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Improved Processing of Titanium Alloys by Metal Injection Moulding

A T Sidambe[1], I A Figueroa [1], H Hamilton[2], I Todd[1]

[1]University of Sheffield, Engineering Materials Department, Sir Robert Hadfield Building Mappin Street, Sheffield, S1 3JD, UK

[2]Johnson Matthey Technology Centre, Blount's Court, Sonning Common, Reading, Berkshire, RG4 9NH, UK

Email: Thwala1@aol.com

Abstract. The commercially pure (CP-Ti) and Ti6Al4V (Ti-64) powders with powder size of sub 45-micron were mixed with a water soluble binder consisting of a major fraction of Polyethylene Glycol (PEG), a minor fraction of Polymethylmethacrylate (PMMA) and some stearic acid as surfactant. The pelletised mix was injection-moulded into standard tensile bar specimens and then subjected solvent debinding by water leaching and thermal debinding in an argon atmosphere. The titanium compacts were then subjected to sintering studies using the Taguchi method. The results of the oxygen impurity levels of the sintered parts are presented in this paper. Titanium parts conforming to Grade 2 requirements were achieved for CP-Ti whilst those conforming to Grade 5 were achieved for Ti-64.

1. Introduction

Metal Injection Molding (MIM) is a well-established, cost-effective method of fabricating small-to-moderate size metal components. MIM has a wide area of applications which include watch cases, radial rotors, turbocharger rotors, automotive parts, surgical tweezers, gas manifolds and fuel nozzles etc. The MIM industry has been driven by reduction in production costs as compared to other methods and MIM has become a mature technique for the fabrication of small and difficult to machine parts with complex shapes.

The MIM cycle begins with preparation of a feedstock by mixing together very fine metallic powder with a binder comprising waxes, polymers, lubricants and surfactants. The resulting feedstock is then granulated. An injection moulding machine is used to heat up the feedstock before injecting it into a mould cavity under pressure. The molten feedstock is allowed to cool, solidify and become what is known as a “green” part. The binder components are then removed by the process of debinding and the brown moulding becomes a highly porous “brown” part. The brown part is sintered at elevated temperature and shrinks during the process typically to more than 95% density. Sintering is considered to be a very important step because it affects the final density and mechanical properties. It has been shown in previous studies that the important factors of the sintering cycle are: heating rate, sintering time, sintering temperature and sintering atmosphere [1-4]. These factors can affect the microstructure, pore size and shape, final density, and final impurity levels on the sintered part. These in turn influence the mechanical properties of the sintered parts. An understanding of the effects of the sintering factors on the final density and mechanical properties can be used to optimise the sintering process [5]. One method that can be used in sintering studies is the Taguchi method.

The Taguchi method is statistically a robust technique which has been proven to be reliable [6]. This method utilizes orthogonal arrays to study a large number of variables with a small number of experiments [7, 8]. An orthogonal array is a balanced matrix that is used to lay out an experimental plan [9] and this approach can reduce research and development costs by simultaneously studying a large number of parameters [10].

The traditional approach to experimental work is to vary one factor at a time, holding all other factors fixed. This method does not produce satisfactory results in a wide range of experimental settings. Screening of process parameters is the key step in Taguchi method to achieve high quality without increasing the number of experiments and cost [11].

The process of estimating the main effects of each factor is called the analysis of means (ANOM) and the effect of a factor level on the deviation it causes from the overall mean response is also widely used to analyse the results. From this analysis, the main effect of each parameter can be estimated and from which the optimum conditions associated with specified property (expected result at optimum condition) can then be predicted using the equation (1).

$$y(A,B,C,D) = \bar{y} + (\bar{y}_A - \bar{y}) + (\bar{y}_B - \bar{y}) + (\bar{y}_C - \bar{y}) + (\bar{y}_D - \bar{y}) \tag{1}$$

Where $\bar{y}$ is the grand average of performance represented by the overall mean of the entire experiment. The values of factor effects $\bar{y}_A$, $\bar{y}_B$, $\bar{y}_C$ and $\bar{y}_D$ depend upon the levels of A, B, C and D when each factor has the most effect.

The Taguchi method also uses a statistical measure of performance called signal-to-noise (S/N) ratio. The S/N ratio takes both the mean and the variability into account. The S/N equation depends on the criterion for the quality characteristic to be optimized and is shown in Equation 2.

$$S/N = -10\log(mean\_square\_quality\_of\_characteristic) \tag{2}$$

Two types of analysis for the S/N ratio, the-larger-the-better and the smaller-the-better, are most usually used. In the-larger-the-better type, the mean square of characteristic is $(1/\text{property})^2$, whereas in the smaller-the-better type the square of the characteristic is $(\text{property})^2$ [12,13].

After performing the statistical analysis of S/N ratio or ANOM, an analysis of variance (ANOVA) needs to be employed for estimating error variance and for determining the relative importance of various factors [14].

In this study, in which the analysis has been confined to the ANOM and ANOVA, titanium was injection moulded and focus was placed on sintering studies. The commercially pure (CP-Ti) and Ti-6Al-4V (Ti-64) powders with powder size of sub 45-micron were injection-moulded into standard tensile bar specimens and then subjected to sintering studies using the Taguchi method described above. The objective of the study is to determine which factors contribute to less oxygen contamination in sintered titanium components. Titanium exhibits high susceptibility to interstitials and shows a very high reactivity with atmospheric components like oxygen, nitrogen and carbon. The quantity of such foreign elements in the alloy is problematic and strongly influences its mechanical properties and too high content of these elements in particular causes a non-tolerable brittleness of MIM parts.

2. Experimental

The CP-Ti and the Ti-64 powders were supplied by Advanced Powders and Coatings (AP & C) and are produced by plasma atomization. Figure 1 is a scanning electron micrograph showing the morphology of the powder as spherical in shape. CP-Ti and Ti-64 chemical composition properties are shown in Table 1 and the particle size distribution is shown in Figure 2 as sub 45μm in size.

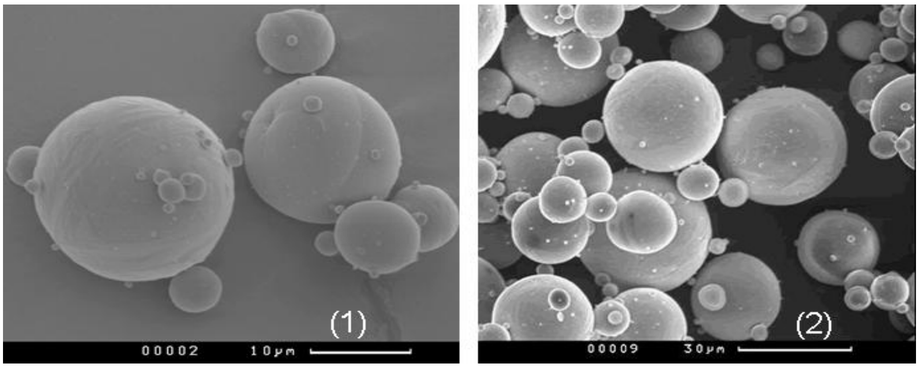

Figure 1: Scanning electron micrograph showing the morphology of the CP-Ti (1) and Ti6Al4V (2) powder

The CP-Ti and the Ti-64 powder were each mixed with a water soluble binder that consists of a major fraction of polyethylene glycol (PEG) and a minor fraction of polymethylmethacrylate (PMMA) with Stearic acid (SA) used as a surfactant. Handling of the materials was carried out in an inert argon atmosphere and the mixing was carried out in the centrifugal Speedmixer^{TM}.

Table 1: CP-Ti and Ti-64 chemical properties

Powder	Mean	Composition (%)							
type	size(μ)	O	C	N	H	Fe	Al	V	Ti
CP-Ti	sub 45	0.143	0.012	<0.05	<0.05	0.06	N/A	N/A	Bal
Ti-6Al-4V	sub 45	0.148	0.04	<0.05	0.008	0.08	6	4	Bal.

The mixing speeds were increased every two minutes as follows: 800, 1200, 1400, 1400, 1600 rpm. The weight ratios of the constituent binder materials were 87:11:2 of PEG, PMMA and SA respectively. The powder loading that was selected is 69 volume %. For the purposes of this study, the CP-Ti specimens have been denoted as MIM 57 whereas the Ti-64 specimens have been denoted as MIM 69. The mixed feedstock was granulated and then injection moulded in a 60 tonne Arburg 320 C injection moulding machine at 120°C. An injection pressure of 1500 bar, packing pressure of 1350 bar and injection speed of 20 cm^3/min were used.

Figure 3 is a schematic showing the dimensions of the standard MIM tensile bar that was moulded. After injection moulding, the mouldings were visually inspected and each weighed for quality control. The green part mouldings were then subjected to solvent extraction by immersing them in a heated water bath containing distilled water for 6 hours at 55°C. This stage of debinding was aimed at removing the PEG component of the binder. The MIM samples were then dried in air for 12 hours.

The parts were then subjected to thermal debinding in order to remove the backbone PMMA component of the binder. This debinding process was done by heating the parts in an Argon atmosphere at a ramp rate of 2.5ºC/min to 350ºC, and holding for 1 hour after which they were heated up again at a heating rate of 2ºC/min to 440ºC and again holding for 1 hour. After that the samples were sintered.

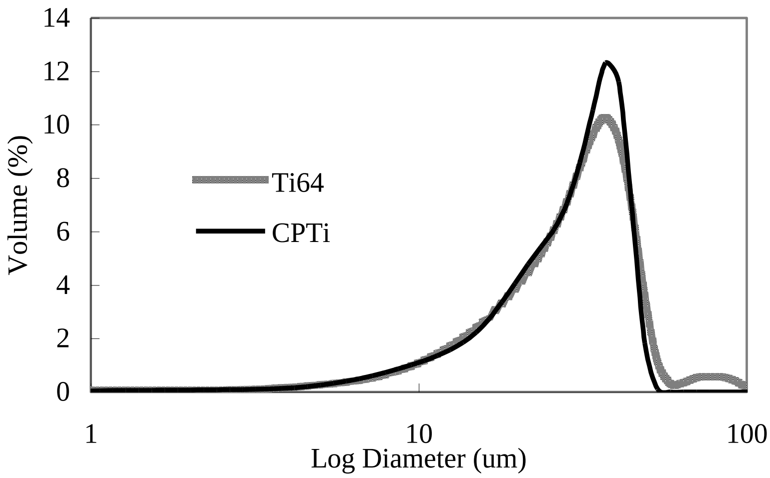

Figure 2: Particle size distribution for CP-Ti and Ti6Al4V

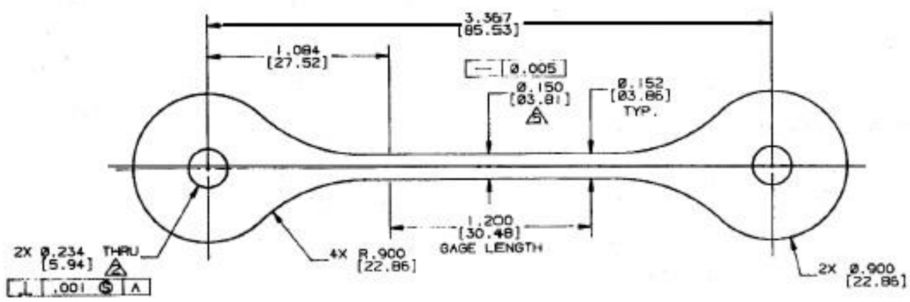

Figure 3: ASTM Tensile specimen drawing for parts produced by metal injection moulding [15]

The sintering parameters were selected according to the Taguchi experimental design methodology using sintering temperatures of 1250°C, 1300°C and1350°C, heating rates of 2.5, 10 and 20°C/min, sintering atmosphere in low flow argon, high flow argon and vacuum as well as sintering times of 1, 2 and 3 hours in an L9 orthogonal array. This means that nine experimental runs with four factors and three levels investigated.

Table 2: Selected process parameters and their respective factors and levels for the sintering experiments

	Factor	Level 1	Level 2	Level 3
A	Sintering Time (hrs)	1	2	3
B	Sintering Atmosphere	Argon High	Argon Low	Vacuum
C	Heating Rate (°C/min)	2.5	10	20
D	Sintering Temp (°C)	1250	1300	1350

Each sintering factor was designed with three levels, as shown in Table 2. Nine experiments were carried out as shown in Table 3. “Argon low” indicates a flow rate of 10 slpm and whereas “Argon high” indicates a flow rate of 20 slpm in the retort of the sintering furnace. A vacuum level of 10^{-3}

mbar was used. Chemical analysis of the samples to determine the impurity levels of oxygen and carbon of MIM specimens was carried out using a conventional LECO melt extraction system

Table 3: Experimental layout and factor distribution of L9 orthogonal array

	Factor1	Factor 2	Factor 3	Factor 4
	A:Sintering Time	B:SinteringAtmosphere	C:Heating Rate	D:Sintering Temp
1(T1)	1	Argon High	2.5	1250
2(T5)	1	Argon Low	10	1300
3(T7)	1	Vacuum	20	1350
4(T9)	2	Argon High	10	1350
5(T3)	2	Argon Low	20	1250
6(T8)	2	Vacuum	2.5	1300
7(T4)	3	Argon High	20	1300
8(T6)	3	Argon Low	2.5	1350
9(T2)	3	Vacuum	10	1250

3. Results

Figure 4 is a photograph illustrating the linear shrinkage undergone by a sintered CP-Ti MIM tensile sample. The dimensional change of the MIM sample after injection moulding, solvent debinding and sintering is shown.

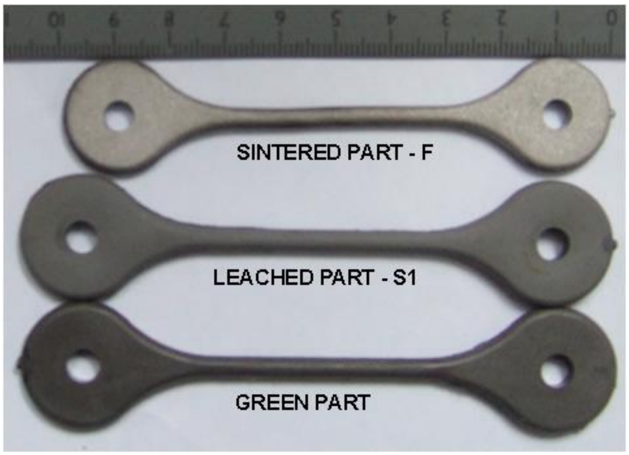

Figure 4: Photograph illustrating the linear shrinkage undergone by a MIM sintered part

The results of oxygen impurity levels as well as the grand average of performance for the nine experimental runs are shown in Table 4. The table of the main effects which shows the values of the measured oxygen impurity levels of CP-Ti and Ti-64 for each factor at all levels is shown in Table 5. Figure 5 shows the response graphs of mean oxygen levels for both CP-Ti (MIM57) and Ti-64 (MIM69) against the sintering factors. For CP-Ti the main effect factors are A1, B1, C2 and D1 (i.e. sintering for 1 hour in high flow argon at a heating rate of 10°C/min at 1250°C) Ti-64 these are A1, B1, C3 and D2 (i.e. sintering for 1 hour in high flow argon at a heating rate of 20°C/min at 1300°C).

Table 4: Results of oxygen impurity levels in CP-Ti (MIM57) and Ti-64 (MIM69)

			Oxygen(%)	
Std	Run	ABCD	MIM57	MIM69
1	T1	1111	0.18	0.19
9	T2	3321	0.20	0.19
5	T3	2231	0.18	0.19
7	T4	3132	0.25	0.15
2	T5	1222	0.18	0.17
8	T6	3213	0.27	0.20
3	T7	1333	0.21	0.17
6	T8	2312	0.30	0.21
4	T9	2123	0.20	0.18
Cu. Gr. Av of Perf.			0.22	0.18

Table 5: Mean oxygen impurity levels of CP-Ti (MIM57) and Ti-64 (MIM69) for each factor at all levels

	Factor	Level 1	Level 2	Level 3
MIM57	A:Sintering Time (hrs)	0.19	0.23	0.24
	B:Sintering Atmosphere	0.21	0.21	0.24
	C:Heating Rate (°C/min)	0.25	0.19	0.21
	D:Sintering Temp (°C)	0.19	0.24	0.23
MIM 69	A:Sintering Time (hrs)	0.18	0.19	0.18
	B:Sintering Atmosphere	0.17	0.18	0.19
	C:Heating Rate (°C/min)	0.20	0.18	0.17
	D:Sintering Temp (°C)	0.19	0.18	0.18

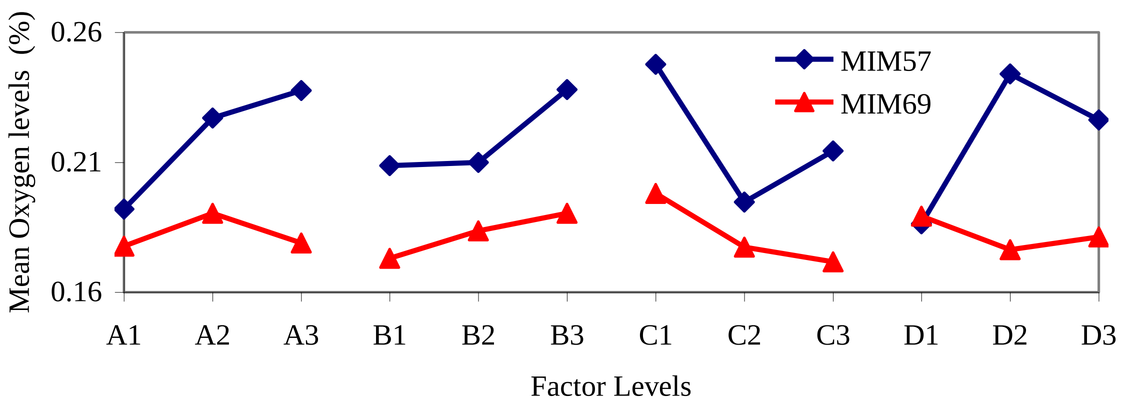

Figure 5: Response graphs for mean oxygen levels for both CP-Ti (MIM57) and Ti-64 (MIM69) against the used sintering factors using the smaller-the-better model

From the results of ANOVA for CP-Ti shown in Table 6, it can be deduced that there are no factors sensitive to the process variation due to a larger contribution of the residual error. There are interactions between factors A and B (larger) and also between C and D which have been treated as errors. The influence of the factors that contribute to high oxygen levels is in the following order from high to low: sintering time, sintering temperature, atmosphere and heating rate.

For Ti-64, Table 7 shows that the heating rate is sensitive to the process variation. There are interactions between factors A and B and also between C and D but they have also been treated as part of the errors. It can also be deduced that the heating rate is the more significant that the other three factors with a contribution of 45.27%, followed by sintering atmosphere which contributes 21.23%.

Table 6: Anova results for CP-Ti mean oxygen impurity levels

Source	Sum of Squares	DF	Mean Square	F Value	Perc. P%
A	0.0031	1	0.0031	1.54	21.40
B	0.0016	2	0.0008	0.4	11.26
C	0.0013	1	0.0013	0.65	9.09
D	0.0024	1	0.0024	1.18	16.42
Residual	0.0061	3	0.0021		41.81
Cor Total	0.0146	8			100.00

Table 7: Anova results for Ti-64 oxygen impurity levels

Source	Sum of Squares	DF	Mean Square	F Value	Perc. P%
A	$2.67\text{x}10^{-6}$	1	$2.67\text{x}10^{-6}$	0.0128	0.012
B	$4.59\text{x}10^{-4}$	2	$2.29\text{x}10^{-4}$	1.10	21.23
C	$9.78\text{x}10^{-4}$	1	$9.78\text{x}10^{-4}$	4.7	45.27
D	$9.60\text{x}10^{-5}$	1	$9.60\text{x}10^{-5}$	0.46	4.22
Residual	$6.25\text{x}10^{-4}$	3	$2.08\text{x}10^{-4}$		28.92
Cor Total	$2.16\text{x}10^{-3}$	8			100.00

Therefore, if the main factors for CP-Ti are A1, B1, C2 and D1 (i.e. sintering for 1 hour in high flow argon at a heating rate of 10°C/min at 1250°C) then the optimum result expected can be roughly estimated calculated using Equation 1 is 0.125% and this represents no oxygen contamination because the powder was found to contain 0.143% oxygen. Similarly, for Ti-64 if the factors are A1, B1, C3 and D2 (i.e. sintering for 1 hour in low high argon at a heating rate of 20°C/min at 1300°C) then the expected oxygen level result can be estimated to be 0.18% for a confidence interval of ±0.02 at 95%CI. It is noted however that only a main effect which exceeds the magnitude of the interactions can safely be used.

4. Discussion

It has already been mentioned in Section 1 that external elements like oxygen strongly influence a component's mechanical properties and that a too high content of these elements in particular causes a non-tolerable brittleness of MIM parts. In this study it has been shown that oxygen levels can be obtained using short sintering time and lower temperatures. However a combination of these factors is not expected to contribute to adequate densification of MIM parts or acceptable residual porosity. This in turn also affects the final mechanical properties. Therefore the processing conditions can either be chosen according to intended application or the optimum processing conditions can be derived through co-optimisation by including factors which contribute to improved tensile strength as well as elongation of MIM parts.

Figure 6 and 7 show all factor levels' contributions towards oxygen levels in CP-Ti and Ti-64 respectively. Also included in these figures are the maximum oxygen levels for Ti Grades according to ASTM B348-06 [16] requirements.

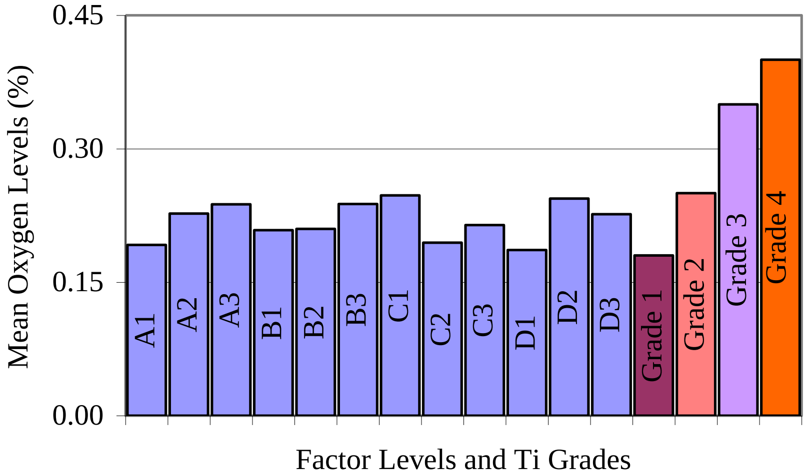

Figure 6: Comparison of factor level oxygen contributions with CP-Ti Grades requirements

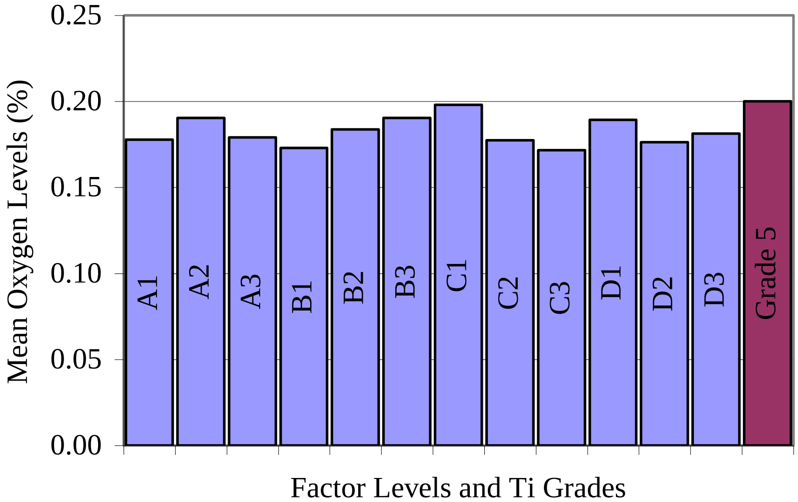

Figure 7: Comparison of factor level oxygen contributions in Ti-64 with Grade 5 requirements

For CP-Ti, Figure 6 shows that all the sintering factors contribute towards oxygen impurity levels which are within specifications for Grade 2 titanium. Therefore, co-optimisation can be performed from parameters contributing towards optimum parameters for elongation as well as tensile strength at the same time avoiding a combination of parameters that could cause oxygen levels to exceed requirements. For example it can be estimated using equation 2 that factors that contribute the highest oxygen levels in CP-Ti, ie A3, B3, C1 and D2 (i.e. sintering for 3 hours in vacuum at a heating rate of 2.5°C/min at 1300°C sintering temperature) would yield oxygen content of 0.311 %, corresponding to levels of Grade 3 titanium.

For Ti-64, Figure 7 shows that all the sintering factors contribute to oxygen impurity levels which are within specifications for Grade 5 titanium. Co-optimisation can be performed from parameters contributing towards optimum parameters for elongation as well as tensile strength at the same time avoiding a combination of parameters that could cause oxygen levels to exceed requirements. For example it can be estimated using equation 2 that factors that contribute the highest oxygen levels in Ti-64, ie A2, B3, C1 and D1 (i.e. sintering for 2 hours in vacuum at a heating rate of 2.5°C/min at 1250°C sintering temperature) would yield oxygen content of 0.221 %.

Based on the factor sensitivities derived from ANOVA, it can be confirmed that there is some latitude in the choice of optimum levels, i.e. B1=B2 in the case of CP-Ti and A1=A3, D2=D3 in the case of Ti-64 which means that these optimum conditions can be interchanged for co-optimisation reasons without affecting the oxygen levels significantly.

5. Conclusion

The feasibility and reliability of Taguchi DOE method to the sintering process of titanium injection moulded components has been successfully verified. For CP-Ti, it has been found that there are no factors sensitive to the process variation. The influence of the factors that contribute to high oxygen levels is in the following order from high to low: sintering time, sintering temperature, atmosphere and heating rate. For Ti-64, it has been shown that the heating rate is sensitive to the process variation and that the heating rate is more significant than the other three factors with a contribution of 45.27%, followed by sintering atmosphere which contributes 21.23%.

6. Acknowledgments

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