RHEOLOGICAL ASSESSMENT OF TITANIUM MIM FEEDSTOCKS

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Abstract

Titanium is an exciting structural material that can offer significant strength-to-weight advantages over currently used alloys. However its Achilles' heal is its costly, energy intensive production process that effectively eliminates it from competing with aluminium and high-strength steels, apart from those critical applications where the metal forms only a small component of the total cost. Current attempts are being made to reduce the cost of titanium products and these recognise the importance of minimising the costs over the total production chain. Powder metallurgy technologies play a crucial role within this, as the output of the existing and potential primary metal production methods is in the form of sponge or powder. By using PM costly re-melting and forming operations can then be avoided, except for large components.

Metal injection moulding is an effective process for producing complex net-shape components in large volumes from metal powders. Nevertheless the commercial use of titanium powders in this process is still in its infancy. There is only one major supplier of feedstock and this utilises a polyacetal-based binder. This gives good green strength but requires a catalytic nitric acid process to remove most of the binder prior to thermal treatment. As this involves additional and expensive equipment plus the potential hazardous nature of the process, there is interest in finding an alternative binder system that can be debound either purely thermally or that involves a less hazardous and more environmentally friendly solvent.

This paper describes the use of capillary rheometry to characterise the influence of temperature and shear rates on the flow behaviour of potential binder systems for titanium MIM feedstock.

1. Introduction

The development of a feedstock involves an interplay of multiple activities, as indicated in Figure 1.

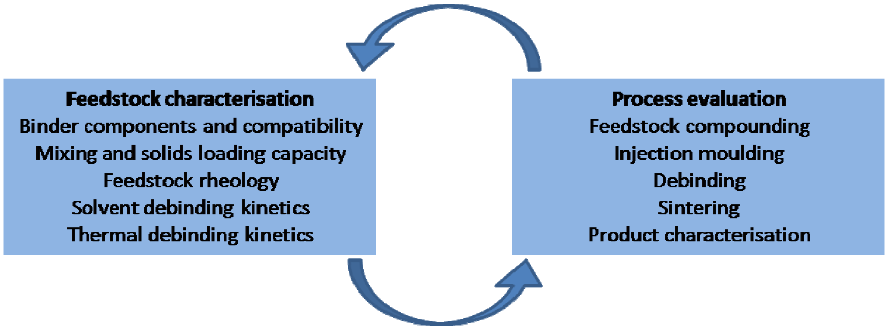

Figure 1: Activities involved in development of a MIM feedstock (adapted from [1])

One of the factors is to optimise the powder loading and this should be at or slightly below the critical value. A schematic representation of this optimum level is shown in Figure 2.

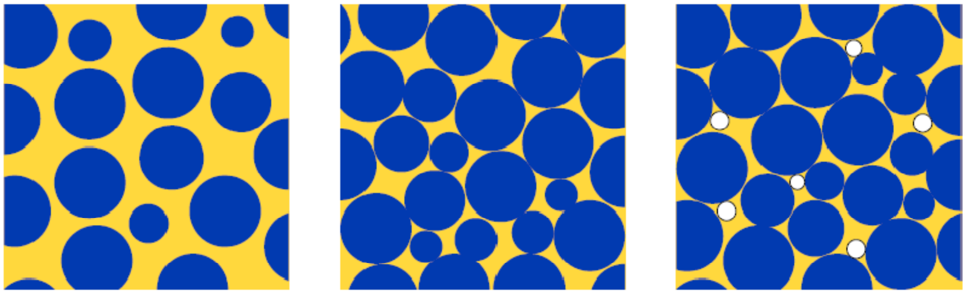
(a) Excess binder
(b) Critical powder concentration
(c) Excess powder

Figure 2: Schematic showing the structures when the powder loading is too low (excess binder), optimal (critical) and too high (excess powder) [1].

When the powder loading is too low, several problems are encountered: the excess binder can separate from the powder during injection moulding leading to in homogeneities in the final part, low brown strength (after debinding) that can result in fracture or even collapse of the shape and large shrinkage during sintering. If the loading is too much then the viscosity becomes too high resulting in difficulties in moulding as well as the formation of voids that result in cracking of the shape during debinding.

Powder loading is usually measured in terms of the volumetric ratio of powder to binder, according to the following formula [1]:

$$\frac{w_p/\rho_p}{w_p/\rho_p + w_b/\rho_b}$$

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where w_p and w_b are the weight fraction of powder and binder and ρ_p and ρ_b are the densities of the powder and binder respectively.

The critical loading can be determined by measuring the density, melt flow, the mixing torque or viscosity of the powder binder mixture. For example, Figure 3 shows the typical increase in viscosity as the critical loading is approached. The exact value will vary depending on the powder particle size and morphology.

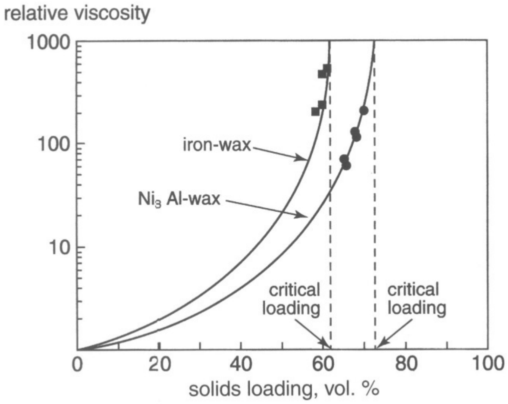

Figure 3: Effect of solids loading on feedstock viscosity for two powder types [2].

If the torque values of the mixer are monitored during feedstock compounding, the mixture shows an increase in mixing resistance as the critical loading is approached. Figure 4 shows the significant increase when changing the loading from 50 to 60vol% (i.e. approaching the critical loading) as compared to the difference between 33 and 50vol%.

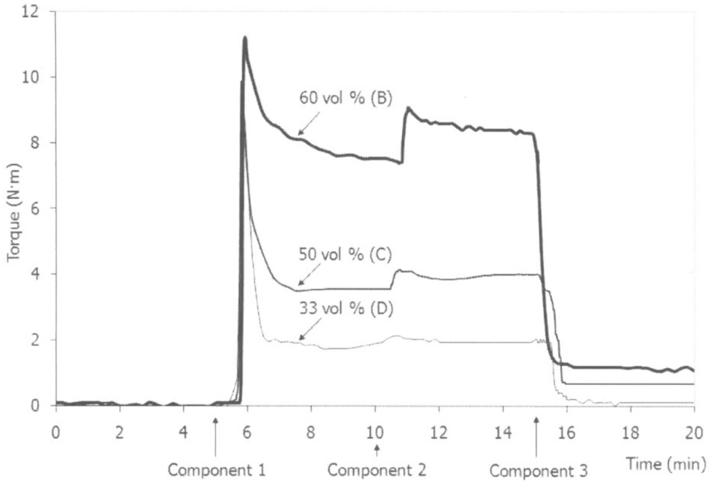

Figure 4: Torque evolution curves during compounding feedstock containing varying powder loadings at 180°C and 180rpm [3].

Based on the above discussion, it is clear that the effect of powder loading is an important criterion in the development of feedstock. A balance needs to be struck between having sufficient loading to maximise the strength in the debound state as well as the final density of the component, and maintaining adequate fluidity for good injectability. The first step in this process is to determine the critical loading value for the specific binder formulation and powder type.

2. Experimental Procedure

A binder system, based on EVA and a wax, was used to prepare feedstock with varying powder loadings. In all three cases the total mass of the binder components were kept constant, while only the mass of the metal powder was increased relative to the overall polymer content.
The various components that were used are the following:
Metal Powder: Ti6Al4V 25 micron atomized powder
Binder: EVA (Elvax 210), wax (Licomont TP EK), lubricant (stearic acid) and EVA plasticiser (Santicizer 261).
Three loadings were initially chosen i.e. 65v/v, 67v/v and 70v/v. The compositions that were used are given below:

Powder: Ti6Al4V **65 v/v**

	Density	**Mass**	**m/o**	**Volume**	**v/o**
Powder	4.42	**210.00**	89.04	47.51	**65.0**
LP:	0.87	0.000	-	-	-
Elvax 210:	0.93	8.966	3.80	9.64	13.19
Licomont	1.10	5.678	2.41	5.16	7.06
Stearic acid	0.94	2.241	0.95	2.38	3.26
Santi. 261	1.07	8.966	3.80	8.38	11.47
Total		235.85	100.00	73.08	100.00
Binder :		25.85	10.96	25.57	

Powder: Ti6Al4V **67 v/v**

	Density	**Mass**	**m/o**	**Volume**	**v/o**
Powder	4.42	**229.00**	89.86	51.81	**67.0**
LP:	0.87	0.000	-	-	-
Elvax 210:	0.93	8.966	3.52	9.64	12.46
Licomont	1.10	5.678	2.23	5.16	6.67
Stearic acid	0.94	2.241	0.88	2.38	3.08
Santi. 261	1.07	8.966	3.52	8.38	10.83
Total		254.85	100.00	77.38	100.00
Binder :		25.85	10.14	25.57	

Powder: Ti6Al4V **70 v/v**

	Density	Mass	m/o	Volume	v/o
Powder	4.42	**250.00**	91.08	56.56	**70.0**
LP:	0.87	0.000	-	-	-
Elvax 210:	0.93	8.490	3.09	9.13	11.30
Licomont	1.10	5.377	1.96	4.89	6.05
Stearic acid	0.94	2.123	0.77	2.26	2.80
Santi. 261	1.07	8.490	3.09	7.94	9.82
Total		274.48	100.00	80.77	100.00
Binder :		24.48	5.40	24.21	

The rheological measurements were conducted with a Ceast SmartRheo capillary rheometer (Figure 5) at shear rates between 900 and 7200 s^{-1}. The capillary diameter was 1mm and the die length was 5mm. The temperatures were varied according to the observed brittleness/fluidity of the resultant extrudate.

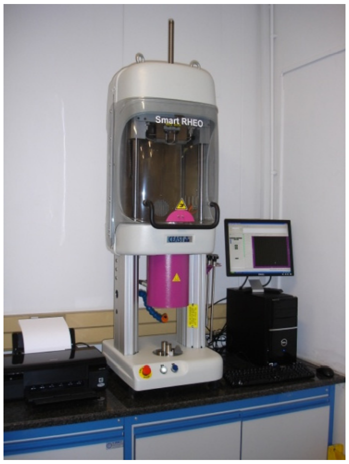

Figure 5: Ceast SmartRHEO capillary rheometer.

3. Experimental Results

The results of the viscosity measurements of the various feedstocks are shown in Figures 6 to 8.

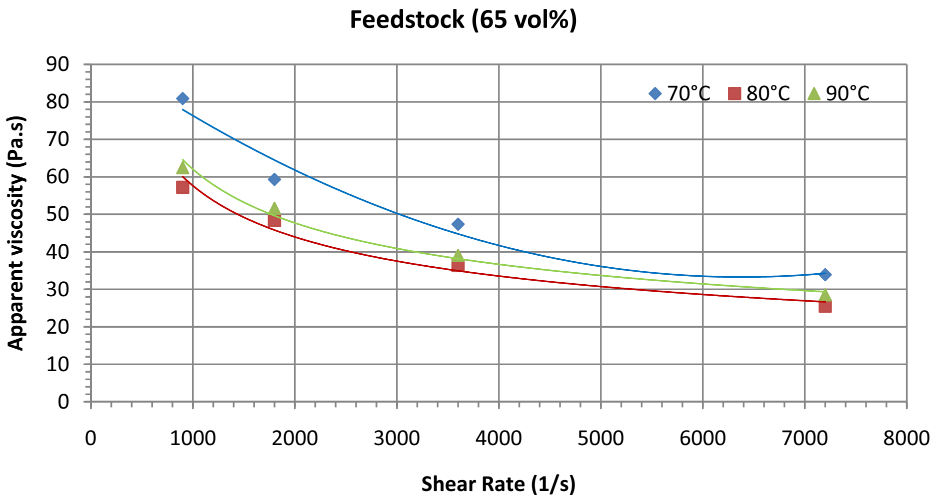

Figure 6: Capillary rheology results for feedstock containing 65 vol% Ti-6Al-4V powder.

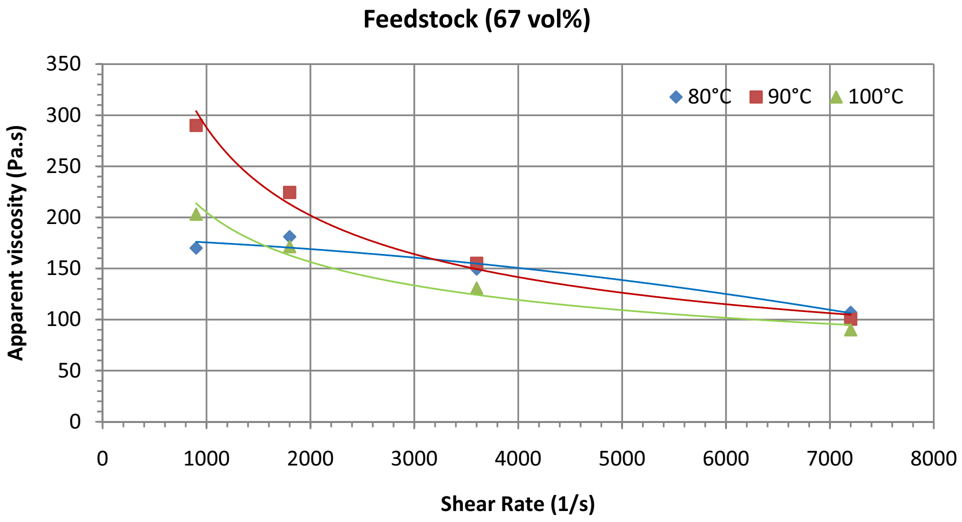

Figure 7: Capillary rheology results for feedstock containing 67 vol% Ti-6Al-4V powder.

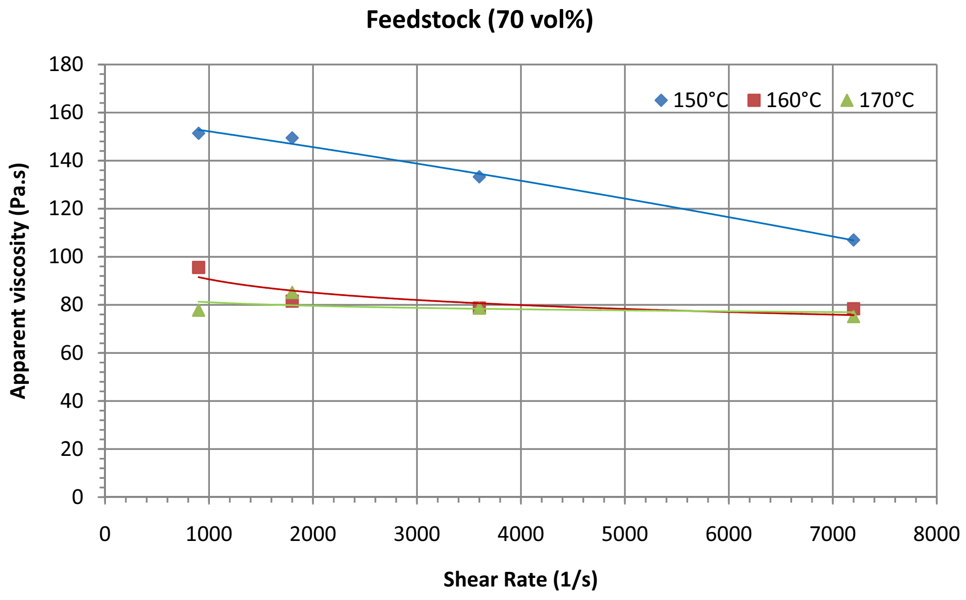

Figure 8: Capillary rheology results for feedstock containing 70 vol% Ti-6Al-4V powder.

As the temperature was increased it was expected that the viscosity should decline however this was not always observed. Figures 6 and 7 reveal an anomalous effect where the opposite can be seen to have occurred. This has been observed in some other binder systems as well and the reason for it is not clear. It may be due to a particular phase change in the binder constituents as it occurs below 100°C but is not observed at higher temperatures (Figure 8).

Nevertheless a consistent effect of powder loading can be found when a shear rate of 900s^{-1} is selected and the temperature to achieve a viscosity of 100Pa.s is determined. Figure 9 shows the increasing temperature required as the loading is raised.

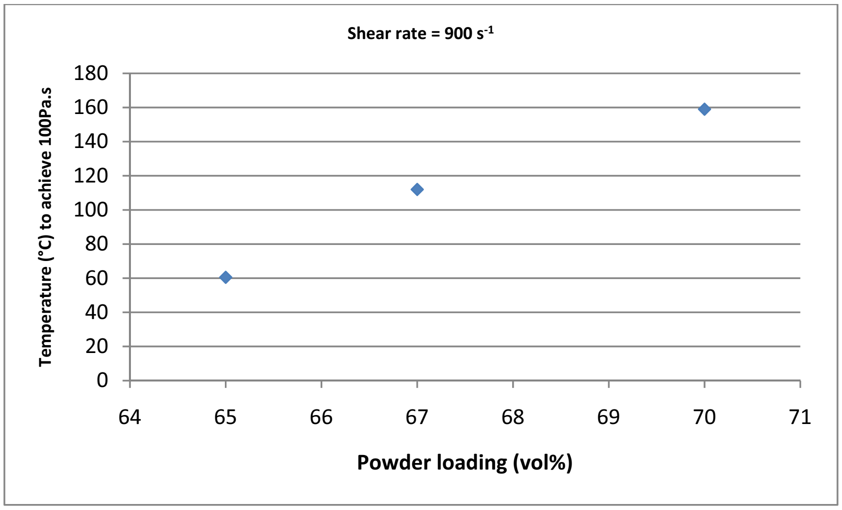

Figure 9: Effect of powder loading on the temperature required to obtain a viscosity of 100Pa.s.

The 70vol% feedstock showed indications of having insufficient green strength and it was felt that addition of more Elvax would be a possible solution. The powder loading was also reduced from 70vol% to 66vol%.

The composition of this new batch is given below:

Powder: Ti6Al4V **66 v/v**

	Density	Mass	m/o	Volume	v/o
Powder	4.42	**219.00**	89.44	49.55	**66.0**
LP:	0.87	0.000	-	-	-
Elvax 210:	0.93	8.966	3.66	9.64	12.83
Licomont	1.10	5.678	2.32	5.16	6.87
Stearic acid	0.94	2.241	0.92	2.38	3.17
Santi. 261	1.07	8.966	3.66	8.38	11.16
Total		244.85	100.00	75.11	100.00
Binder :		25.85	10.56	25.57	

Rheological tests results for this feedstock are given in Figure 10.

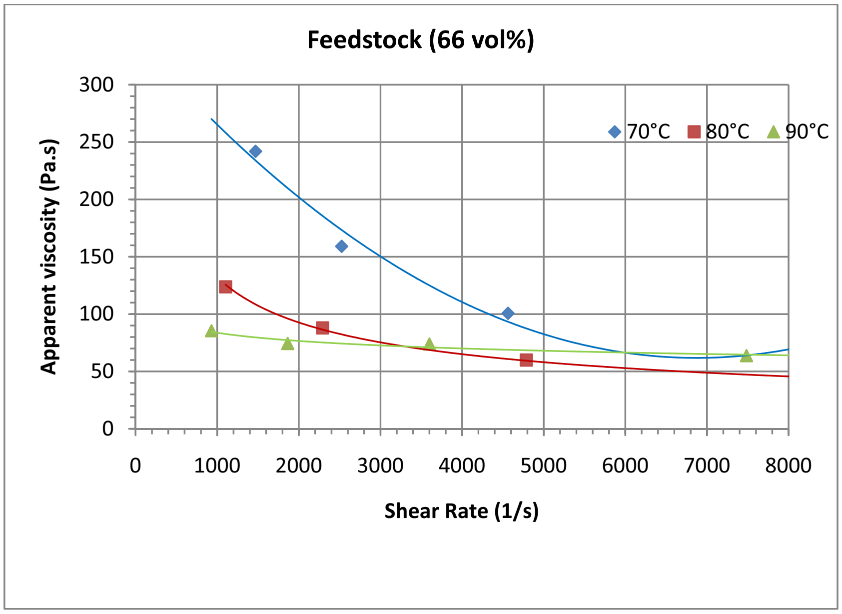

Figure 10: Capillary rheology results for feedstock containing 66 vol% Ti-6Al-4V powder.

The temperature required for the 66vol% feedstock to give a viscosity of 100Pa.s was calculated and was seen to fit the previously determined powder loading vs viscosity trend (Figure 11).

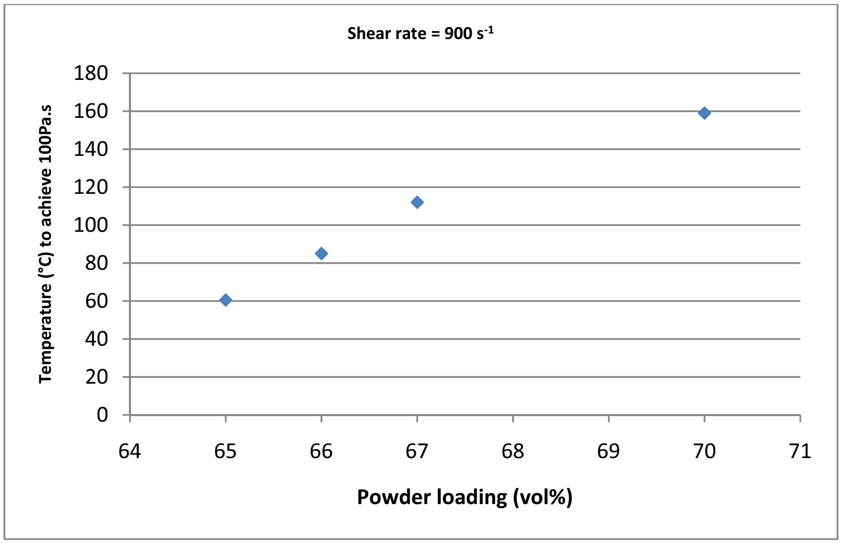

Figure 11: Effect of powder loading on the temperature required to obtain a viscosity of 100Pa.s.

4. Conclusions

Feedstocks of Ti-6Al-4V powder and a wax-EVA binder were prepared with varying levels of powder loading. An upper limit of approximately 70vol% has been suggested in literature however this is dependent on parameters such as powder particle size and shape as well as the binder system used.

In the present work, the loadings chosen ranged from 65 up to 70vol% and the viscosity measurements were determined in a capillary rheometer.

It was observed that at temperatures below 100°C the effect of temperature on fluidity was not predictable as some stiffening was observed as the test temperature increased.

However, if a shear rate that is representative of the injection moulding process is selected (i.e. $900s^{-1}$), it was found that increasing the powder loading caused the temperature to achieve the same viscosity (e.g. 100Pa.s) to rise significantly.

The optimum powder loading, based on the observed behaviour of this binder system, is considered to be between 66 and 67vol%.

References

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Have worked as a physical metallurgist for 26 years, with experience in alloy design (nickel-based superalloys and zinc die casting alloys), aero-engine failure investigations, repair of aero-engine components (by brazing, recoating and thermal treatments) and more recently titanium powder metallurgy.