The Effect of Particles Shape and Size on Feedstock Flowibility and Chemical content of As-sintered NiTi Alloys

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Abstract. This paper presents a comparative study of two different titanium powders in fabrication of NiTi alloys by metal injection moulding (MIM) route. Two batches of powder mixture consisted of Ni-Ti and Ni-TiH₂ with atomic ratio (at%) of 50-50 were prepared. TiH₂ powder was used as a substitution for pure Ti powder owing to its relatively cheaper cost and has been claimed favourable in producing less impurity uptake in sintering process. The binder system used for both mixtures comprised of composite binder of palm stearin (PS) and polyethylene (PE) at weigth ratio (wt%) of 60-40. The flow behaviour of the mixtures was analysed using a capillary rheometer at different shear rates and temperatures. The results showed that owing to irregular shape of TiH₂ compared to Ti powder, the viscosity of the feedstock was significantly higher, thus required greater temperature in order to improve the mouldability of the feedstock. Nevertheless, both feedstocks exhibited pseudoplastic, a shear thinning behavior with shear rate and temperature, desirable properties for injection moulding process. Samples prepared with Ni-Ti feedstock were sintered in a high vacuum furnace, while Ni-TiH₂ feedstock was sintered in a tube furnace under a flowing of Argon gas. The results showed that the impurity contents (Carbon and Oxygen) for both feedstocks were almost comparable, suggesting NiTi alloy samples prepared with TiH₂ powder is an attractive route for manufacturing of NiTi alloys.

1. Introduction
NiTi alloy is considered as one of the promising candidates used in biomedical applications, especially for bone implants due to its unique shape memory effect (SME) and pseudo-elasticity (PE) which is not found in many conventional metallic materials such as stainless steel and titanium alloys. In the other hand, mechanical behaviour of the alloy exhibits very close properties to bone compared to others [1]. Processing of NiTi alloy by powder metallurgy (PM) route, specifically by metal injection moulding (MIM) has been extensively studied by Ismail [1]. One of the important attributes in the MIM is the flow behaviour of the prepared feedstock via rheological test. The success of feedstock flow through die orifice during rheological test is strongly influenced by powder characteristics in terms of size and shape, relative fraction between powder and binder and processing parameters such as temperature and pressure. These attributes are significantly important to ensure the part is successfully moulded with uniform density which leading to further densification via debinding and sintering processes.
In processing of NiTi alloy by PM route, the use of TiH₂ as substitution to pure Ti powder has been investigated by several researchers [2-3] owing to several advantages such as (i) cheaper than pure Ti powder, (ii) capable to be sintered in argon flow atmosphere despite expensive route of vacuum sintering (iii) better phase homogeneity via sintering process and (iv) low impurity uptake particularly oxygen and carbon. Most of the TiH₂ powder used by researchers is irregular in shape, considered as sufficient when conventional compaction and sintering method is employed as irregular shape powder provides better powder interlocking mechanism. However, in MIM route, owing to the flow of powder-binder mixture via small flow path in mould cavity, starting powders with spherical shape is highly required as it greatly reduces friction during moulding, thus improve mouldability. Irregular powder will increase inter-particle and reduce the packing density compared to spherical shape. This circumstance will probably lead to powder-binder separation during injection moulding and further sintering process cannot be preceded. Generally, the powder size of less than 20 µm is required and the irregular shape powder is undesirable for injection moulding process[1]. The irregular size of TiH₂ will increase the inter-particle friction and reduce the packing density compared to spherical shape. It is believed that processing improvement can be done by tailoring the powders blend with different size and shape where different particles size produce better moulding capacity when mixing the finer spherical shape with irregular coarse powder [4-5].

In this proposed research, the effect of TiH₂ substitution in processing of NiTi by MIM route is investigated, taken into account the feedstock rheology, injection moulding, sintering and impurity contents after the sintering process. The low impurity uptake, particularly O₂ and C after sintering process is significantly important as it leads to better mechanical and corrosion resistance of the NiTi alloy. The result is compared with previously done formulation using elemental Ni and Ti powder mixtures [6].

2. Materials and Method

Figure 1 shows the SEM images of the elemental Ti, TiH₂ (after ball-milled) and Ni powders used in the present work. Clearly, different morphology can be observed; Ti powder shows spherical shape with very fine surface finish while the TiH₂ powder is irregular and the surface texture is rough. The Ni powder is also spherical in shape but the surface is rougher than the Ti powder. The average particle size measured by a Malvern® particle size analyser were Ti =10.86 µm, TiH₂ = 26.66 µm and Ni = 7.87 µm. Due to greater size of the as-received TiH₂, the powder was ball milled at a speed of 300 rpm in a ball mill to reduce the particle size, resulting the mean particle size of 9.77 µm.

![Figure 1. SEM of starting elemental powders: (a)Ti (b) TiH₂ and (c) Ni](image)

Feedstock preparation was done by mixing the powder mixtures and binder system using an internal mixture, Haake Rheomix at mixing temperature of 150°C for 2 hours. The flow behaviour of the feedstock was then characterized using a Rosand RH2000 capillary rheometer. The tungsten carbide die having a diameter and length of 1 mm and 16 mm, respectively was used resulting in an aspect ratio (L/d) of 16. The pelletized feedstock was loaded into the preheated chamber at a constant heating rate of 5°C/min and at the temperature range of 110-150°C for feedstock A, while 150 - 170°C
for feedstock B at a constant shear rate within the range 5 – 8000 s\(^{-1}\). Tensile shape sample in accordance with ASTM 638-type V standard [7] were then injection moulded using a manually operated injection moulding at a temperature range between 130°C and 170°C. All moulded samples were then subjected to solvent extraction using n-heptane solution at 50°C to remove the primary binder of palm stearin. Samples prepared from feedstock A were sintered in a high vacuum furnace at a sintering temperature of 1150°C as reported in previous work [6], while samples from feedstock B were sintered in an argon gas flow tube furnace at 1100°C as investigated by Chen [3]. The chemical contents of the sintered parts were determined using a Leco Melt Extraction Machine (LECO TCH 600) to determine the impurity levels (Carbon and Oxygen) for each sample.

3. Results and Discussion

3.1 Viscosity vs Shear Rate

Figure 2 shows the result of flow behavior for (a) Ni-Ti feedstock and (b) Ni-TiH\(_2\) feedstock, clearly both feedstock formulations demonstrate almost similar pattern of flow; viscosity decreasing with shear rate. This common behaviour for injection moulding materials is also known as shear thinning or pseudoplastic in which increasing of shear allows small particles to fill within the gap between large particles and feedstock homogeneity and fluidity are improved [8,9]. It is also noticed that the value of viscosity for Ni-TiH\(_2\) feedstock is significantly higher, approximately 30 times greater than the Ni-Ti feedstock, indicating greater friction of the feedstock attributed from the irregular shape and rough surface of TiH\(_2\) powder. Ismail [1] has highlighted in his work that the recommended viscosity for feedstock is the range of 10 and 1000 Pa.s at the injection moulding operating temperature. It was also observed that the required temperature for Ni-Ti feedstock to exhibit good flow was relatively lower, in the range of 130 and 150°C, while for Ni-TiH\(_2\) feedstock was in the range of 150 and 170°C. This shows that higher temperature is needed during actual injection moulding in order to reduce the inter-particle friction as well as bonding between particle and binder. However, too high moulding temperature will cause other problems, especially powder-binder separation and flashing, thus feedstock may not be proceeded to injection moulding process.

![Figure 2. Variation in viscosity and shear rate for a) Ni-Ti feedstock, b) Ni-TiH\(_2\) feedstock](image)

3.2 Shear sensitivity index (n)

One of the information that can be extracted from the rheological analysis is the level of shear sensitivity or generally referred as \(n\) index. It is determined from the slope of logarithmic plots of shear stress versus shear rate. The \(n\) index values below than 1 is generally reported by many researchers [1, 6, 8-11], indicating pseudoplastic flow which is the required flow in injection moulding process. In the rheological finding by Ismail [1] using Ni and Ti powder mixtures, the optimal range of \(n\) was in the range of 0.5 and 0.7. Feedstock with greater than 0.7 exhibited very viscous flow resulted in short-shot defects, while too low \(n\) values resulted in jetting flow leading to binder separation. Figure 3 compares the \(n\) values for both feedstocks, clearly Ni-Ti feedstock exhibited better flowbility in comparison with Ni-TiH\(_2\) feedstock owing to spherical shape Ti powder. The results also show that increasing
the barrel temperature resulted in $n$ values increases, corresponding to better flowability as suggested by Yimin et al. [10]. They claimed that greater value of $n$ will result in less sensitivity of viscosity changes with shear rate.

![Graph showing sensitivity index (n) vs. temperature for Ni-Ti and Ni-TiH2 feedstocks.

**Figure 3.** Sensitivity Index (n) a) Ni-Ti feedstock, b) Ni-TiH2 feedstock

### 3.3 Activation Energy (E)

Another aspect that commonly investigated is the flow activation energy of the feedstock. Table 1 compares the $E$ values for two batches of feedstock. Low $E$ value is preferable which indicates viscosity is not strongly influenced by temperature and desirable for injection moulding. Low temperature sensitivity on viscosity is desirable for a good quality of MIM feedstock. Agote el al. [11] have stated that the value of $E$ determines the sensitivity of the viscosity to temperature which generally should be as small as possible in order to avoid any sudden viscosity changes [10]. The flow activation energy of evaluated feedstock can be attained from the slope of graph ln against (1/T). The result clearly shows that Ni-TiH2 feedstock exhibited higher $E$ value, indicating higher sensitivity during moulding attributed to higher viscosity of the feedstock.

| Feedstock   | Flow activation energy (kJ/mol) |
|-------------|---------------------------------|
| A (Ni-Ti)   | 16.1                            |
| B (Ni-TiH2) | 55.72                           |

**Table 1. Flow activation energy for both feedstock**

### 3.4 Injection Moulding and Chemical Contents

Both feedstocks were successfully injection moulded to tensile shape as shown in Figure 4 in the range of 140 and 170°C. It was observed that owing to irregular shape of TiH2 powder and higher viscosity, a greater temperature was used for feedstock B to ensure good flowability. After sintering process the samples were tested using LECO TCH 600 to determine impurities containing oxygen and carbon of the as-sintered sample. The sintering environment is different where feedstock A (Ni-Ti) was sintered using high vacuum environment and feedstock B (Ni-TiH2) using low cost tube argon furnace. Table 2 shows the impurity contents for the as-sintered parts in comparison with other related published research using MIM of elemental Ni and Ti powders. It shows that both feedstocks have low chemical contents that suitable for biomedical implant. It can be seen that the impurity of oxygen in the present work is almost double and the carbon is comparable with the previous work. The lower impurity contents were because of employing a powder with lower initial impurity contents [1, 12]. However, all previous studies using MIM route show an increase of impurity from the initial powder, particularly oxygen. Thus, maintaining the low oxygen content comparable to that contained in the initial powder is almost difficult. Furthermore, the use of binder system which mainly comprised of hydro-carbon and several stages involved in MIM give the greater tendency for the impurities to be introduced prior to sintering process. However, the carbon concentration can be reduced to a minimum value if suitable binder can be identified and optimized process parameters are used.
Figure 4. Green parts after been removed from mould cavity

Table 2. Comparison of impurity contents between present and previous works

| Reference | Composition | Conditions | Impurity contents (wt%) |
|-----------|-------------|------------|------------------------|
|           |             | Sintering Temperature (°C) | Atmosphere | O₂ | C |
| Feedstock A (Ni-Ti) | 50.0at.% Ni - 50.0at.% Ti | 1150 | Vacuum | 0.498 | 0.117 |
| Feedstock B (Ni-TiH₂) | 50.0at.% Ni - 50.0at.% TiH₂ | 1100 | Argon | 0.426 | 0.119 |
| [1] | 50.9at.% Ni-49.1at.% Ti | 1150 | Vacuum | 0.200 | 0.062 |
| [12] | 50.9at.% Ni-49.1at.% Ti | 1100 | Vacuum | 0.3524 | 0.112 |

From the present work, results show that sintering of NiTi alloy starting with elemental powders of Ni and TiH₂ in an argon tube furnace following metal injection moulding process seems to be attractive for several reasons; (i) low cost of TiH₂ and argon tube sintering and (ii) comparable impurity uptake with vacuum sintered condition (Feedstock A). Further improvement is in progress in order to minimize the impurity uptake, thus improving the mechanical behaviour and biocompatibility of the sintered NiTi alloy.

4. Conclusions
It can be concluded that spherical shape powder has better rheological behaviour compared to irregular powders. Both feedstock exhibited shear thinning which is the desired flow behaviour for injection moulding. Feedstock A containing Ni-Ti exhibited better rheological properties in terms of viscosity range, low shear sensitivity index and activation energy in comparison with Feedstock B containing Ni-TiH₂. This resulted in low injection temperature during injection moulding. From the sintering point of view, samples prepared with TiH₂ powder and sintering in an argon atmosphere exhibited a comparable impurity uptake with samples sintered in vacuum condition, thus providing better insights for future works on NiTi alloy processing by MIM route.

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