# Sintering of gamma Titanium Aluminide (TiAl) Alloys Aided by Small Additions of Copper

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Titanium aluminide alloy powders are difficult to sinter unless assisted with pressure. This investigation explores the use of sintering aids to enable pressureless sintering of Ti-48Al-2Cr-2Nb in order to take advantage of the conventional powder metallurgy (PM) approach for low-cost near-net shape fabrication. Thermodynamic calculations using Thermo-Calc and Ti-alloys database TTTI3 predict that copper (Cu) is a potential sintering aid for Ti-48Al-2Cr-2Nb. The effect of Cu additions from 0 to 2 at. % on the sintering of Ti-48Al-2Cr-2Nb was accordingly assessed at 1375℃ with 120 min isothermal holding in vacuum. The sintered density increased from (73. 9 ± 0. 6)% theoretical density (TD) without Cu to > (98 ± 0. 5)%TD with an addition of 2 at. %Cu, demonstrating the significant effectiveness of Cu as a sintering aid for Ti-48Al-2Cr-2Nb. The enhanced densification is attributed to liquid formation. A minor Cu- and Cr-enriched phase was detected with additions of ≥ 1. 0 at. %Cu. The as-sintered microstructures and phase constituents were analysed by scanning electron microscopy equipped with an Energy Dispersive Spectroscopy (EDS) microanalysis system and X-ray diffraction analysis.

***Keywords***: *Titanium aluminide, powder metallurgy, sintering aids, copper*

## 1. Introduction

TiAl based alloys are promising high temperature structure materials which combine the advantages of low density, high temperature specific strength, good oxidation resistance and high stiffness[1-3]. Much effort has been made to optimize the composition of TiAl based alloys[4-6]. The second generation TiAl alloy, Ti-48Al-2Nb-2Cr (48-2-2), better known as the GE alloy, was developed by Huang in 1991[7,8]. The alloy has excellent mechanical properties compared with other TiAl based alloys. As a result, it has replaced Ni-based superalloys for the 6th and 7th turbine stages of blades in the new generation 225 — 340 kN thrust class engines (GEnx) made by GE Aircraft Engines[9].

Powder metallurgy is an attractive approach to the fabrication of TiAl based alloys because of its near-net-shape capability, greater materials utilization, and attributes of producing more homogenous microstructures[10,11]. However, TiAl based alloys can only be sintered with the assistance of an external field such as current and/or pressure, e. g. by spark plasma sintering[12-14] or hot isostatic pressing[15,16]. These processes require the use of special cans or dies with limited geometric flexibility. In addition, the cost of fabrication is high.

For conventional sintering of pre-alloyed TiAl powders, near full densification requires near solidus sintering. Gerling et al.[17] sintered γ-TAB (Ti-47Al-4 (Mn, Nb, Cr, Si, B) (at. %) alloy powder to 96%TD at 1410℃ for 240 min in vacuum. Recent work by Limberg et al.[18] showed that sintering of Ti-45Al-5Nb-0. 2B-0. 2C (at. %) (TNB-V5) to 99. 5%TD required 120 min at 1500℃. Zhang et al.[19] sintered Ti-45Al-8. 5Nb-0. 2W-0. 2B-0. 02Y (at. %) to 96. 2% TD at 1480℃ for 120 min (optimum sintering parameters). Apart from increased energy consumption, sintering at higher temperatures with longer times leads to significant grain coarsening, which is detrimental to as-sintered mechanical properties.

A previous study[20] has indicated that small additions of copper (<2 at. %) improve the resistance of Ti-48Al-2Cr-2Nb to oxidation without noticeably affecting the mechanical properties while additions of 2-4 at. %Cu are disadvantageous. The presence of copper is believed to reduce the concentration of chromium in the scale, which favours the formation of a more continuous, and thus more protective, alumina layer on the surface[20]. Copper thus has the potential to be a useful modifier to the GE gamma TiAl alloy from an oxidation resistance standpoint. No work has been reported on the role of copper as an elemental additive in the sintering of the GE alloy. This study investigates the effect of copper additions in the range from 0 to 2 at. % on the sintering densification of Ti-48Al-2Cr-2Nb and the mechanism by which the enhanced densification occurs.

## 2. Experimental Procedure

Gas atomized γ-TiAl alloy powder with a nominal composition of Ti-48Al-2Cr-2Nb (at. %) was used. The powder has 99. 9% purity with a size range of 45-145μm. CERAC elemental copper powder (99. 9% purity, <45μm) was used as copper additions.

Pre-alloyed Ti-48Al-2Cr-2Nb powder is not compactable at room temperature. To enable green shape formation for sintering, a simple coating method was developed. An ethanol-nylon solution was prepared where 1. 5 wt. % of nylon powder was dissolved into ethanol at 100℃. The γ-TiAl alloy powder was first mixed with Cu powder of a required concentration in a Tubular mixer for 60 min. Then the powder mixture was immersed into the ethanol-nylon solution and a thin layer of nylon coated on the powder after vaporisation of ethanol. The coated powder was cold-pressed at 600 MPa in a floating uniaxial die of circular cross section using a hand operated Carver hydraulic press. The resulting green samples were right cylinders, 9-11mm in height and 10 mm in diameter, with the green density falling in the range of (71. 9 ± 0. 8)% TD. The theoretical density of the powder mixture was calculated following the mixture rule[21)]

$$\rho_{th} = 100/\sum_{i}(m_i/\rho_i)$$

where $m_i$ is the mass percentage of constituent $i$ in the alloy and $\rho_i$ is its density, of which, the pore-free density of the Ti-48Al-2Cr-2Nb alloy used is 4 g/cm$^3$.

Sintering was conducted at 1375℃ in vacuum ($10^{-3}$-$10^{-4}$) in an alumina tube furnace. The samples were heated and cooled both at a rate of 4℃/min. Prior to isothermal holding, the samples were held for 120 min at each of 400℃, 500℃ and 600℃ to thoroughly remove nylon. Sintered densities were measured by the Archimedes method according to the ASTM standard B328. The pore filling liquid is Mobil DTE25 oil with a specific gravity of 0. 87 and the test liquid was hydrofluoroplyether heat transfer fluid with a specific gravity of 1. 68.

Samples for metallographic investigation were prepared from sintered samples and the polishing was finished with colloidal silica. The microstructure was studied using a scanning electron microscopy (SEM) (Model JEOL 6460L, Japan) equipped with an Energy Dispersive Spectroscopy (EDS) microanalysis system. The phase constituents were identified by X-ray diffraction (XRD) using the characteristic wave length of Kα line for Cu (1. 5418Å. Thermo-Calc for Windows (TCW5) from Thermo-Calc Software AB (2006) and Ti-alloy database from Thermo-Tech Limited (v. 3 2006) were used to calculate the liquid phase fractions of the Ti-48Al-2Cr-2Nb-(0-2)Cu system.

## 3. Results and Discussion

Figure 1 shows the density of Ti-48Al-2Cr-2Nb-(0—2)Cu sintered at 1375℃ for 120 min in vacuum, as a

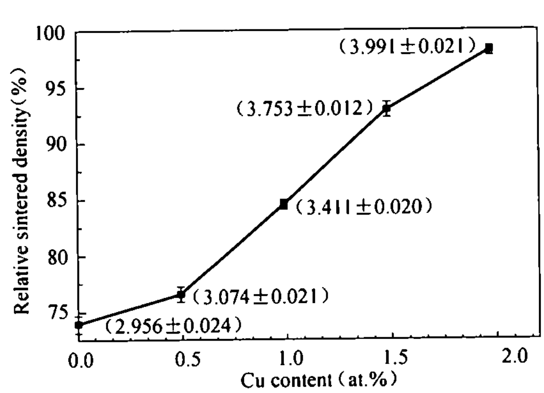


**Figure 1.** The effect of Cu additions on the sintered density of Ti-48Al-2Cr-2Nb-xCu alloys (x=0, 0. 5, 1. 0, 1. 5, 2. 0) at 1375℃ for 120 min. The figures in the brackets are real sintered densities (g cm$^{-3}$)

function of copper addition level. Small additions of copper were found to be exceptionally effective in enhancing the sintering of Ti-48Al-2Cr-2Nb. In the absence of Cu the density increased only slightly from (71. 9 ± 0. 6)% TD (green density) to (73. 9 ± 0. 6)%TD after 120 min isothermal holding at 1375℃. Although necking by sintering occurred between some particles, loose powder particles are readily noticeable in the sintered microstructure (Figure 2a). In contrast, the sintered density increased consistently from (76. 6 ± 0. 8)%TD to (98 ± 0. 5)%TD with increasing copper content from 0. 5 at. % to 2 at. %.

The corresponding microstructures are shown in Figure 2. Most powder particles remained to be essentially spherical with an addition of 0. 5 at. %Cu after sintering (Figure 2b). However, substantial sintering occurred with an addition of 1 at. %Cu (Figure 2c). Further increasing the Cu content to 1. 5 at. %Cu resulted in a well-sintered microstructure with isolated pores at grain junctions (Figure 2d). The microstructure containing 2 at. %Cu was almost fully dense with only a few small pores present (Figure 2e).

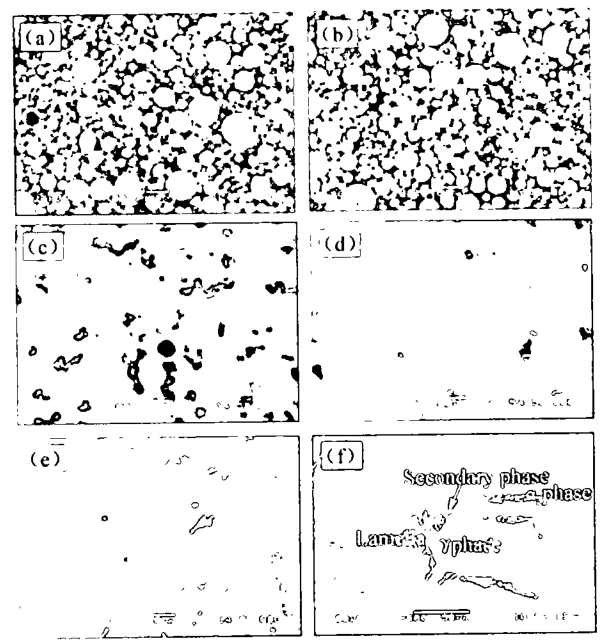


**Figure 2.** Backscattered electron microstructures of Ti-48Al-2Cr-2Nb-xCu alloys sintered at 1375℃ for 120 min in vacuum: (a) x=0, (b) x=0. 5, (c) x=1. 0, (d) x=1. 5, (e) x=2. 0, and (f) a magnified view of the microstructure shown in (e)

The sintered microstructure shows a duplex structure composed of equiaxed gamma grains and pockets of lamellae (Figure 2f). In addition, a minor phase (bright) was observed with an addition of ≥ 1. 0 at. % Cu (Figure 2c — 2e); its presence increased with increasing Cu content. XRD analyses of the phase constituents in each sample are shown in Figure 3. Interestingly, only two phases were detected, namely the γ phase and the $\alpha_2$ phase ($Ti_3Al$). X-ray diffraction failed to detect the minor phase due probably to its small volume fraction.

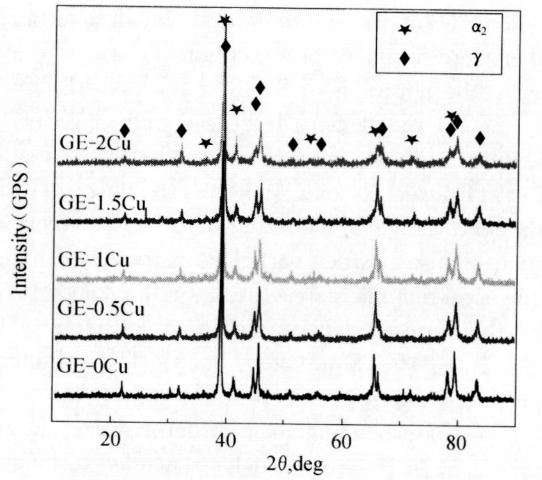

**Figure 3.** XRD patterns of Ti-48Al-2Cr-2Nb-xCu (GE-xCu) alloy sintered at 1375℃ for 120 min in vacuum (x=0,0.5,1,1.5,2)

EDS point and line analyses were used to analyse the three phases observed in the sintered microstructure of Ti-48Al-2Cr-2Nb-2Cu (Figure 4). The compositions of each phase are summarised in Table 1. The γ phase (labelled phase 1 in Figure 4) contains 47.72% Ti, 46.75% Al, 1.63% Cr, 2.06% Nb and 1.84% Cu, where the ratio of Ti to Al is almost equal to one. The $\alpha_2$ phase (labelled phase 2 in Figure 4) has an average composition of 56.78% Ti, 36.75% Al, 3.36% Cr, 1.9% Nb and 1.225% Cu. These results reveal that the presence of copper is very limited (1% − 1.5%) in both the γ and $\alpha_2$. The third phase (labelled phase 3 in Figure 4) is featured by a large presence of Cu and Cr, containing 37.36% Ti, 33.59% Al, 12.84% Cr, 2.2% Nb and 14% Cu. It differs from the γ and $\alpha_2$ phases. Transmission electron microscopy will be necessary to define the crystal structure of this Cu- and Cr-enriched phase.

**Table 1.** EDS analyses of the three phase regions indicated in Figure 4 in Ti-48Al-2Cr-2Nb -2Cu sintered at 1375℃ for 120 min

| Elements | Phase 1 | | Phase 2 | | Phase 3 | |
|---|---|---|---|---|---|---|
| | at. % | error % | at. % | error % | at. % | error % |
| Ti | 47.72 | 0.39 | 56.78 | 0.38 | 37.36 | 0.22 |
| Al | 46.75 | 0.24 | 36.75 | 0.25 | 33.59 | 0.17 |
| Cr | 1.63 | 0.63 | 3.36 | 0.64 | 12.84 | 0.34 |
| Nb | 2.06 | 0.7 | 1.9 | 0.67 | 2.2 | 0.41 |
| Cu | 1.84 | 1.46 | 1.22 | 1.47 | 14 | 0.82 |

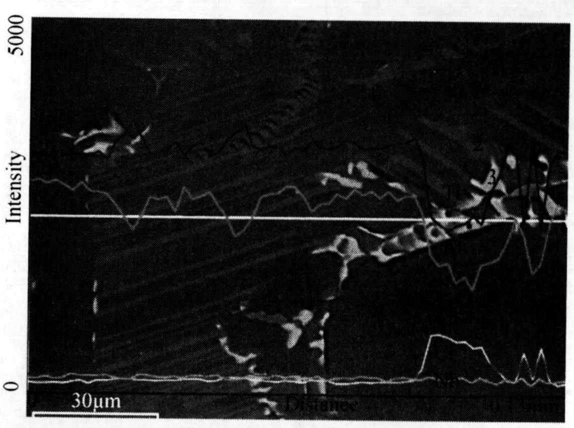

**Figure 4.** EDS line analysis of Ti-48Al-2Cr-2Nb-2Cu sintered at 1375℃ for 120 min

To understand the densification induced by small additions of Cu, Thermo-calc was used to predict the phase constituents of Ti-48Al-2Cr-2Nb-xCu (x = 0, 0.5, 1, 1.5, 2.0) at the sintering temperature, 1375℃. It is assumed that the system was close to equilibrium in the late stage of the 120 min isothermal holding. The predictions are summarised in Figure 5. The solidus temperature of the GE alloy Ti-48Al-2Cr-2Nb decreases substantially with increasing Cu content (Figure 6). As a result, sintering of Ti-48Al-2Cr-2Nb occurs in the solid state while sintering of Ti-48Al-2Cr-2Nb-xCu (x=0.5−2 at. %) occurs in the presence of a persistent liquid. For instance, the mole fraction of the liquid in the Ti-48Al-2Cr-2Nb-2Cu alloy is predicted to be 0.275, which is sufficient to lead to near full densification. The Thermo-Calc predictions well explain the experimental observations. The enhanced sintering by Cu is thus attributed to the liquid formation at the selected sintering temperature.

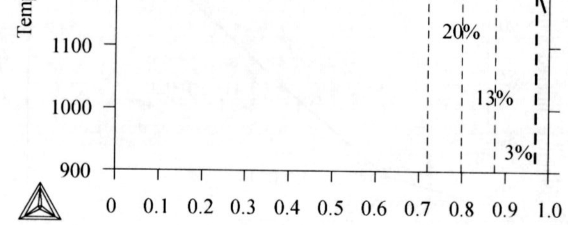

**Figure 5.** Thermo-Calc predictions of the liquid and solid fractions in the Ti-48Al-2Cr-2Nb-xCu alloys (x=0,0.5,1,1.5,2) in the temperature range from 900℃ to 1600℃

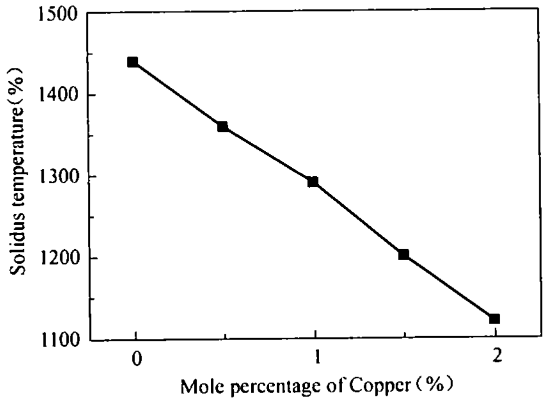


**Figure 6.** Solidus temperature of Ti-48Al-2Cr-2Nb-xCu as a function of Cu content

## 4. Summary

Small additions of copper (≤ 2 at. %) can effectively enable the sintering of pre-alloyed Ti-48Al-2Cr-2Nb powder and make the alloy from essentially non-sinterable below 1400℃ to readily sinterable without the assistance of pressure. Thermo-Calc predictions reveal that small additions of Cu are remarkably effective in lowering the solidus temperature of the alloy (a decrease of > 300℃ by an addition of 2 at. %Cu). The enhanced sintering is attributed to liquid formation at the sintering temperature. The finding is important for the design of sinterable titanium aluminide alloys.

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## REFERENCES

1) Y. W. Kim, Jom. 1989;41: pp. 24-30.
2) W. Smarsly, H. Baur, G. Glitz, H. Clemens, T. Khan and M. Thomas, Minerals, Metals & Materials Soc. 2001; pp. 25-34.
3) F. Appel, H. Clemens, U. Lorenz, M. Oehring and J. D. H. Paul, Intermetallics. 1998;6: pp. 667-672.
5) Y. W. Kim and D. M. Dimiduk, Minerals, Metals & Materials Soc. 1996;531-543.
6) T. T. Cheng, M. R. Willis, I. P. Jones, Intermetallics. 1999;7: pp. 89-99.
7) Y. W. Kim, Minerals, Metals & Materials Soc. 1995;637-654.
8) S. C. Huang, U. S. patent 4879092. 1989.
9) "GE Aviation", Internet: www. geae. com. Oct. 16, 2009.
10) C. F. Yolton, U. Habel and Y. W. Kim, Metals & Materials Soc. 2003;215-228.
11) L. Zhao, J. Beddoes, P. Au and W. Wallace, Adv. Perform. Mater., 1997;4: pp. 421-434.
12) A. Couret, G. Molenat, J. Galy and M. Thomas, Intermetallics. 2008;16: pp. 1134-1141.
13) Y. H. Wang, J. P. Lin, Y. H. He, Y. L. Wang and G. L. Chen, Intermetallics. 2008;16: pp. 215-224.
14) H. Jabbar, J. P. Monchoux, M. Thomas and A. Couret, Mater. Res. Soc. Symp. Proc. 2008;1128: pp. 1103-1104.
15) F. F. R. Gongalves, C. M. De Neto, C. A. A. Cairo, E. T. Galvani and V. A. R. Henriques, 63DG Congresso Anual da ABM: 63rd ABM International Annual Congress. 2008.
16) G. E. Fuchs, MRS Syrup. Proc. 1993;288: pp. 847-852.
17) R. Gerling and F. P. Schimansky, Materials Science and Engineering A. 2002;329-331: pp. 45-49.
18) W. Limberg, T. Ebel, F. P. Schimansky, R. Hoppe, M. Oehring and F. Pyczak, Euro PM2009-Powder Injection Moulding-Materials II. 2009.
19) H. M. Zhang, X. B. He, X. H. Qu and L. M. Zhao, Materials Science and Engineering A. 2009;526: pp. 31-37.
20) B. Dang, J. W. Fergus, W. F. Gale and T. Zhou, Oxid. Met. 2001;56: pp. 15-32.
21) G. B. Schaffer, S. H. Huo, J. Drennan and G. J. Auchterlonie, Acta Materialia. 2001;49: pp. 2671-2678.