Neutron Diffraction Analysis of the Non-Equilibrium Solidification of Al-Fe and Al-Ni: Part I

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Recycling of aluminum alloys is a general practice in foundries. In these recycled Al alloys, Fe is almost invariably present as an impurity. By forming intermetallics such as $Al_{13}Fe_4$, Fe can result in significant damage to aluminum alloys. Thus strategies have to be developed to modify the negative effect of Fe. One of them is by physical processing such as rapid solidification processing (RSP) to increase the solubility of Fe or obtain finer dissemination of Al-Fe precipitates. Among the atomization techniques, Impulse Atomization (IA) is one innovative approach, which is capable of producing droplets of controlled size with relatively narrow distribution and a predictable cooling rate. During rapid solidification, the undercooling and/or high cooling rates attained by the liquid can result in a non-equilibrium (metastable) phase formation in the microstructure. The presence of these non-equilibrium phases produced by RSP allows greater flexibility and control of the final microstructure to yield good high temperature strength with sufficient ductility, high elastic moduli and excellent thermal stability, superior to those obtained by more conventional ingot metallurgy and casting techniques. In order to tailor the processes, to obtain data such as undercooling, cooling rate in IA process is important. However, these parameters are difficult to collect due to the characteristics of the rapid solidification process. Therefore, simulated experiment such as levitation experiments at reduced gravity (PFC) was conducted to make these measurements. For comparison, terrestrial experiments are conducted as well.

In the previous transmission electron microscope (TEM) study on IA Al-Fe powders, we found the existence of metastable Al_mFe, stable phase $Al_{13}Fe_4$ and primary α-Al. The TEM characterization on PFC and terrestrial droplet revealed $Al_{13}Fe_4$, eutectic $Al_{13}Fe_4$ and unknown Al-Fe intermetallic in PFC sample while $Al_{13}Fe_4$, eutectic $Al_{13}Fe_4$ in terrestrial sample. Metastable Al_mFe (m = 4.0-4.4) was not found in the microstructure for both samples. Neutrons are highly penetrating, allowing the non-destructive investigation of the interior of materials. This makes it as a very complementary tool to TEM.

Al-Ni alloys are of great interest to the aerospace industry because of their low density and high temperature capabilities. It is believed that the improved mechanical properties result from reduced microsegregation and formation of metastable phases during rapid solidification processing. Understanding the evolution of microsegregation during rapid solidification is necessary to control the microstructure and the properties of these alloys. To study the effect of different processing parameter such as composition and cooling rate on the microstructure evolution of Al-Ni alloys, rapidly solidified powders of Al-20at%Ni and Al-31.5at%Ni were produced using IA in Helium and Nitrogen atmospheres, respectively. Two different particle sizes, 325 and 780 μm, were studied using neutron diffraction technique. The formation of different phases and their quantity are to be compared to droplets solidified in micro-gravity (TEXUS) to investigate the effect of cooling rate, undercooling and convection in the melt.

Neutron diffraction measurements were performed on the C2 neutron powder diffractometer, located at the NRU reactor. C2 consists of an 800-wire BF3 detector, floating on an epoxy dance floor. Measurements were performed using a wavelength of 1.33 Å taken from a Si(531) monochromator at 92.7° take-off angle. The atomized powders were placed inside a vanadium can of internal diameter 5 mm, and volume 1 cm^3. The spherical droplets (diameter about 6 mm) obtained from the reduced gravity and terrestrial conditions were measured without placing them inside a can. Both types of samples were placed onto posts on a multispecimen changer, consisting of a linear translator that was bolted to the sample table of the diffractometer. Beam defining slits were used to illuminate only the sample volume. In addition, the aluminum posts were shielded with cadmium. Both of these precautions ensure that the diffraction pattern is solely from phases in the sample.

Figure 1 shows the neutron diffraction patterns of Al-Fe IA powders. Three different compositions (0.61 wt %, 1.90 wt %, 8.0 wt %), below denoted as Al-0.61Fe, Al-1.90Fe and Al-8.0Fe, have been conducted for neutron diffraction. The positions of diffraction peaks obtained from literature crystallographic data are shown in the figures as well. By comparing the pattern obtained by means of Rietveld refinement calculation and the experimental patterns, it was found that in Al-0.61Fe, metastable Al_mFe is the only intermetallic in the structure. This is consistent with the TEM observation on the same powder, which shows that the microstructure consists of dendritic/cellular α-Al with eutectic Al_mFe –α-Al decorating at the dendritic/cellular walls. For Al-1.90Fe, neutron diffraction shows the existence of Al_mFe as well. This is again, consistent with the TEM investigation of the microstructure. The TEM observation shows similar microstructure compared with that in Al-0.61Fe but with more eutectic volume percentage. The neutron diffraction analysis for Al-1.90Fe suggests the possible existence of Al_6Fe, but not very strongly. Al_6Fe is another metastable phase formed at lower cooling rate comparing with Al_mFe. However, extensive TEM observation has not identified this phase. In Al-8.0Fe, the primary intermetallic phase, as revealed by the neutron diffraction analysis, is still Al_mFe. This confirms what found in TEM observation. Neutron diffraction shows the possibility for the existence of Al_6Fe as well. Indeed, in the TEM observation, we did find the eutectic and the

selected area diffraction (SAD) analysis suggests it is eutectic Al6Fe–α-Al. Neutron diffraction also suggests the existence of $Al_{13}Fe_4$, but not very certain. Again, TEM observation found fine needles and coarse blades in the microstructure and SAD analysis identified they were $Al_{13}Fe_4$, supporting the neutron diffraction results. The uncertainty about the existence of $Al_{13}Fe_4$ in neutron diffraction analysis may come from the limited volume fraction of $Al_{13}Fe_4$ in structure. Thus the TEM results show that TEM is complementary to neutron diffraction analysis in this aspect.

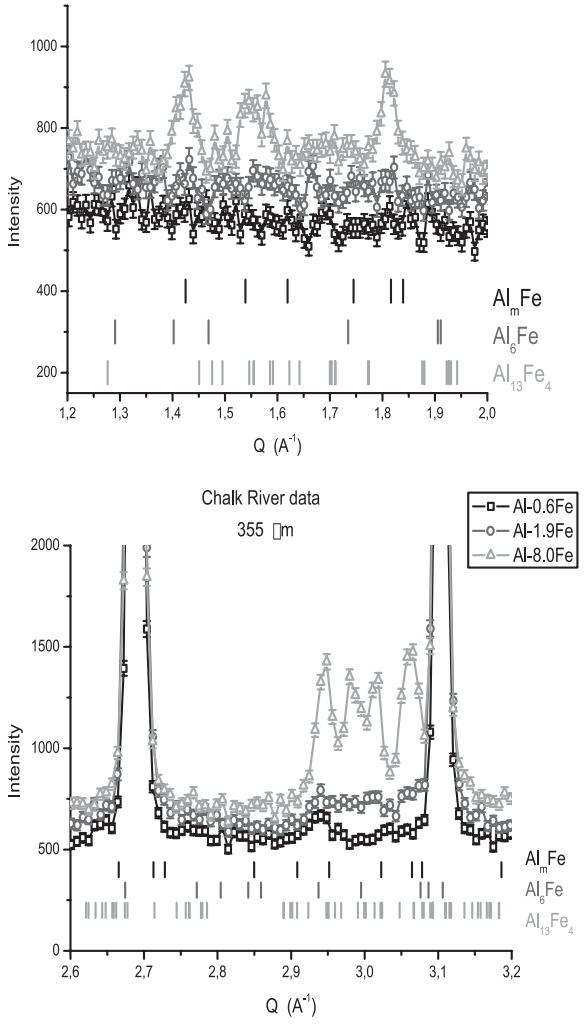

Fig 1. *Neutron diffraction patterns of Al-Fe IA powders for three different compositions (0.61 wt %, 1.90 wt %, 8.0 wt %), denoted as Al-0.61Fe, Al-1.90Fe and Al-8.0Fe.*

The neutron diffraction indicates samples may contain some other phase as no diffraction peak exists at 2.979 $Å^{-1}$ for any of the three phases of Al_mFe, Al_6Fe and $Al_{13}Fe_4$. However, it might be that this peak originates from a strongly distorted Al_6Fe phase. Further work need to be done on this.

Figure 2 depicts the diffraction patterns and the computed peaks from Rietveld refinement. The diffraction patterns suggest the existence of $Al_{13}Fe_4$ in both PFC and terrestrial samples, which is consistent with the TEM observation. Furthermore, neutron diffraction analysis points out that there is metastable Al_mFe in both structures as well, which was not obtained in the extensive TEM observation. Since the information TEM supplied is from the thin foil prepared from a slice from the spherical droplet (~ 6 mm in diameter), it is quite possible that Al_mFe is not in the area we observed. This shows, on the other hand, neutron diffraction is complementary to TEM observation. Although quantitative information has not been obtained yet, we postulate the quantity of Al_mFe is not much considering the post annealing effect of the droplet because its cooling rate is much slower than that of atomized powder.

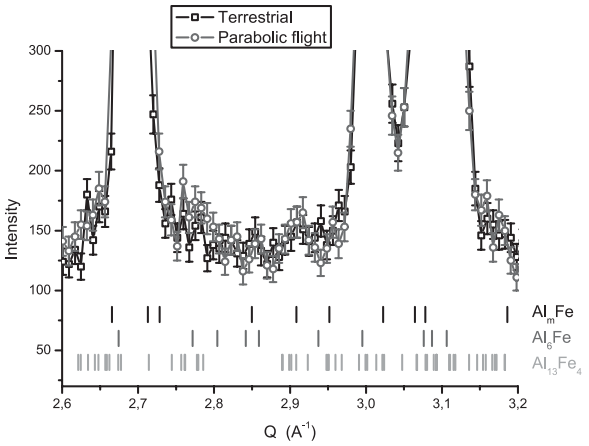

Fig 2. *Diffraction patterns and the computed peaks from Rietveld refinement.*

The neutron diffraction shows the intensity difference of the Al diffraction peaks at about 2.7 and 3.1 $Å^{-1}$ for PFC and terrestrial samples (see Figure 3). This is due to texture effects arising from the difference in solidification of the two samples. Remarkably enough there seems to be no texture effects for Al_mFe or $Al_{13}Fe_4$ that indicates that the crystallites are small and randomly oriented. Thus no orientation correlation between the Al and the Al_mFe or $Al_{13}Fe_4$ crystallites seems to exist.

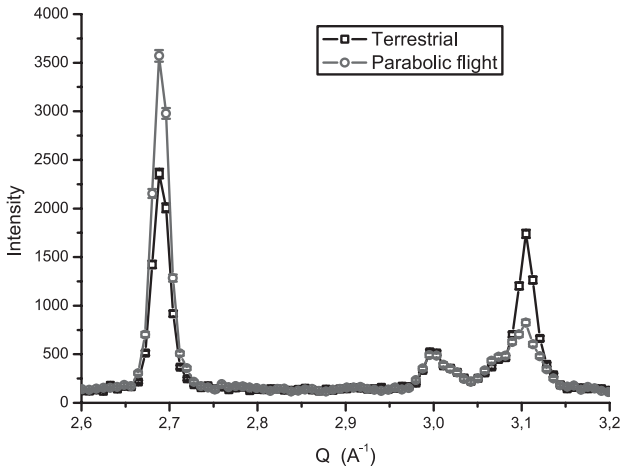

Fig 3. *Neutron diffraction shows the intensity difference of the Al diffraction peaks at about 2.7 and 3.1 $Å^{-1}$ for PFC and terrestrial samples.*

In the current study, the neutron diffraction results of TEXUS sample prepared from TEXUS44 sounding rocket campaign

were used to compare those of IA results. Figure 4 shows the neutron diffraction pattern of Ni-Al IA powders and Rietveld refinement calculation results. In the Figure, the black vertical bars correspond from above to the positions of diffraction peaks of the Al phase, the Al_3Ni_2 phase and the Al_3Ni phases, respectively.

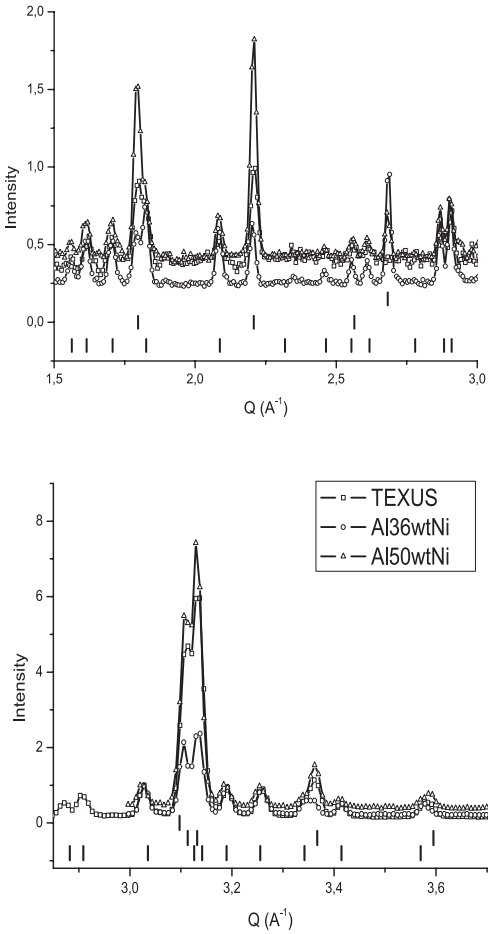

Fig 4. *Neutron diffraction pattern of Ni-Al IA powders and Rietveld refinement calculation results. The black vertical bars correspond from above to the positions of diffraction peaks of the Al phase, the Al_3Ni_2 phase and the Al3Ni phases, respectively, from top to bottom.*

One striking difference is that the TEXUS sample does not contain any Al phase (see the peak at about 2.68 A^{-1}). This is a very interesting result that needs further investigation to find the reason behind it. When comparing the TEXUS and IA samples a larger difference in phase content can be seen. Looking on the two peaks at about 1.8 A^{-1}, the ratio R between the amounts of Al_3Ni_2 and Al_3Ni varies significantly. From the variation of R it is obvious that IA(Al50wtNi) > TEXUS > IA(Al36wtNi). Further investigation on the neutron diffraction results is underway to quantify different phases shown in the patterns.

In conclusion, neutron diffraction analysis reveals the existence of eutectic metastable Al_mFe in IA powders with composition of Al-0.61wt%Fe and Al-1.90wt%Fe. This is consistent with the TEM observation. For Al-8.0wt%Fe, neutron diffraction study indicates primary Al_mFe in the microstructure together with Al_6Fe and $Al_{13}Fe_4$. This is again confirmed by the TEM observation. However, for large droplets obtained from PFC and terrestrial, neutron diffraction suggests the existence of Al_mFe while TEM observation does not reveal it. This shows that as a powerful tool to supply 3D information, neutron diffraction is complementary to TEM observation.

Neutron diffraction has also shown a striking difference between TEXUS sample and IA atomized Al-Ni, i.e. the TEXUS sample does not contain any Al phase. Based on this, further characterization can be preformed to disclose the phase formation sequence and mechanism.