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Economical Sintering of Titanium Powder

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The development of new processes for the production of low-cost titanium metal powder brings with it the potential for wider application of titanium components. In order for the full potential to be realized, low-cost fabrication techniques are also required. One such technique is the powder metallurgy press-and-sinter method, avoiding higher-cost refinements such as powder forging or hot isostatic pressing. The sintering of powders of titanium and simple titanium alloys has been examined with a view to identifying alloy compositions and sintering conditions that give rise to rapid densification and favourable mechanical properties. Both solid-state and liquid phase sintering have been examined.

Keywords: *titanium (Ti), powder, sintering*

1. Introduction

The economical sintering of titanium and titanium alloys has been the objective of a large body of published research. Some of this work is summarised in Table 1,[1-11] which provides an appreciation of typical powder types, compaction pressures and sintering conditions. Results are included for blended elemental powders, cold uni-axial compaction (and some cold isostatic pressing) and sintering without applied pressure.

The emphasis in much of the research was on the development of microstructure and mechanical properties. Our interest is more in sintering behaviour and densification, which of course have a profound influence on properties and applications of sintered titanium components.

In this paper we present the results of a preliminary exploration of some possible methods of achieving sintering of titanium-based blended elemental powders at relatively low temperatures. The final goal is to design alloys specifically for efficiency in sintering, but to date only simple binary alloys have been investigated.

2. Method

Hot pressing and reduction of particle size are common methods of increasing the rate of densification of titanium powder compacts. We have not examined these techniques, opting instead to confine ourselves to low-cost alternative procedures. Cylinders 10 mm in diameter and 10 mm in height were prepared for dilatometry by cold, uni-axial compression in a floating cylindrical die. Die wall lubrication was applied in the form of a thin film of Acrawax C powder. Composition was altered by mixing elemental powders with HDH titanium powder supplied by CERAC and Sumitomo. Sintering was carried out in a Netzsch DIL 402C dilatometer under a vacuum of about 1 Pa. Our objective was to identify some practical approaches to sintering titanium alloys to high density at temperatures low enough to minimise problems associated with reactions between the alloys and components of the sintering furnace.

3. Results

The effect of the compaction pressure on the sintering of 100% CERAC, -100 mesh, hydride-dehydride (HDH) titanium powder was examined in a preliminary experiment. Figure 1 shows a reduction in shrinkage during sintering as the compaction pressure is increased. Figure 2 shows the effect of compaction pressure on density.

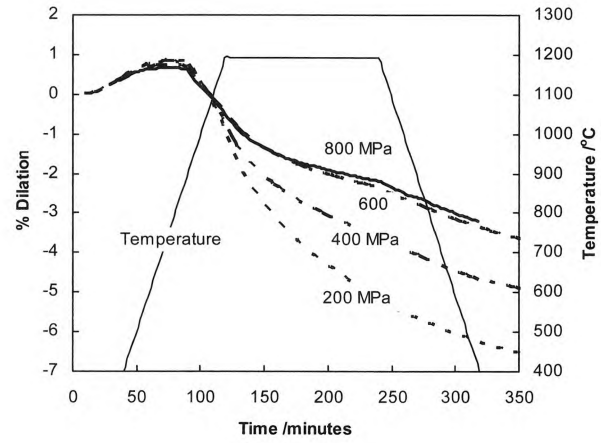

Figure 1. Effect of compaction pressure on shrinkage of CERAC HDH Ti powder heated at 10 K/min to 1200°C and held 2 hours at that temperature.

It is well known that diffusion and sintering rates are higher in the high-temperature β phase of titanium than in the closer-packed α phase [12]. Cycling through the α-β phase transition has been examined as a method of accelerating sintering [13]. Figure 3 shows that for both CERAC and Sumitomo -100 mesh HDH powder there is an acceleration of sintering on heating through the transition at about 880°C. Part of the acceleration is due to changes in microstructure and local stresses due to transformation, but this component appears to persist for only a few minutes. There is a similar disturbance in sintering rate on cooling.

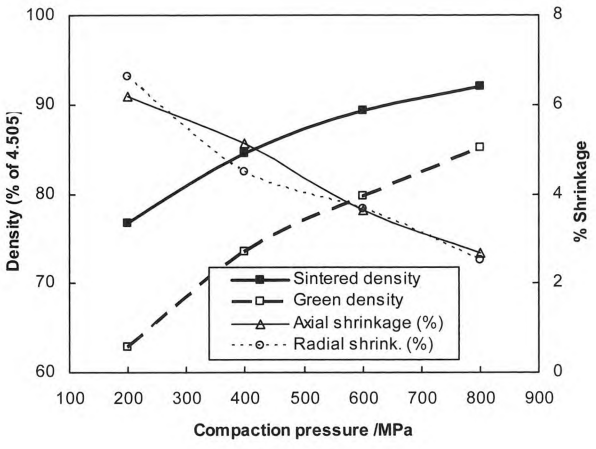

Figure 2. Effect of compaction pressure on green and sintered density and on axial and radial shrinkage during sintering of CERAC HDH Ti powder at 1200°C for 2 hours.

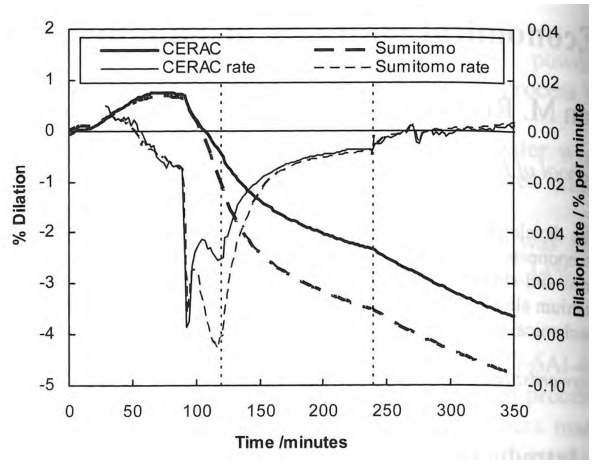

Figure 3. Dilatometer traces for HDH Ti compacted to 80% green density at 600 MPa (CERAC) or 78% green density at 500 MPa (Sumitomo), heated at 10 K/min to 1200°C, held 2 hours, and cooled at 10 K/min (also the first derivative after subtracting thermal expansion).

Table 1. Conditions for economical sintering of blended elemental Ti alloys (or Ti plus master alloy powders). Most sintering was carried out in vacuum of about 1 MPa (occasionally under Ar). Heating rates were typically 10 K/min (5-20 K/min).

Composition	Powder type	Size	Compact. pressure	Green density	Sintering temp.	Sinter. time	Sintered density	Ref.
		(μm)	(MPa)		(°C)	(hr)		
CP Ti	-	<40	196	?	1000-1400	1	87-96%	1
CP Ti	Sponge	~90, ~50	400-600	83, 88%	1260	2-3	95, 98%	2
CP Ti	Armstrong	100-200 agglom.	1050	91%	1350	0.2-16	92%	3
	Sponge	<45, <75, <150		85, 87, 94%			97, 99, 98% (1)	
CP Ti	HDH	8	200 (CIP)	86%	1250	0.5	90%	4
Ti-1Fe	-	<40 (Ti)	196	?	1000-	1	88-97%	1
Ti-5Fe					1400		90-97%	
Ti-10Fe							91-97%	
Ti-6Al-4V	HDH, Hunter sponge	<150 (Ti), <44 (master alloy)	?-?	?-?	1260	4	97.5-99.6% (2)	5
Ti-5Al-4V + TiB	Sponge (Hunter Ti)	150 (Ti)	392	?	1300	1-16	?	6
	HDH (Kroll Ti)	9-40 (Al_3V)	(CIP)					
		3 (TiB_2)						
Ti-6Al-4V	-	<100, 100-200 (Ti)	320	76-79%	1350	4	84-95% (3)	7
		<100 (master alloy)	640	83-89%			89-96%	
		<100, <20 (Al)	960	88-93%			91-98%	
		<100, <40 (V)						
Several alloys	Sponge	~90, ~50 (Ti)	400-600	80-87%	1260	2-3	88.6-97.5%	2
		5-50 (master alloys)						
Ti-5Al-3V-2Fe-2Mo	HDH	<150 (Ti)	?-?	?-?	1260	4	98.5-99.8% (2)	5
		<44 (master alloys)						
Ti-7Mo-4Fe-1Al-1V	HDH	<40 (Ti)	392	?	1300	4	99%	8
		10, 9 (master alloy)	(CIP)					
Ti-6Al-2Fe-0.1Si	HDH	<150 (Ti)	to 600		1300	3	<95%	9
		<44 (Ti)	100				>95%	
Ti-5Al-2.5Fe	GA, GA, OR	50, 33, 77	200	?	700, 1000,1400	2	?, ?, 85%	10
Ti-2,3Al-1Fe-1-5Zr	-	<55 (Ti)	483	-	1250	-	(4)	11

(1) Maximum densities, (2) Similar densities for HDH and sponge, (3) Range due to particle sizes, (4) Pycnometry data.

The dilation rate curves in Figure 3 display two clear minima (shrinkage rate maxima). The first is coincident with the α-β transition. The second is due to an increase in shrinkage rate as the temperature was raised, followed by a decrease after the hold temperature was reached.

The results of thermal cycling through the transition temperature are shown in Figure 4. The shrinkage rate increased for a short time after transformation in each cycle, both on heating and on cooling. The acceleration in the first heating stage was much greater than in the subsequent heating and cooling stages, and greater densification was obtained by simply heating to 1200°C. Oscillations at 800°C and 1000°C in the dilation rate for the compact subjected to thermal cycling are due to small instrumental artefacts.

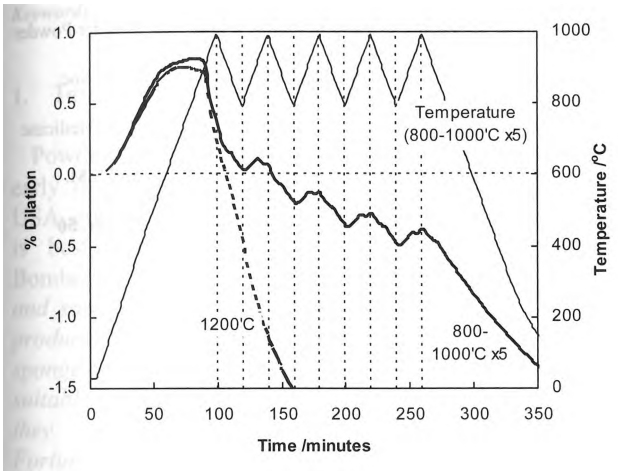

Figure 4. Dilatometer traces for CERAC Ti compacted at 600 MPa and cycled between 800 and 1000°C at 10 K/minute (full lines) or heated at the same rate to 1200°C for two hours (dashed line).

Although thermal cycling through the phase transition does not seem to be a practical method of accelerating the sintering of titanium, designing PM alloys with lower transition temperatures is certainly feasible.

Temporary alloying with hydrogen is one approach [14]. The sintering of titanium with blended elemental additions of β-stabilising elements has been reported briefly by several authors [1,4,15-21].

We have used additions of Ni, Co, Fe, Mn, Cu and Si to examine sintering behaviour, although the mechanical properties of these binary alloys would not be satisfactory in many applications due to the embrittling effect of intermetallic compounds.

Figure 5 displays the effect of nickel additions, and temperature, in increasing the rate of shrinkage of titanium powder compacted at 400 MPa (green density 74-76% of theoretical). During continuous heating, transient liquid is probable at temperatures above the Ti-Ni eutectic at 942°C. Some liquid phase is present under equilibrium conditions at 1200°C for 9% Ni and 1300°C for 7% Ni, but a large increment in sintering rate was not observed for these compositions under continuous heating at 10 K/minute.

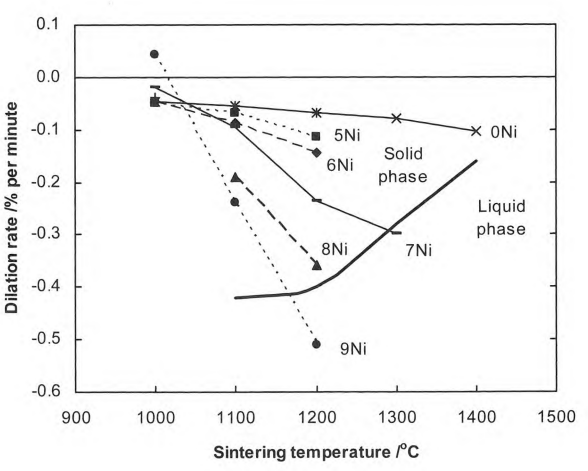

Figure 5. Shrinkage rate for CERAC Ti with 0-9% Ni powder (by weight) compacted at 400 MPa and heated at a rate of 10 K/min. The approximate boundary between solid state and some liquid phase at equilibrium is also shown.

In fact the presence of liquid phase is detrimental to densification of HDH titanium powder, as large pores develop due to gas evolution. Dilatometer traces for several alloys maintained at a temperature where a small amount of liquid was present are presented in Figures 6 and 7.

After initial shrinkage during solid state sintering, the compacts expanded when the temperature was high enough for a small amount of liquid to form and the density reached about 90% of theoretical [22].

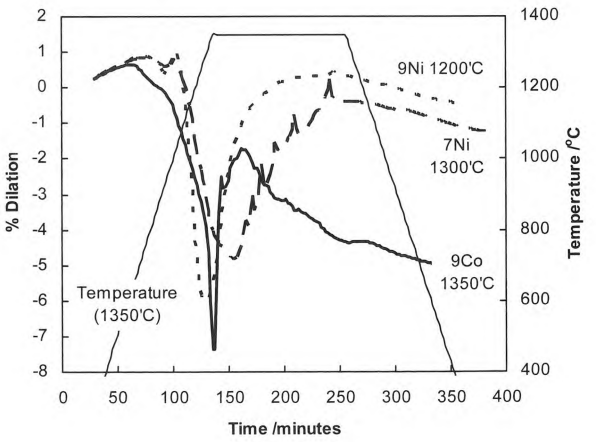

Figure 6. Dilatometer traces for alloys with some liquid phase at the peak sintering temperature (all based on CERAC Ti powder and compacted at 400 MPa except 9% Co based on Sumitomo Ti powder).

For comparison with Figure 4, sintering rates for various binary compositions on heating at a constant rate are listed in Table 2. Silicon and nickel additions appear to offer good prospects for increasing the densification or lowering the sintering temperature of titanium alloys. Silicon has the added advantage of reducing the theoretical density of the alloy.

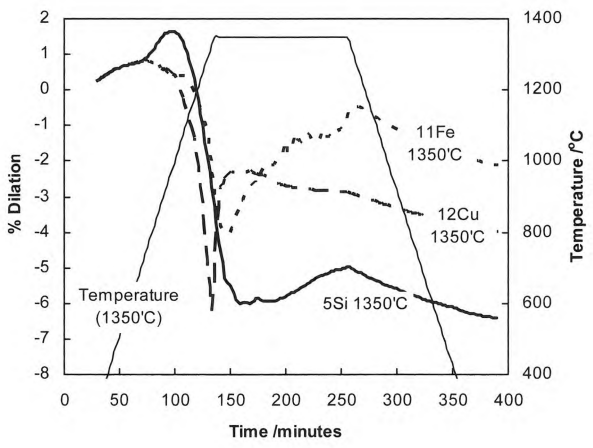

Figure 7. Dilatometer traces for other alloys with some liquid phase at the peak sintering temperature (based on CERAC Ti powder and compacted at 400 MPa).

Table 2. Dilation rates in % per minute of CERAC Ti and binary alloys compacted at 400 MPa and heated at 10 K/minute to 1200, 1300 and 1400°C.

Alloy	1200°C	1300°C	1400°C
CERAC Ti	-0.068	-0.080	-0.103
5% Ni	-0.114	-	
7% Ni	-0.237	-0.298	
9% Ni	-0.511	-	
7% Co	-0.077	-0.099	
5% Fe	-0.080	-	
11% Fe	-0.075	-0.198	
5% Mn	-0.090	-	
10.5% Cu	-0.084	-0.110	
5% Si	-0.165	-0.216	

4. Conclusion

Our work on the sintering of titanium alloys is in its early stages but some prospective methods for accelerating densification or reducing the sintering temperature have been identified. Principal among these is the addition of a high-diffusivity alloying element such as nickel. Some unproductive approaches and potential pitfalls have also been noted. Liquid-phase sintering appears to be precluded by severe swelling, and cycling through the α-β transition is not as effective as simply raising the sintering temperature.

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REFERENCES

1) S. Sakaguchi: Met. Technol. (Japan) **55** (1985) pp.29-32.
2) G. Korb and P. Schretter: *Proc. Conf. Horizons of Powder Metallurgy*, Dusseldorf, Part II, pp.939-942.
3) S.J. Gerdemann and D.E. Alman: *Proc. 2000 Intl. Conf on PM and Particulate Materials*, New York, pp.12.41-12.52.
4) Y. Liu, L.F. Chen, H.P. Tang et al: Mater. Sci. Engng. **A418** (2006) pp. 25-35.
5) T. Fujita, A. Ogawa, C. Ouchi and H. Tajima: Mater. Sci. Engng. **A213** (1996) pp.148-153.
6) Z. Fan, H.J. Niu, B. Cantor et al: J. Microscopy **185** (1997) pp.157-167.
7) O.M. Ivasishin, D.G. Savvakin, V.S. Moxson et al: Mat. Tech. & Adv. Perf. Mat. **17** (2002) pp.20-25.
8) T. Saito, H. Takamiya and T. Furuta: Mater. Sci. Engng. **A243** (1998) pp. 273-278.
9) M. Hagiwara, S.J. Kim and S. Emura: Scripta Mater. **39** (1998) pp. 1185-1190.
10) R.P. Siqueira, H.R.Z. Sandim, V.A.R. Henriques and J.F.C. Lins: Mater. Sci. Forum **498-499** (2005) pp.55-60.
11)M. Chandrasekaran, Z.S. Xia, L.K. Kiong et al: Mater. Sci. Technol. **21** (2005) pp.185-190.
12) Y. Mishin and Chr. Herzig: Acta Mater. **48** (2000) pp.589-623.
13) K. Akechi and Z. Hara: Powder Metallurgy **24** (1981) pp.41-46.
14) F.H. Froes: Intl. Mater. Rev. **49** (2004) pp.227-245.
15) H. Kyogoku, S. Komatsu, I. Tsuchitori and T. Toda: J. Jpn. Soc. Powder Powder Metall. **42 (1995)** pp.1052-1056.
16) W. Wei, Y. Liu, K. Zhou and B. Huang: Powder Metallurgy **46** (2003) pp.246-250.
17) K. Majima, M. Kihara and K. Shoji: J. Jpn. Soc. Powder Powder Metall. **32** (1985) pp.294-300.
18) K. Majima, Y. Yoshimura and K. Shoji: J. Jpn. Soc. Powder Powder Metall. **34** (1987) pp.205-210.
19) Y. Ikeda, S. Takaki, M. Kamada and Y. Tokunaga: J. Jpn. Soc. Powder Powder Metall. **40** (1993) pp.774-779.
20)M. Thieme, K.-P. Wieters, F. Bergner et al: J. Mater. Sci. Medicine **12** (2001) pp.225-231.
21) A.G. Kostornov, L.G. Galstyan, S.A. Mnatsakanyan and S.M. Agayan: Powder Metall. Metal Ceram. **25** (1986) pp.909-911.
22) R.J. Low, I.M. Robertson and G.B. Schaffer: Scripta Mater. **56** (2007) pp.895-898.