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Interstitial elements in titanium powder metallurgy: sources and control

E. Baril*, L. P. Lefebvre and Y. Thomas

The effect of interstitials on the mechanical properties of cast and wrought titanium alloys has been extensively reported but less information is available on the effect of contamination during PM processing. The sources of interstitial contamination when processing titanium powders by compaction, isostatic pressing, powder injection moulding (PIM) and innovative foaming processes are reviewed, focusing specifically on oxygen. The initial powder characteristics (surface area, size), process parameters (time, temperature) and environment (atmosphere, binder, support) may all have significant impact on the final interstitial content. It is, therefore, important to identify and control the sources of contamination by interstitials. A case study on PIM is provided to illustrate the relative contribution of the different sources.

It is well established that the mechanical properties of dense titanium and titanium alloys are sensitive to the presence of interstitial solutes such as oxygen, nitrogen, carbon and hydrogen, which tend to increase the elastic modulus and yield strength and reduce the ductility.[1] Nitrogen has generally the most significant effect, followed by oxygen and carbon. While nitrogen and carbon are usually not found at high concentration in dense titanium, oxygen is a common contaminant due to its high solubility in and high affinity for titanium. At low concentration, oxygen occupies octahedral sites of the α-titanium lattice; it increases the lattice parameters as well as the c/a ratio in the crystal, resulting in a volumetric change of 0·0013 nm^3/at.-%O.[2,3] The oxygen atoms interact with both the hydrostatic and shear stress fields of dislocations, affecting both edge and screw dislocation motion. Therefore, increasing oxygen content results in an increase of the yield strength, hardness and fatigue resistance at a given stress level, whereas it decreases the ductility and impact resistance by restricting twinning and prismatic slip.[4]

Since interstitial elements significantly affect the properties of titanium, standards have been established on the chemical requirements for orthopaedic and dental applications.[5–9] These standards specify maximum permissible interstitial contents for different manufacturing processes[11–13] and demonstrate the capability of wrought material, casting and PM processes to keep the oxygen concentration at low levels. The PM standard allows the highest oxygen content in the final component (0·30 wt-%) for Ti–6Al–4V alloy. Oxygen in porous titanium coatings for surgical implants has also been addressed in a standard.[10] According to this standard, the maximum content of oxygen in the powder used for such coatings must be <0·4 wt-%. The standard does not, however, specify the amount of oxygen in the final coating.

The high specific surface area of powders means that the potential of increased interstitial contents from surface contamination (oxidation, nitriding, carburising, etc.) is significant. The sources of interstitials contamination when processing titanium powders and their respective importance will now be reviewed, focusing specifically on oxygen.

Sources of interstitial contamination

Figure 1 illustrates typical PM steps and related variables that may affect interstitial contamination.

It should be noted that accuracy of chemical analysis is important in assessing oxygen in titanium, inert gas fusion being the most common technique. While the technique is normalised,[14] the results are highly sensitive to the sampling and measurement procedures. The reliability of the technique has been assessed in a round robin testing campaign conducted on $-45\ \mu$m cp Ti and Ti–6Al–4V powders at four laboratories certified to serve the aerospace and medical sectors.

As can be seen in Table 1, large variations were observed. The powder supplier was able to reproduce (within 4% variability) the results reported in the powders certificate of analysis and one laboratory (S) gave results relatively close (within 10%, but slightly above) to those reported by the supplier. The other laboratories provided values much higher (B) or well below (G) the certificate of analysis. The results clearly show that values from certified laboratories cannot be taken for granted unless their procedures have been validated and blind controlled to confirm their reliability and suggest that some laboratories need to be trained and monitored specifically for the analysis of titanium powders.

The authors' laboratory (NRC-IMI) has installed an inert gas fusion oxygen analyser (LECO TCH-600) and developed sampling, analytical and monitoring procedures for titanium powder. Once training and monitoring procedures were in place, the standard deviations achieved on SP3-126 (Ti) powder were 0·011 wt-%, which corresponds to variability below 4·4%. These values are, nevertheless, above the 1·5% variability values reported by the analytical equipment manufacturer.[15]

Powder production

The oxygen content of the starting powder is mainly determined by its manufacturing process, size distribution, surface area, chemistry, and storage conditions. These factors affect the two contributors to total oxygen content: surface oxide and oxygen in solid solution. The oxygen in solution mainly comes from the chemistry of the raw material and the powder manufacturing process. The amount of oxygen in the surface oxide

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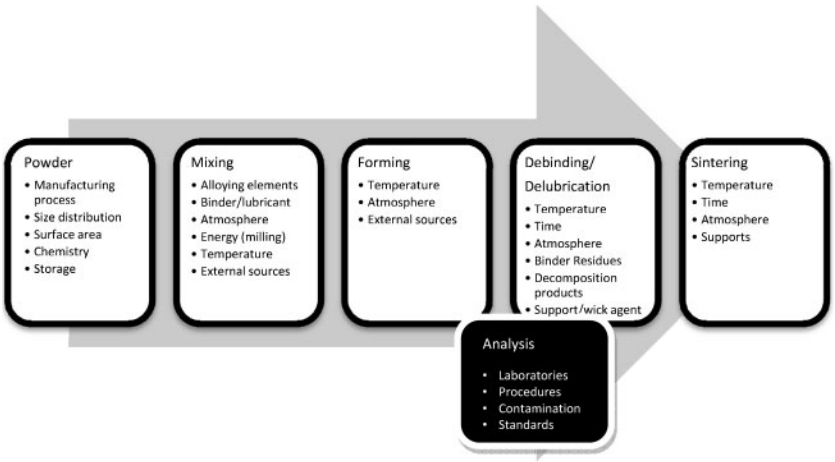
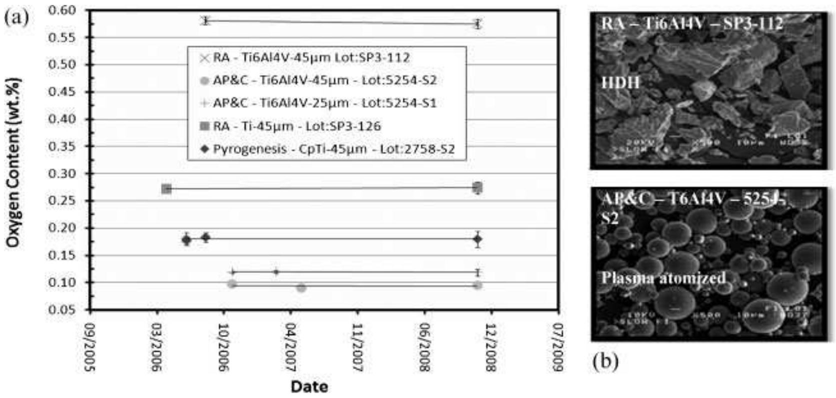


1 Source of interstitial oxygen contamination in typical PM processes



2 *a* Oxygen content of titanium powders stored in unsealed steel containers in air under uncontrolled conditions; *b* morphology of HDH and plasma atomised powders

depends on the specific surface area of the powder (particle size distribution and shape) and thickness of the oxide layer. The oxide layer thickness, on the other hand, depends on processing (exposure to oxygen at moderate temperature) and the storage conditions.

Figure 2 presents the total oxygen content of various titanium powders and the effect of storage on oxygen pick-up. Commercial purity (cp) Ti and Ti–6Al–4V powders from two manufacturers (Reading Alloy: HDH and AP&C-Pyrogenesis: plasma atomised) were analysed over a period of 2·5 years of storage in normal conditions (unsealed steel containers filled with air of uncontrolled humidity between 20 and 60% RH). The effect of particle size distribution and surface area can clearly be seen with the plasma atomised powders (5254-S1 and 5254-S2). Both powders were from the same atomisation batch but were sieved at -25 μm (S1) and -45 μm (S2), with specific surface areas of 0·1233 and 0·0717 $m^2 g^{-1}$ respectively. The surface area difference (i.e. 0·0516 $m^2 g^{-1}$) results in an increase of oxygen content by 0·0237 wt-% (an oxygen increase of 4·59 mg m^{-2}). Assuming the increase is directly related to surface oxidation (ρ=4·23 g cm^{-3}, O_{TiO2}=40·1 wt-%), this represents a 3 nm TiO_2 passivation layer, which is typical of oxide layers naturally formed on titanium at room temperature (2–7 nm).[16] The immobilisation of this oxygen in the passivation layer means that the interstitial content (in solution in titanium) in these powders should be ~0·062 wt-%. This is close to the level in commercially available high purity titanium (0·04 wt-%) and indicates that, apart from oxidation of the new surfaces created, there is practically no oxygen pick-up during atomisation.

HDH powders show significantly higher oxygen contents than the plasma atomised powders, associated with both the higher surface area due to their irregular shape (0·137 and 0·176 $m^2 g^{-1}$ for SP3-126 and SP3-112) and higher soluble content. Assuming a 3 nm TiO_2 passivation layer, the oxygen in solid solution represents 0·200 wt-% (SP3-126) and 0·484 wt-% (SP3-112).

During the 2·5 year exposure, the containers were opened several times and closed without purging with neutral gas; consequently, the powders were exposed to air. The results in Fig. 2 therefore show the relative resistance to oxidation of the titanium powder when stored and manipulated in a laboratory environment without use of a glove box or neutral gas cover.

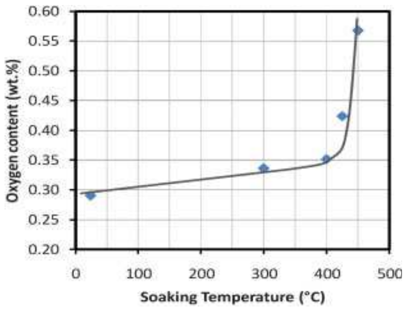
Powder mixing and compaction

In most PM processes, the titanium powders are mixed with lubricants, binders and/or alloying elements. The contribution of the mixing procedure is negligible unless mixing is done at high temperature and/or energy. With high mixing energies, such as those involved in mechanical alloying, the titanium particles may deform and/or break, leading to the exposure of new surfaces that will be passivated when exposed to air. The creation of the new oxide film increases the oxygen content in the final powder mixture.

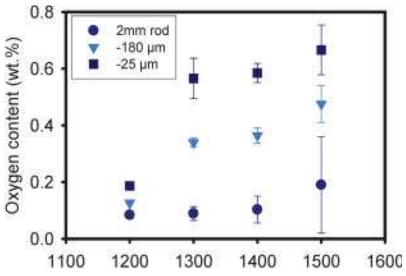
Additives such as binders or lubricants can also represent important sources of interstitial contamination. Consequently, these additives must be carefully selected to avoid oxygen pick-up during processing. Unless the powder/additives mixture is exposed at high temperature in the presence of oxygen, the forming (moulding, compaction, extrusion, foaming) of titanium powders does not cause important oxygen pick-up. Any pick-up usually comes from reaction with remaining oxygen in the debinding atmosphere and to a lesser extent from decomposition products.

Table 1 Round robin results on oxygen analysis (wt-%) on -45 μm hydride/dehydride (HDH) powders conducted with four certified laboratories serving aerospace and medical sectors

Sample	Certificate of analysis	G	B	S	B2	Supplier	Average (labs)	Standard deviation (labs)
SP3-126 (Ti)	0·25	0·109	0·63	0·276	0·221	0·26	0·30	0·20
SP3-112 (Ti–6Al–4V)	0·54	0·220	0·66	0·570	0·503	0·53	0·50	0·17



3 **Oxygen content in titanium foams exposed for 60 min at various temperatures in argon containing 20 vol.-%O_2**



4 **Oxygen content of loose titanium powders and 2 mm rod after exposure for 60 min in 10^{-6} torr vacuum**

Debinding/delubrication

Thermal processing is often used to decompose and eliminate binders and/or lubricants used during the forming step. Since decomposition usually takes place in inert atmospheres free of oxygen, these additives must have clean decomposition characteristics to avoid reaction with titanium during debinding.

Several formulations have recently been developed for the powder injection moulding of titanium. These formulations, which generally include compounds among polyethylene, polypropylene, polymethylmethacrylate, polyethylene glycol, ethylene vinyl acetate, paraffin wax, naphthalene and stearic acid,[17,18] have decomposition temperatures between 200 and 500°C. Thus, thermal debinding profiles must be optimised to the binder system used. Some compounds such as PEG leave excessive residues (oxygen and carbon) if not sufficiently removed during the water based initial debinding treatment.

Thermal debinding is usually done at moderate temperatures to ensure the complete decomposition of the binder while minimising oxygen pick-up. Figure 3 presents the oxygen pick-up of titanium foams (0·05 m^2 g^{-1}; initial oxygen content: 0·29 wt-%)[19] exposed for 60 min at various temperatures in argon containing 20 vol.-%O_2. It can be seen that oxidation dramatically increases above 400°C: below that temperature, the oxidation is not dramatic even in an atmosphere containing 20%O_2. This confirms that no special care is required when mixing or shaping titanium powder below 400°C (unless very fine powders are involved). This also indicates that the debinding/delubrication process should be done at temperature below 400°C.

Sintering

High temperature vacuum sintering is generally preferred for titanium PM components. Since sintering occurs at temperature above 1000°C, the passivation layer is dissolved and the oxygen goes into solution.[19] The titanium surface then becomes highly active and will react with oxygen, even at very low concentration in the atmosphere. The initial surface area of the powder, the sintering time–temperature profile and the sintering support are the main factors affecting oxygen pick-up. Figure 4 presents the effect of surface area (-25 and -45 µm powder and dense 2 mm rod) on the oxygen pick-up during exposure for 60 min in a 10^{-6} torr vacuum. It can be seen that oxygen pick-up increases significantly with temperature and also with the surface area of the medium (powder or rod). Other variables, such as sintering time and supports, have been analysed elsewhere.[20–22]

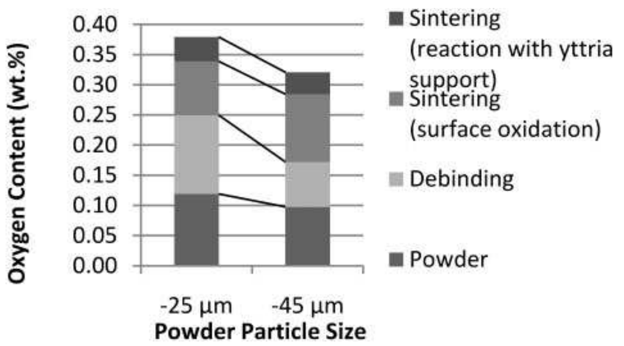
The surface of titanium is repassivated during exposure to air after vacuum sintering, resulting in additional oxygen pick-up. This effect is minimal for dense components but can be important for porous components.[19] The formation of this new oxide film contributes to the total oxygen content but should not have an important impact on the final mechanical properties of the components, on which the effect of oxygen in solution is predominant. The oxide film does, however, confer corrosion resistance and biocompatibility on titanium and titanium alloys.

Case study

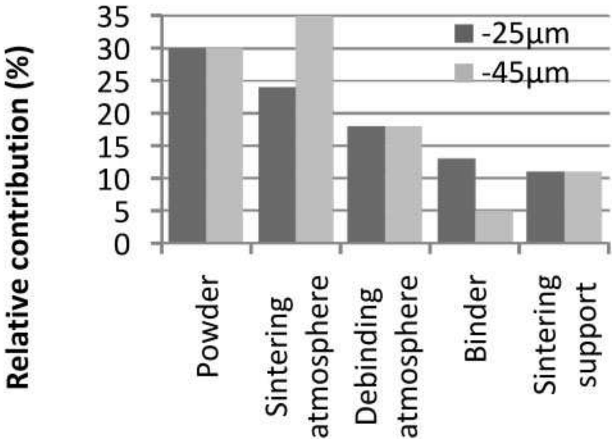
In order to evaluate the relative contribution of different sources of oxygen, a study of a titanium PIM process has been carried out. Titanium alloy PIM components have great potential in high value markets such as defence, medical and aerospace applications and the requirement to meet specified properties is critical in penetrating these markets.[23] Understanding and controlling interstitial contamination are an important component of these developments.

For this case study, two Ti–6Al–4V powder particle size distributions were used: -25 and -45 µm. The feedstock was composed of 66 vol.-% of powder in a polyethylene–paraffin wax–stearic acid binder system. Debinding was conducted for 10 h between 100 and 450°C in repurified argon (4 L min^{-1} Ar with 10^{-8} ppm O_2). Sintering was done under vacuum for 3 h at 1300°C. To monitor independently the effect of each variable, reference powders were placed in a BN crucible to avoid contamination from the binder or oxide support. Figure 5 compares the absolute contributions of the powder, debinding, sintering and support to the total oxygen content in the component. As expected, the -25 µm powder had higher oxygen content than the -45 µm powder, the major contributors being the initial powder and the debinding process.

When normalised, the contributions can be ranked in a Pareto graph (Fig. 6). This analysis indicates that the final oxygen content is principally affected by the initial oxygen content of the powder and the interaction with trace oxygen in the vacuum sintering furnace. Interestingly, powder size and surface oxidation do not change the



5 **Absolute contributions of powder, debinding and sintering cycles on final oxygen content of titanium PIM components**



6 **Pareto plot of contributions of main PIM variables to final oxygen content in Ti components**

relative ranking of the powder, debinding and sintering support contributions. They do, however, impact on the ranking of the binder and sintering atmosphere contributions. The binder contributes more significantly to oxygen pick-up for the smaller particles. This may be due to the larger surface area available for the reaction with binder components. The relative contribution of the sintering atmosphere is less important for the smaller particles as a result of their faster densification and the faster reduction of surface area during sintering. The reduction of the exposed titanium surface minimises oxygen pick-up during sintering.

The Pareto graph helps to identify areas of potential improvement in the process. Since the major contribution comes from the powder, reduction of the powder oxygen content would be beneficial. However, the Ti–6Al–4V powders employed were already low in oxygen (<0·11 wt-%) and potential for further improvement is limited without significant cost penalty. Improved sintering conditions will, however, contribute significantly to the reduction of the total oxygen content without major cost implications. Optimisation of the sintering time–temperature schedule and use of *in situ* oxygen getters could further reduce the total oxygen content. Other improvements such as the reduction of the debinding peak temperature will also contribute to the reduction of the oxygen content in the final components.

Conclusions

Oxygen in solution has detrimental effects on the ductility of titanium components. Therefore, its maximum content is generally specified and must be controlled in most applications.

The following conclusions can be drawn on the basis of the present review:

- analysis of oxygen content can be tricky and must be done with care and good controls according to standard procedures
- the oxygen content of the final components is mainly determined by: (i) powder oxygen content (process, size distribution, specific surface area) and (ii) thermal processes above 400°C
- when carefully optimised, binders have minimal impact on the total oxygen content
- at temperatures below 200°C, oxidation of titanium is minimal and no special care is required to minimise oxygen pick-up.

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