A comparison of Ti–Ni and Ti-Sn binary alloys processed using powder metallurgy

Hung-Wei Liu, D. Paul Bishop, Kevin P. Plucknett*

Materials Engineering, Department of Process Engineering and Applied Science, Dalhousie University, 1360 Barrington St., Halifax, Nova Scotia, Canada

ABSTRACT

The simple press-and-sinter powder metallurgical technique has provided an economical route for the manufacture of components from lightweight alloys, including titanium. However, the issue of residual porosity is limiting Ti alloy use in demanding applications. The presence of a liquid phase during sintering can potentially facilitate diffusion, leading to improved densification. In the present work a comparison of liquid phase sintering mechanisms is undertaken, with either persistent or transient liquid formation, for Ti–Ni and Ti–Sn alloys, respectively. Samples are produced using blended elemental powders, with up to 10 wt% alloying addition. Compacts were uniaxially pressed, and sintered at 1200–1400 °C. The benefit of Ni addition is significant in terms of sintering, with close to full density ($\sim$99.5% of theoretical) achieved for optimised conditions. Sn additions also exhibit a beneficial sintering response, particularly at lower temperatures (< 1250 °C) and for lower concentrations (i.e. 2.5 wt%), with densities exceeding 98.5% of theoretical achieved under optimal conditions. The hardening effect is clear for both alloy groups compared to commercially pure-Ti, whereas there was generally an adverse effect on the tensile properties.

1. Introduction

Commercially pure titanium (CP–Ti) exhibits excellent corrosion resistance properties and is widely applied in marine or chlorine containing environments, such as in reaction vessels and heat exchangers [1–3]. Compared to stainless steels or other corrosion resistant metals and alloys, CP–Ti also provides a high strength-to-weight ratio, and is consequently favourable for application as a structural material in environments with mass constraints.

Despite these outstanding characteristics, titanium and its alloys are considered to be expensive, due to the complicated metal extraction and manufacturing processes that are required. In addition to the raw materials expense, the manufacturing steps used generally account for up to 60% of the total component costs [4]. The conventional ingot metallurgical processing method includes melting-and-casting, forging or other thermal-mechanical process steps, and potentially a considerable amount of final machining, adding further fabrication expense [5].

Conversely, the powder metallurgical (PM) processing approach, which has gained considerable acceptance in the high volume processing of other light metals, such as aluminium [6],

holds the potential to providing an economical processing route for CP–Ti and related alloys [7]. Successful development of Ti PM processing would then have the opportunity for expanding application into a variety of industries, including automotive, aerospace and biomedical. The near-net-shape PM approach maximises the material utilisation and reduces the need for using complex fabrication processes (e.g. vacuum–arc remelting and various hot working procedures) [5]. However, in order to achieve full densification, hot isostatic pressing (HIP) is generally necessary for titanium, which adds further expense. Typical press-and-sinter PM components generally retain some porosity, even with optimised sintering treatments. Previous work has demonstrated densities of $\sim$98% of theoretical for CP–Ti, via a conventional press-and-sinter PM approach [8]. Residual porosity therefore remains to be overcome to attain improved mechanical performance. In particular, the ductility suffers considerably from the presence of porosity.

To boost the sintering densification, alloy additions are sometimes introduced to generate a secondary liquid phase; for example adding Cu or Fe to Ti [9–12]. The presence of the liquid phase during sintering provides an effective diffusion route for mass transport. Therefore, voids are ideally eliminated, with a reduced sintering time or lower temperature potentially offering equivalent densification levels. Depending on the alloying additions, a liquid phase may exist at the sintering temperature (i.e. persistent) or might only occur during the early diffusion stage at

* Corresponding author.
E-mail address: kevin.plucknett@dal.ca (K.P. Plucknett).

lower temperatures (i.e. transient).

For the Ti–Ni system, a persistent liquid phase is expected at some target sintering temperatures, based on the phase diagram (i.e. the β+liquid region) [13], and for blended elemental mixtures the heating process encounters several intermediate eutectic temperatures in the binary system. The lowest of these occurs at 942 °C for Ti with 28 wt-% Ni. As can be anticipated, the liquid phase volume will therefore vary with both the Ni content and sintering temperature. In addition to introducing a liquid phase at elevated temperature, Ni has been found to reduce the diffusion activation energy [14], and therefore has a high diffusivity in Ti–Ni alloys [12], which promotes greater inter-diffusion. Some densification improvements have been confirmed in PM processed Ti–2Ni and Ti–5Ni (in at%) alloys [14].

Conversely, there is no eutectic reaction in the Ti–Sn system. A transient liquid phase can initially expected to be created from the low melting temperature Sn, which will then form a binary Ti-based solid solution, resulting in solid-state sintering at elevated temperature. Early research using sponge Ti powder has shown promising results arising from Sn additions. It was demonstrated that Sn (varied from 2.5 to 15 wt%) improved both the compaction behaviour and the sintered density (which increased from 95.6% up to 97.9%), with a concurrent small reduction in tensile elongation (decreasing from 20% to 14%) [15]. However, Hsu et al. have reported that Sn (< 5 wt%) in an as-cast Ti–Sn alloy noticeably improved both bending strength and modulus [16]. While PM studies of Sn additions in Ti have been relatively limited, generally demonstrating minimal benefits, Sn additions have been investigated for biomedical applications [17–19]. This is due to good biocompatibility as well as the ability to modify the modulus of cast titanium alloys (e.g. Ti–(Ta–Nb–Zr) [17,18] or Ti–Cu [19]), in order to avoid the'stress shielding' caused by a high modulus difference between the popular Ti–6Al–4V implant material and human bone [20].

In the present work, the Ti–Ni (persistent liquid phase) and Ti–Sn (transient liquid phase) binary systems, both with up to 10 wt% alloying addition, are evaluated and compared in terms of their benefits on the sintering response and the consequent mechanical properties, when following a conventional PM-based press-and-sinter processing route. Relatively fine Ti and alloying addition powders have been specifically chosen for this study, with the sizes selected to optimise particle packing during compaction (the sintering addition powders are approximately one third the diameter of the Ti powder).

2. Experimental methods

The Ti used in the present research was a CP-grade hydride/dehydride (HDH) powder (−325 mesh, 99.5% purity), obtained from Alfa Aesar; C, H, O and N analysis for this powder is presented in Table 1 [8]. The alloying Ni powder (type 123, 100% grade) was obtained from Vale Inco. The Sn powder (−325 mesh, 99.8% purity grade) was also obtained from Alfa Aesar. The individual particle size distributions of the as-received powders were determined using Malvern Master Particle Sizer 20600.

The binary Ti compositions were prepared by adding Ni or Sn powder, in various weight percentages, from 2.5 to 10 wt%, to the

Table 1
The analyzed carbon, hydrogen, nitrogen and oxygen contents of the as-received HDH powder (in wt%).

	C	H	O	N
HDH Ti powder	0.030	0.077	0.70	< 0.007

HDH-Ti (balanced). In addition, a further 1.5 wt% Licowax LC lubricant was also incorporated to ease the friction between die walls and particles during the compaction process. The powders were then blended using Turbula T2F mixer for 30 min to provide a homogeneous mixture. The blended powders were uniaxially pressed into two sample geometries: (i) cylindrical discs of 15 mm diameter × ~7 mm thickness (~4 g of powder) for sintering density measurements and microstructural evaluation, and (ii) rectangular bars of dimensions $12.8 \times 12.8 \times 76.5$ mm^3 (~41 g of powder) for tensile test samples. Samples were uniaxially pressed in a floating tungsten carbide die at 300 MPa, using Instron hydraulic compaction press (Satec 5594-200HVL). In order to evaporate out the lubricant, the pressed compacts were initially heated in a tube furnace to 400 °C, at a rate of 10 °C/min, and held at temperature for 30 min under constant nitrogen flow. After cooling, they were sintered in a high vacuum (10^{-5} torr) furnace (Materials Research Furnaces J-8x10-WM-1650-VG), with a hold time of 2 h, at various temperatures ranging from 1100 °C to 1400 °C. The nominal heating and cooling rates were both programmed at 10 °C/min, although a natural furnace cool occurred below ~400 °C. A minimum of two samples were prepared for each geometry–composition–temperature combination. The liquid phase quantity of the Ti–Ni binary system, for the sintering temperature range that was examined, was estimated through use of the commercial thermodynamics software package FactSage™ 6.4.

Sample green densities were calculated geometrically from the compact dimensions and mass. The sintered densities were determined in accordance with the MPIF Standard 42 (ASTM Standard B328). Selected samples were subsequently sectioned and cold mounted in resin. The surface was initially ground using 500 grit SiC paper, followed by polishing with 9 and 3 μm diamond particle suspensions, and then finally with a colloidal silica suspension (0.05 μm). The polished samples were subsequently etched using a modified Kroll's solution. Microstructures were characterised with Olympus BX-51 optical microscope (OM) and Hitachi S-4700 scanning electron microscope (SEM). The SEM was equipped with Oxford Instruments energy dispersive X-ray spectroscopy detector (EDS) to identify sample chemistry. The sample pore size distributions were determined by image analysis (Media Cybernetics Image-Pro 6.3) of the OM micrographs. Individual pore size was determined from the Feret diameter measurement. The size data compiled for statistics consisted of between 1000 and 5000 individual pore measurements for each individual sample. Crystalline phase compositions were identified using Bruker D8 Advance X-ray diffraction (XRD).

Cylindrical 'button end' tensile samples were machined from the rectangular bars after sintering. Tensile property evaluation was performed using Instron hydraulic test system (Satec 5594-200HVL) equipped with a 50 kN load cell. Strain was measured with a clip-on extensometer (Epsilon 3542) that remained attached to the sample through the point of fracture. As such, the reported strains to failure represent the sum of the elastic and plastic components. A minimum of two samples were tested for each composition-temperature combination. The hardness of sintered samples was evaluated using Rockwell indentation testing (Leco R-660), with measurements made within the Rockwell'A' scale. Each hardness value is the average of four indentation tests.

3. Results and discussion

3.1. Liquid phase volume prediction

One fundamental difference between the Ti–Ni and Ti–Sn systems relates to their liquid phase forming mechanisms during sintering. As highlighted in Fig. 1, the Ti–Ni system experiences the