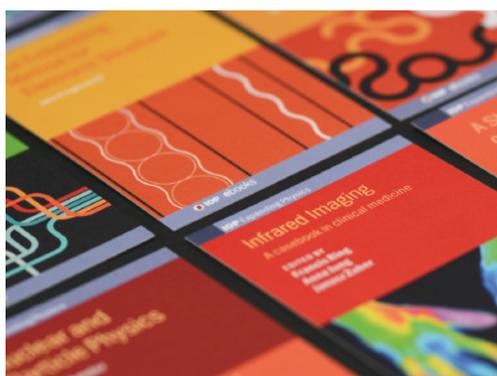# Study of phase formation in metal injection moulding through real time neutron diffraction

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Study of phase formation in metal injection moulding through real time neutron diffraction

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Abstract. The sintering of metal injection moulded stainless steel was investigated using *in situ* neutron diffraction with different sintering temperatures, from $1270°C$ up to $1390°C$, with sintering profiles that were based on those used in industry. The production of an unwanted high temperature phase, δ-ferrite, was observed during sintering and is seen to be retained in the final product after sintering. Ferrite production during sintering acts to speed up the sintering process by forming in the grain pores but is unwanted in the final product as it is a soft and malleable phase. The ferrite that was formed at high temperature was observed to not completely disappear during cooling as a result of the coexistence of dual high temperature phases delta-ferrite and gamma-austenite during the high temperature soak. This suggests the segregation of the alloying elements between the two phase which changes the composition of the phase grains and allows the ferrite to exist during cooling, resulting in the unwanted phase in the final product.

1. Introduction
Metal injection moulding (MIM) is the process of producing small and delicate castings, as small as 300 microns across and 30 mg in weight, without the need for melting but with near liquid cast strengths. The process is to make a mould which is 10 to 20% oversize and inject this with a mix of metal powders and an organic binder. The binder is then cooked away at around $600°C$ leaving a porous material and then the casting is heated to around $1400°C$, to allow densification to occur, shrinking the sample to the final size with a near to liquid casting strength.

17-4PH stainless steel was looked at as it is the most common precipitation hardened stainless steel and contains around 17 wt.% chromium and 4 wt.% nickel along with other alloying elements which gives it high strength and good corrosion resistance [1]. Chromium is a ferrite-stabilising element while nickel is an austenite-stabilising element [2]. The high temperature δ-ferrite phase is wanted during sintering as it acts to speed up the sintering by forming in the pores between the grains but is unwanted in the final sample. Previous investigations of MIM 17-4PH have focused on the shrinkage rates during the sintering [1]. It was found that 17-4PH can only be sintered to near-full density in pure hydrogen or a vacuum [3, 4, 5]. This investigation looks at the phase composition during the sintering process too better understand the densification process which leads to insights into the sintering of metal injection moulded
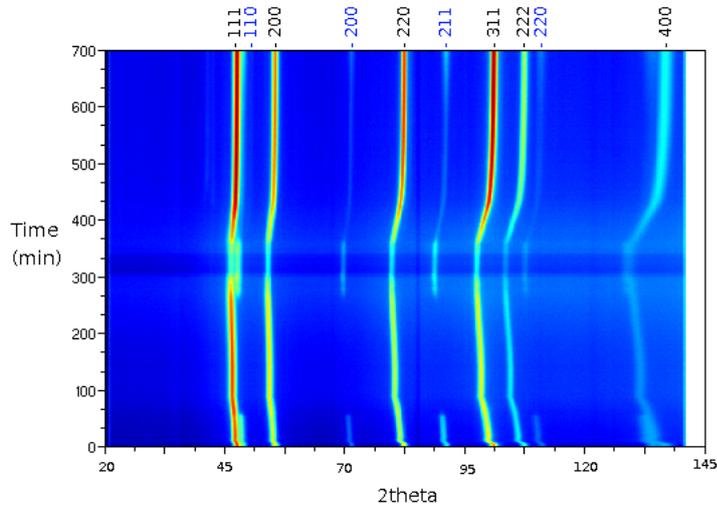
Figure 1: The diffraction pattern intensity as a function of 2θ, with intensity represent by colour, blue low intensity, red high intensity as it varies with time. The sample is heated to a maximum of 1390°C. The reflections are labeled with austenite black and ferrite in blue. Wavelength of the neutrons used was 1.664 Å.

stainless steel that can be used to optimise sintering profiles. The relationship between the shrinkage rate, shown in Figure 1 in ref [1] and phase composition is explored and the source of the production of ferrite in the final sample suggested.

2. Experimental

The samples were produced for the neutron diffraction experiments by a MIM manufacturer [6]. The samples were first debindered before being sintered in the beam. The sintering process as used by ref [6] involves a fast heating ramp of 10°C/min up to 50°C below the maximum temperature then 3°C/min up to the maximum. The sample is then held at that temperature for an hour before cooling at 10°C/min down too 1000°C where the furnace is turned off and the sample allowed to cool to room temperature.

The sintering was done in a vacuum furnace while on WOMBAT, the High Intensity Powder Diffractometer at ANSTO [7] using the 115 reflection on the Ge monochromator with a wavelength of 1.664 Å. This allowed diffraction patterns to be collected in real time and the phase transformations to be observed. Upon heating the steel went through two phase changes first from the α-ferrite to γ-austenite then to a δ-ferrite phase. A time resolution of about 1 min for each diffraction pattern was used as this is quick enough to see the phase changes as they happen and also long enough to get a large number of counts in the diffraction pattern. One of the evolution of diffraction patterns shown in Figure 1. The sintering was done with a range of maximum temperature ranging from 1270°C to 1390°C. Sintering temperature are listed in Table 1.

3. Results and Discussion

Rietveld analysis was performed using MAUD[8, 9] on every diffraction pattern collected for each of the sintering profiles. This allowed quantitative phase analysis as a function of time and temperature to be performed. The results of the weight fraction for austenite and ferrite for one of the sintering profiles with a maximum temperature of 1390°C is shown in Figure 2. The temperature profile used for the 1390°C sinter was reproduced from ref [1] too allow easier comparison with their shrinking rate data.

The sample that was sintered at 1270°C didn't reach a temperature high enough to enter the δ-ferrite phase. The amount of ferrite remaining in the sample depended on the maximum temperature reached, with the highest amount found, around 10.6% Wt, with the sample sintered at 1390°C and around 1.2% and 1.5% found with the samples sintered at 1330°C and 1360°C
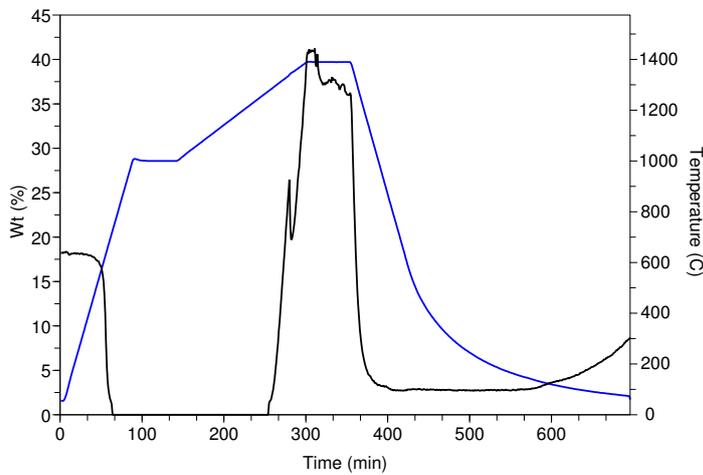
Figure 2: Weight percent vs time for α or δ-ferrite in black. Temperature vs time in blue. The sample is heated to a maximum of 1390°C.

Sintering temperature	δ-ferrite max Wt %	α-ferrite final Wt %	Final volume (mm^3)	% Shrinkage
1270	0	0	3094	9.6
1330	4.8	1.2	3093	10.0
1360	22.4	1.5	2692	12.8
1390	42	10.6	2406	

Table 1: The debinding temperature relating the maximum ferrite found at high temperature and the final ferrite in the sample. The final volume is given to represent the amount of shrinkage, initial volume was 4236 mm^3.

respectively. Looking at Table 1 shows the relationship between sintering temperature and shrinkage of the sample with relation to the amount of ferrite in the sample. There is little difference between the shrinkage when sintered at 1270°C and 1330°C but sintering at 1360°C results in much more shrinkage. The production of δ-ferrite acts to increase the rate of sintering of the sample where this is seen in our samples with little or no δ-ferrite not shrinking as much as sample that entered further into a pure δ-ferrite phase.

It can be seen that 1360°C versus 1330°C gives almost the same ferrite phase fraction after cooling, but the much higher δ-ferrite at high temperature gives better shrinking at higher temperature, Table 1, which means better densification and stronger component. This is only true if the sample is not quenched from high temperature. This explains why the experimentally derived profile finds it best to slowly cool to 1000 C before quenching as this reduces the ferrite that remains in the sample.

It is suggested that the high temperature dual phase allows the segregation of the stabilising compounds into their preferred phases due to their different solubility in different phases. The result is a δ-ferrite with a higher amount of chromium and γ-austenite with a higher amount of nickel in their local grains. So the δ-ferrite attains more chromium and less nickel which shifts its position in the phase diagram and allows the ferrite to exist during cooling and in the final product. It was also observed that the higher temperature which results in the higher amount of δ-ferrite caused more ferrite to remain in the sample which suggests a greater amount of segregation occurred between the two high temperature phases.

The relationship between the shrinkage of the sample, Figure 1 in ref [1] and the phase composition, Figure 2, to be seen with the major shrinkage occurring with the production of a δ-ferrite phase which acts to close up the pores in the sample. While the phase change into the

high temperature δ-ferrite acted to increase the shrinkage, which can be seen by the different final densities of the 1330°C and 1360°C sintered steel, the segregation of the alloying elements has to be inhibited to prevent the δ-ferrite being stabilized to lower temperatures: this maintains the desired mechanical properties of the final product.

To prevent the segregation of the alloying elements the two phase system at high temperature has to be avoided. The steel has to be either sintered at a lower temperature in a pure austenite phase but for a much longer time as the δ-ferrite acts as a catalyst for shrinkage, or heated up higher to a pure δ-ferrite phase. This will prevent segregation because there is only one phase but large grain growth is likely to occur in the δ-ferrite. Grain growth may have negative effects on the physical properties especially when dealing with very small and delicate objects since δ-ferrite grains can grow to 2-3 mm in size. Large grains also result in bad mechanical properties.

Sintering with an oscillating temperature around the δ-ferrite phase change temperature could allow for a faster sinter because δ-ferrite will form in the grain pores, with the additional benefit of having a shorter time in a dual δ-ferrite/γ-austenite phase region which could decrease the segregation of alloying elements and in turn decrease the amount of ferrite in the final product. Alternatively because little shrinking happens while at the maximum temperature, Figure 1 in ref [1], the hold at that point could be removed. So the sample is heated to the maximum temperature then is immediately cooled. This should have no effect on the densification of the sample but will reduce the time needed for sintering and also reducing the ferrite in the final sample.

Further work could involve the use of a scanning electron microscope (SEM) to observe the final samples microstructure which will give the ability to see which alloying elements are undergoing segregation in different phases. Also the effects of varying the heating and cooling rates the final phase composition could be investigated along with removing the high temperature soak in the sintering cycle.

4. Conclusion

This research has been able to show like never before the phase transitions happening during the sintering of the metal injected moulded stainless steel. It leads to insights into the sintering of metal injection moulded stainless steel which cannot be done using any other technique. The phase composition during the sintering has been shown and it has been suggested that the production of δ-ferrite in the final product can be reduced by minimising the time in the high temperature dual phase while still allowing the complete densification of the sample. This means a lot less additional processing after the sintering is require to remove the ferrite in the sample. This can be used to optimize sintering profiles used in industry.

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