spray Atomisation** |
| **75.0** | **75-106** | **Spray Atomisation** |
| **75.0** | **<38** | **Spray Atomisation** |
| **77.5** | **75-106** | **Spray Atomisation** |
| **79.5** | **<355** | **Impulse Atomisation** |
| **80.0** | **75-106** | **Spray Atomisation** |
| **82.5** | **75-106** | **Spray Atomisation** |

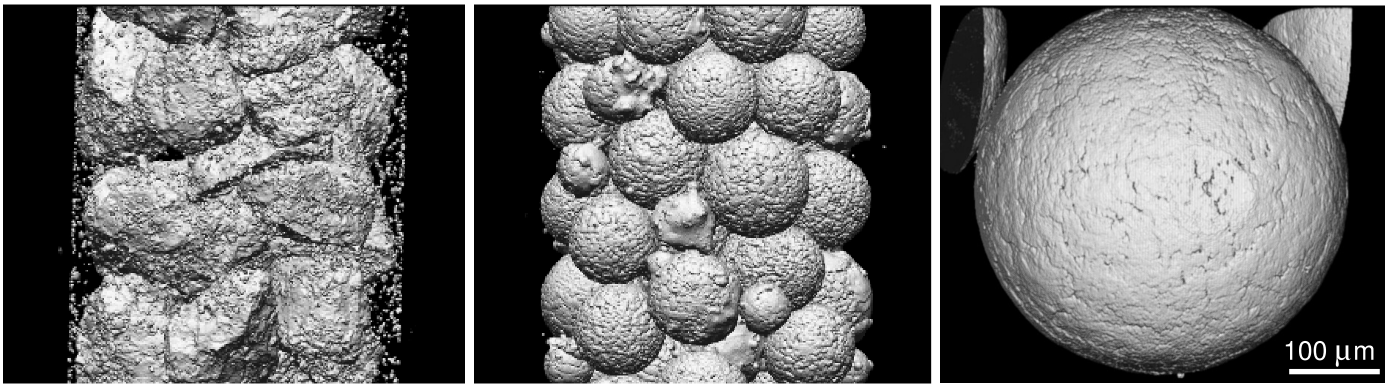
*Table 1. List of non-leached samples scanned during the allocated beamtime.*

| Initial composition (at%Al) | Size range (microns) | Production route |
|---|---|---|
| 68.5 | 90-180 | Cast-and-Crush |
| 68.5 | 75-106 | Spray Atomisation |
| 68.5 | <355 | Impulse Atomisation |
| 75.0 | 75-106 | Spray Atomisation |
| 82.5 | 75-106 | Spray Atomisation |

*Table 2. List of leached + passivated samples scanned during the allocated beamtime.*

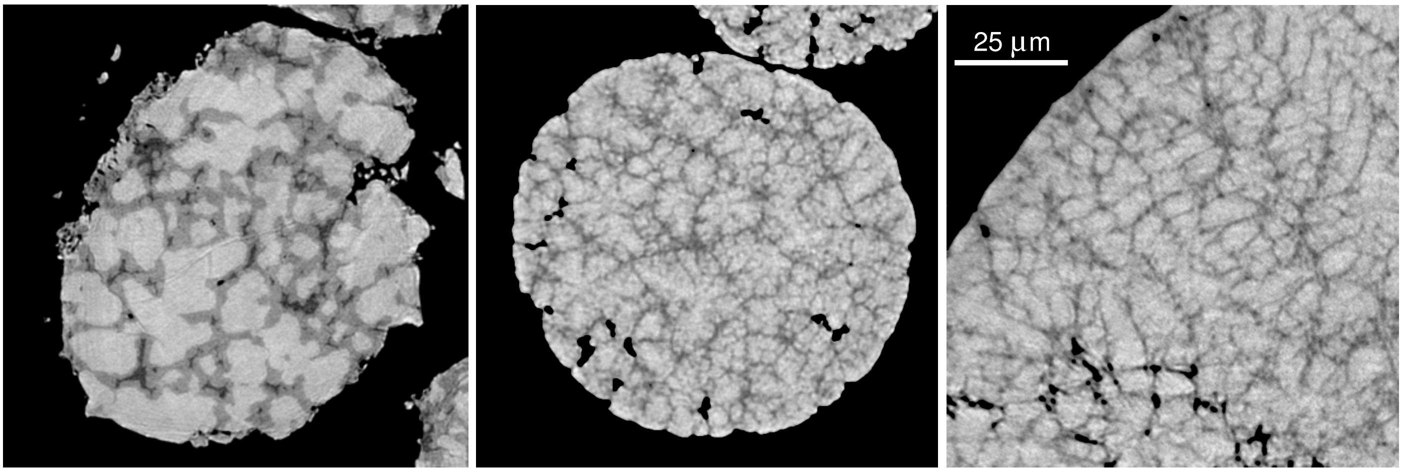
**Results**

*Powders before leaching :*




(a) (b) (c)

*Figure 1. Reconstructed volume of Ni-68.5at%Al powders produced by, (a) Cast-and-Crush, (b) Spray Atomisation, (c) Impulse Atomisation.*



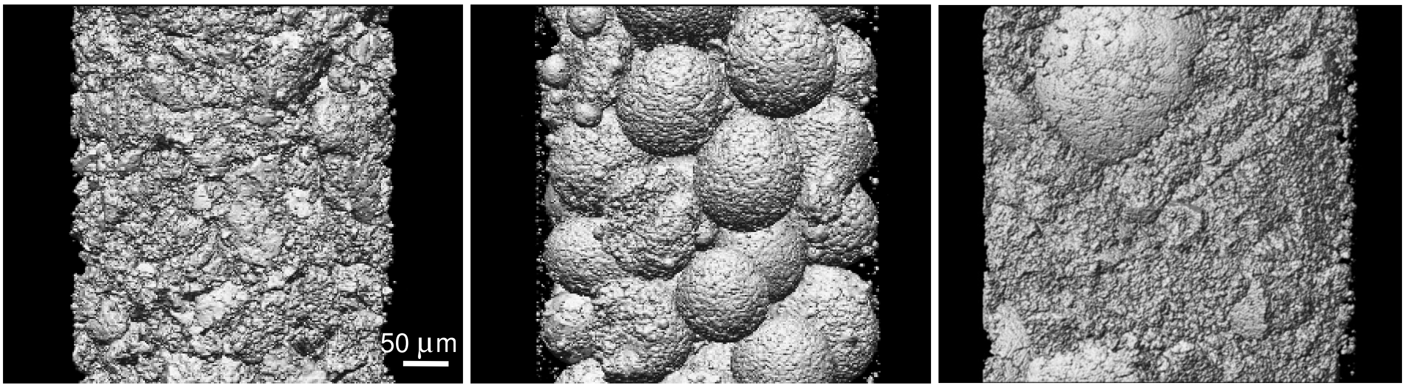

(a) (b) (c)

*Figure 2. Numerical slice of Ni-68.5at%Al powders produced by, (a) Cast-and-Crush, (b) Spray Atomisation, (c) Impulse Atomisation.*

Different grain shapes were observerd for the different production methods (figure 1). Cast-and-crushed grains are facetted, rough and brittle with a lot of dust. Spray atomised grains are mainly spherical and many of them present satellite droplets. This is due to the numerous collisions occuring between droplets when using this solidification technique. Droplets solidified by Impulse Atomisation are spherical and do not present such features. The spatial resolution was sufficient to distinguish the solidification microstructures inside the droplets (figure 2). More or less dendritic microstructures are obtained depending on the

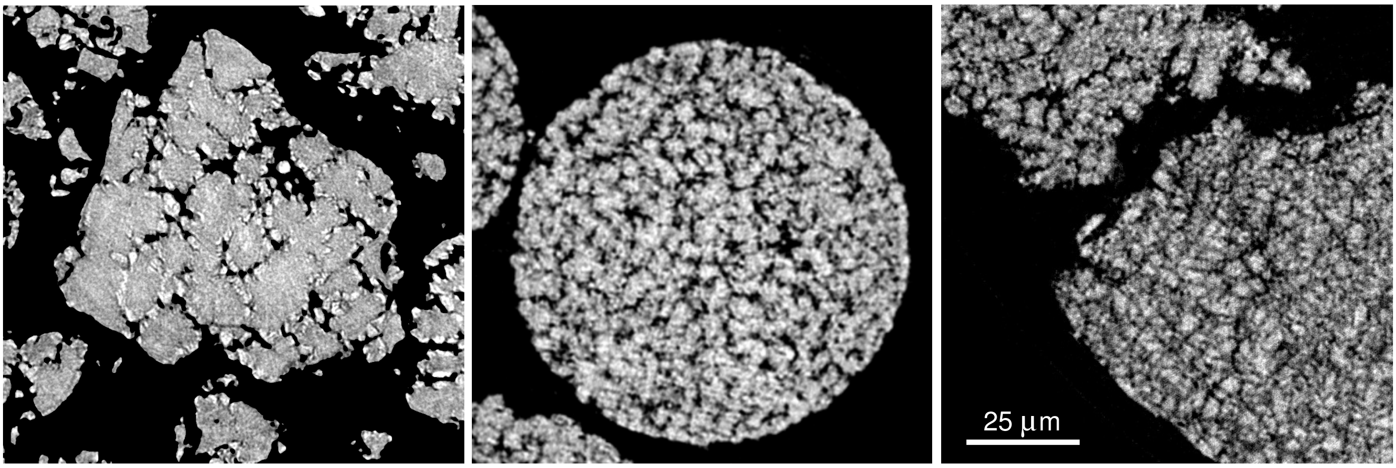
production technique, intial composition and size of the droplet. 3D visualisation allows characterisation of the microstructure morphology such as secondary arm spacing of the dendritic grains. Three different phases can be noticed : white $Ni_2Al_3$, light grey $NiAl_3$ and dark grey eutectic. Numerical thresholds can separate these phases for big microstructures and an evaluation of the phase content of indiviudal droplets can thus be performed.

*Leached powders :*




(a) (b) (c)

*Figure 3. Reconstructed volume of leached Ni-68.5at%Al powders produced by, (a) Cast-and-Crush, (b) Spray Atomisation, (c) Impulse Atomisation.*




(a) (b) (c)

*Figure 4. Numerical slice of leached Ni-68.5at%Al powders produced by, (a) Cast-and-Crush, (b) Spray Atomisation, (c) Impulse Atomisation.*

Visualisation of the investigated volume (figure 3) shows that many of the spray atomised droplets kept a spherical shape after leaching, whereas cast-and-crushed as well as impulse atomised grains broke into several pieces during this step. Indeed removal of the eutectic phase and aluminium in the $NiAl_3$ and $Ni_2Al_3$ leads to a fragile skeletal structure which can break due to stirring of the NaOH solution. The final microstructure of the catalyst is visible (figure 4) and morphological analyses are feasible.

## References


[1] D.J.Jarvis and D. Voss, Materials Science and Engineering: A, 583 (2005) 413-414

[2] F. Devred, B.W. Hoffer, A.D. Langeveld, P.J. Kooyman and H.W. Zandbergen, Appl. Catal. A 244 (1991) 291-300

[3] U. Dahlborg, M. Calvo-Dahlborg, ILL Experimental Report 5-21-965 (2007)