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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 give a greater pore volume after leaching, as well as enhancing mechanical and rheological properties. Impulse Atomisation (IA) is a further 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 the one available on HRPT and 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

Nanotomography experiments were carried out on powders produced by the casting-and-crushing, spray atomised before and after leaching, and impulse atomised processes. 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 trapped into capillaries filled with epoxy resin or coated with epoxy resin at the top of capillary holders. 12h at 400°C then 6h at 600°C annealings were performed in order to avoid the formation of bubbles inside the resin during exposure which would prevent exploitation of the collected data. Pictures were recorded at different angles and positions of the samples with a FReLoN camera. Four different positions are necessary to retrieve the phase from pictures however five positions were used since the samples significantly moved when exposed to X-rays during the first scan. The beam energy was set to 17.5 keV in order to optimise the X-ray flux. Final voxel size was 60 nm, corresponding to a field of view of 90 µm.

14 droplets 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)	Diameter (microns)	Holder	Production route
68.5	**-**	**Top of capillary**	**Spray atomisation**
75.0	**83**	**Trapped into resin**	**Spray atomisation**
77.5	**>90**	**Trapped into resin**	**Spray atomisation**

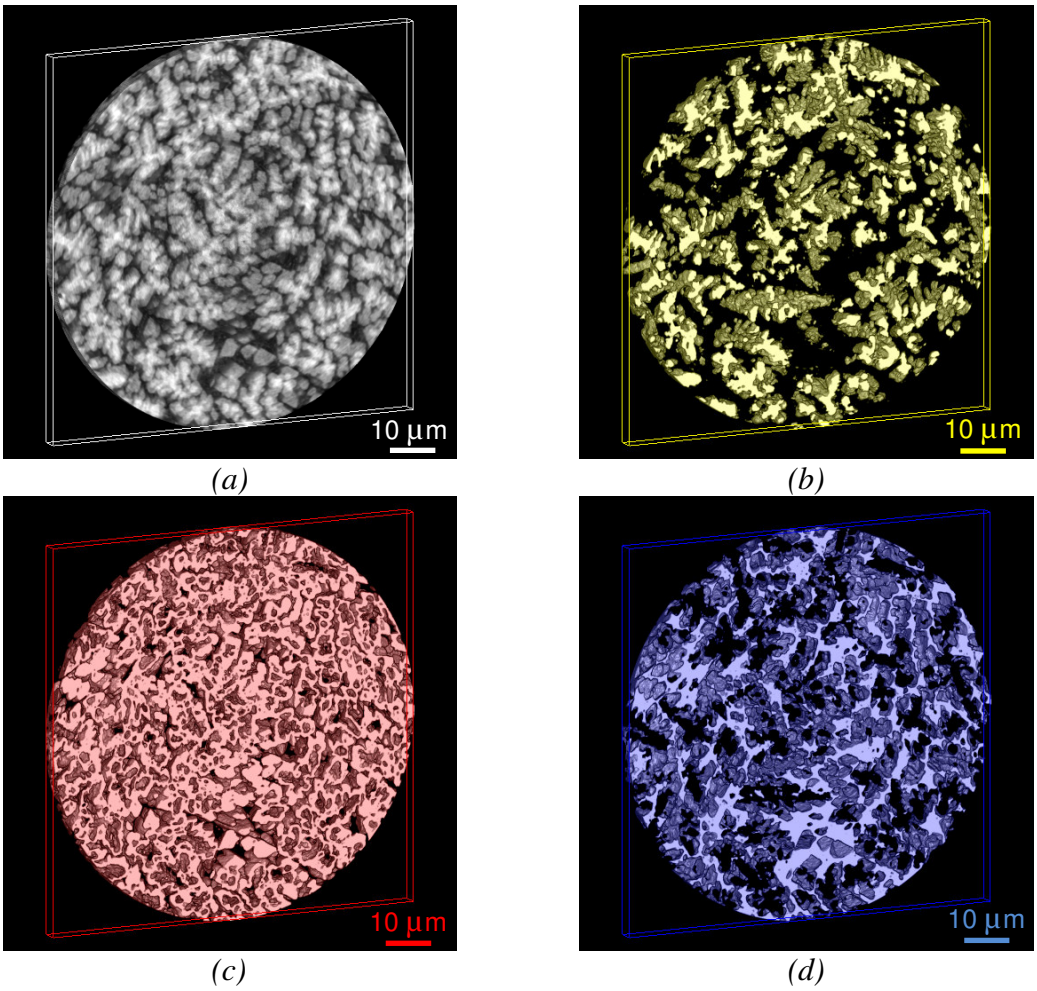
Table 1. List of leached samples scanned during the allocated beamtime.

Initial composition (at%Al)	Diameter (microns)	Holder	Production route
68.5	**79**	**Trapped into resin**	**Spray atomisation**
68.5	**83**	**Top of capillary**	**Impulse Atomisation**
68.5	**86**	**Top of capillary**	**Impulse Atomisation**
75.0	**-**	**Trapped into resin**	**Cast-and-Crush**
75.0	**85**	**Trapped into resin**	**Spray atomisation**
75.0	**60**	**Trapped into resin**	**Spray atomisation**
75.0	**45**	**Trapped into resin**	**Spray atomisation**
77.5	**≈90**	**Top of capillary**	**Spray atomisation**
77.5	**>90**	**Trapped into resin**	**Spray atomisation**
79.5	**86**	**Top of capillary**	**Impulse Atomisation**
80.0	**≈90**	**Trapped into resin**	**Spray atomisation**

Table 2. List of non-leached samples scanned during the allocated beamtime.

Results

Powders before leaching :

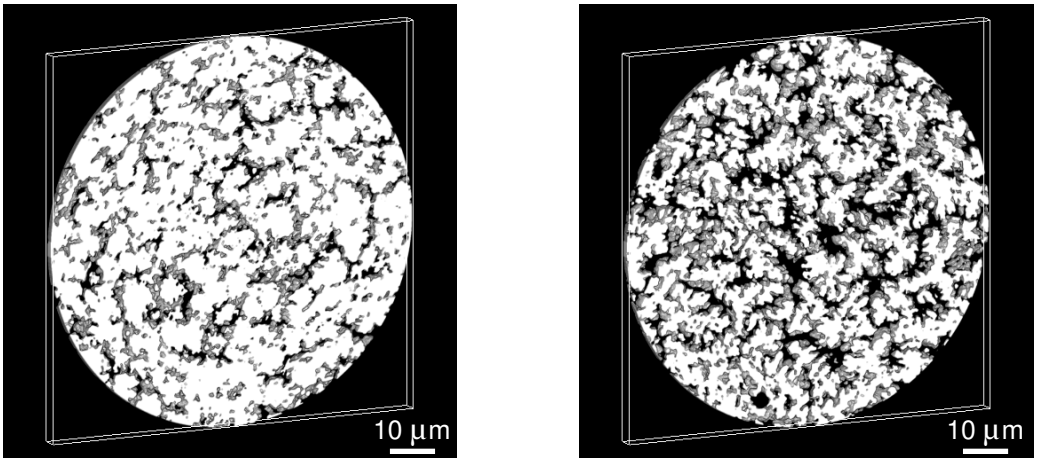


(a) *(b)* *(c)* *(d)*

Figure 1. 1.2 µm thick cylindrical cross sections showing *(a)* the inner microstucture of a Ni-77.5at%Al droplet, *(b), (c)* and *(d)* 3D distribution of the Ni_2Al_3, $NiAl_3$, and eutectic phases respectively.

Numerical slices were obtained by phase retrieval. An approximately 1 µm thick shell around the dropelts could not be rendered with a good contrast due to the occurrence of an important phase contrast on the surface of the droplets. However the inner microstructure is clearly visible as shown in figure 1a. 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 when the droplet did not move significantly during the data acquisition. A precise evaluation of the phase content of indiviudal droplets can thus be performed as well as the visualisation of the phase distribution in 3D (figure 1b,c and d).

Leached powders :



(a) *(b)*

Figure 2. 0.6 µm thick cylindrical cross sections of leached *(a)* Ni-75.0at%Al and *(b)* Ni-77.5at%Al powders produced by spray atomisation.

Visualisation of the inner microstucture of leached and passivated droplets was performed (figure 2). It shows that the final microstructure of catalyst is more dendritic when the initial content in aluminium increases. This is in agreement with the morphological evolution observed for the precursor droplets. Morphological characterisations such as porosity, surface area or sphericity are feasible and will help to improve the understanding of the relations between structure and activity of the catalyst powders.

References

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[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)