Effect of Temperature on Densification, Microstructural Evolution and Mechanical Properties of Ti-5Al-1Mo Developed via Spark Plasma Sintering

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Abstract. Titanium alloys are ideally suited for advanced aerospace structures and industrial applications because of the combination of high strength, low density, good toughness, stiffness, and good corrosion resistance at cryogenic to elevated temperatures. This paper investigates the effect of temperature on alloy densification, microstructure evolution and mechanical properties of Ti-5Al-1Mo processed by Spark Plasma Sintering (SPS). Ti, Al, Mo elemental powders with 94, 5 and 1 wt.% respectively were mixed thoroughly for 8 hrs to attain homogeneity. The mixed powders were consolidated at sintering temperature of 800°C, 1000 °C, 1100 °C, pressure of 50 MPa, holding time of 10 min, and sintering rate of 100 °C/min. The compacted samples were characterised using scanning electron microscopy (SEM), equipped with energy dispersive X-ray spectroscopy (EDS) and X-ray diffractometry techniques. Compacts hardness was also investigated using Vickers micro-hardness tester. Almost fully densified compacts were obtained for samples sintered at 1000 °C and 1100 °C, the microstructures show that the sintered compacts are chemically homogeneous with the Al fully diffused into the CP-Ti matrix. The microhardness increases with increasing temperature with the maximum value being 290.35 HV.

1. Introduction
Titanium (Ti) matrix composites have attracted significant attention among engineering industries for several applications due to their attractive properties which include high specific strength, low density, stiffness, good toughness, and excellent corrosion resistance at cryogenic and at elevated temperature [1-4]. Ti alloy compositions can be designed to contain varying alpha (α) or beta (β) phases proportions based on application or property requirements [5]. The near-alpha (near-α) alloys are mostly used in aeroengines, particularly at the compressor section because these alloys possess the best creep resistance at temperatures between 400 and 600 °C of all Ti-alloys [6-8]. The near-α contains about 1 to 2 wt.% of β stabilisers (such as Mo, V, Nb and Ta) which stabilises β phase (about 5-10%) into the microstructure of the Ti matrix at ambient temperature [5, 7]. The stabilised β phase allows a two-phase strengthening mechanism by controlling the morphology, proportion and dispersion of the α/β phases. Aluminium (Al) is the major major α stabiliser known to enhance the creep strength, tensile strength and also the elastic modulus of Ti [7]. The solubility of Al
is high both in the α and β-phases of Ti and it also reduces the density of the alloy; However, the amount of Al that can be introduced to the Ti matrix is limited due to the formation of a intermetallic phase(s) of titanium aluminide (Ti-Al) which is brittle when the Al content exceeds 8 wt.% [7]. Considering the ternary system of Ti-Al-X, the Ti-Al-Mo system is of special category because it is composed of Mo atoms which has the best capability for stabilising β phase compared to other transition elements [9]. The addition of Mo in α-Ti grains tends to enhance workability and improves the tribological behaviour of Ti-based alloys while keeping their hardness at very high level [10, 11]; Furthermore, this alloying element also trap vacancies, thereby limiting creep relaxation [12]. Aluminium has a stabilising equivalence exactly inverse to that of Mo, thus the two systems can be combined to provide a qualitative view of Ti alloy stability [13].

A study on conventional sintering technique for titanium powders reveals that sintered sample’s full densification in a vacuum environment is feasible only at high temperatures in the range of 1100 to 1400 °C and longer holding time [14]. However, Spark plasma sintering (SPS) has the benefit of rapidly achieving full densification at relatively lower temperatures. SPS entails the application of pressured spark impact, external mechanical pressure and heat (generated by the passage of a pulse current with high energy through the powder particles) simultaneously [15, 16]. Generally, the sintering reaction involves ion diffusion process within an electric field in conjunction with plastic deformation by thermal diffusion.

This study entails the consolidation of Ti-5Al-1Mo powder by SPS method. It investigates the effect of sintering temperature on densification, phase transformation, microstructure evolution and hardness of the metal matrix composites. This route is expected to provide a novel way of rapidly consolidating Ti-5Al-1Mo near alpha Ti-based alloy and promote its usage in industries.

2. Experimental Procedure
2.1 Powder feedstock and preparation
The Ti, Al and Mo powders with properties presented in Table 1 were used in this study. Elemental powders of commercially pure (Cp) Ti matrix consisting of Ti, Al and Mo powders with weight % ratio of 94:5:1 respectively was loaded to cover up to 15% volume of a plastic container. The Ti-Al-Mo powder in the container was blended in a WAB TURBULA SYSTEM SCHATZ turbula mixer at a speed of 48rpm for 8 hrs. Blended powders characterisation was done using Scanning Electron Microscopy (SEM) incorporated with Energy Dispersive X-ray Spectroscopy (EDS) to explore its morphology and confirm the homogeneity of the powders. Figure 1 shows the backscattered electron image (BSE) and the EDS of admixed powder of Ti, Al and Mo.

| Role          | Element | Supplier                              | Purity (%) | Size (µm) | Density (g/cm³) | Melting Point (°C) |
|---------------|---------|---------------------------------------|------------|-----------|-----------------|-------------------|
| Matrix        | Cp Ti   | TLS Technik GmbH & Co                 | 99.8       | -25       | 4.5             | 1670              |
| Reinforcement | Al      | TLS Technik GmbH & Co                 | 99.5       | -25       | 2.7             | 660               |
| Reinforcement | Mo      | CERAC                                 | 99.9       | 2-4       | 10.28           | 2623              |

2.2 Sintering
The blended powders were sintered using the SPS machine (model HHPD 5, FCT Germany). Measured weight of the admixed powder was emptied into a graphite mould system containing a die, upper punch, and lower punch. Graphite foil was employed on the inner wall of the die before the
powder was poured to aid easy removal of sintered sample. Ti-5Al-1Mo was sintered at three different temperatures (800, 1000 and 1100 °C), heating rate of 100 °C/min, pressure of 50 MPa and holding time of 10 min under vacuum level of 10⁻² torr. The temperature during the sintering process was monitored using a pyrometer. The sintered compacts were left to cool to ambient temperature, removed and then sand blasted to remove graphite contaminants.

2.3 Densification
Densities of sintered samples were measured using a densitometer that works using the principle of Archimedes. The density was measured to explore the impact of sintering temperature on the composites. The density value recorded was the average taken from 10 measurements on each sample. The percentage densification was calculated by comparing the measured density to the theoretical density of each compact using equation 1 and 2.

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\frac{1}{\text{Theoretical density of TiAlMo}} = \frac{\text{Mass fraction of Ti}}{\text{Density of Ti}} + \frac{\text{Mass fraction of Al}}{\text{Density of Al}} + \frac{\text{Mass fraction of Mo}}{\text{Density of Mo}}
\]

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\% \text{ Densification} = \left( \frac{\text{Sintered sample's density}}{\text{Bulk sample's theoretical density}} \right) \times 100
\]

2.4 Microhardness
The Vickers microhardness values of the samples were measured by using microhardness tester (FUTURE-TECH FM 800) using a load of 1 Kgf and holding time of 15 s on well-polished surfaces of the sintered Ti-5Al-Mo. The microhardness value reported was the average taken from 5 measurements on each sample.

2.5 Sintered compact characterisation
The SPS compacts were cut transversely, grounded with Emery papers, polished and etched using Kroll reagent with composition of 92 vol.% H₂O, 2 vol.% HF and 6 vol.% HNO₃ for investigating the microstructure in the alloyed zone. The microstructure evolution and elemental composition of the sintered samples were characterised by SEM incorporated with EDS. X-ray diffractometer (PW1710 Philips) with Cu Kα radiation of wavelength 0.154nm, set at 10°-90° angular range with a step size of 1°/min at 45 kV and 25 mA) in combination with X'Pert High Score Plus software was employed to analyse the phases present in the sintered compacts.
3. Results and Discussion

3.1. Powders (Elemental and Mixed) Characterisation

The effectiveness of the mixing done by the turbula mixer was observed by the homogeneity (evenly distribution) of the powders as observed in the back scattered electron (BSE) micrograph in figure 1. The analysed weight percentages of Ti, Al and Mo powders are very close to the mixed value of each element. The XRD patterns (Figure 2) for the as-received elemental Ti, Al and Mo powders shows only the peaks of α-Ti, Mo, and Al respectively.

![Figure 2. XRD patterns of elemental powders](image)

3.2. Effect of temperature on sintered samples properties

Figure 3 shows the influence of sintering temperature on the spark plasma sintered sample’s density and hardness. The sample sintered at 800 °C has a relative density of 81.81%, while fully densified samples of 99.95% and 99.43% relative density were obtained at sintering temperatures 1000 and 1100 °C respectively. Full densification observed in samples sintered at 1000 and 1100 °C are ascribed to the influence of liquid phase sintering that is accompanied with higher uniaxial pressure and heating leading to formation of necks between Ti particles and also the annihilation of porosity as the temperature increases till the end of the sintering holding time. Vickers hardness of the samples was found to increase with decreasing porosity. This is evident as the sample sintered at 800 °C has the least hardness value of 155.15 HV. The measured maximum hardness of 290.35 HV was attained at sintering temperature of 1000 °C. This is in order with the hardness value (245 to 320 HV) reported by Mouritz and Adrian [8] for several α and near α titanium alloys.

From the SEM micrographs shown in Figure 4, it can be observed that the Ti-5Al-1Mo sintered at 800 °C (Figure 4a) has a thin grey Al and white Mo boundary that has locally developed on the surface of nearly all the Ti particles that are in direct contact with the Al particles. This can be attributed to the fact that Al melted to liquid phase and spread throughout the Ti particles which are undergoing necking trying to close up the pores during the sintering process. There was partial interfacial diffusion between the Ti particles and the alloying elements (Al and Mo); this is an indication that sintering (densification) process is not completed. Pores are visible on the micrographs of compacts sintered at 800 °C which agrees with the result of the low densification obtained for the sintered sample. The sintered samples at 1000 °C and 1100 °C sintering temperature are almost fully dense with no evidence of pores nor apparent defects; This is also consistent with the measured values of the density.
Figure 3. Density and microhardness of bulk alloys sintered at various temperatures

Figure 4. SEM micrograph of spark plasma sintered Ti-5Al-1Mo at various temperatures: (a) 800 °C; (b) 1000 °C; (c) 1100 °C

The alloy compacted at 1000 °C and 1100 °C (Figure 4b and c) exhibits morphology which is comprised of a Widmanstatten lath-like morphology with a lamellar α and small ‘basketweave’ retained β phase,
which is an indication that the produced compacts are near-\(\alpha\) titanium alloy, and this is consistent with the phases obtained in the XRD patterns in Figure 5. The secondary \(\alpha\) phase (\(\alpha'\)-phase i.e phase exhibiting lighter contrast) represents a typical lamellar lath-like morphology being initiated from the grain boundary of the \(\alpha\) layer (phase exhibiting the darker contrast in the micrographs) as shown in Figure 4d. It can also be deduced that Mo particles impeded the kinetics of formation of the \(\alpha\) phase.

![XRD Patterns](image)

Figure 5. XRD patterns of (a) Admixed Ti-5Al-1Mo powder; Sintered samples at (b) 800 °C; (c) 1000 °C; (d) 1100 °C

This permitted the development of dispersed basketweave microstructures of secondary \(\alpha\)-phases at the grain boundaries, which would increase the strength and fatigue resistant of the alloy [17]. It was established by EDS analysis of samples sintered at 1000 °C and 1100 °C that there were Mo rich portion which helped in the pinning down of the \(\beta\)-phase as the sintered samples cooled down to room temperature.

XRD analyses confirmed the presence of \(\alpha\)-Ti, Al and Mo phase in the admixed powder (Figure 5a) and there was no formation of any Ti-Al intermetallic phase. The characteristics peaks corresponding to \(\alpha\)-Ti, \(\beta\)-Ti and \(\text{Al}_8\text{Mo}_3\) phases are found in the patterns of the sintered samples with \(\alpha\)-Ti as the major phase. There was no noticeable diffraction peak of \(\beta\)-Ti phase in sample sintered at 800 °C; two peaks of \(\beta\)-Ti phase were seen at 1000 °C at 2-theta angle of 38.759° and 83.156° and two other peaks were added for 1100 °C sample at 55.973° and 70.162°. This can be explained in line with the fact the sintering at 800 °C does not reach to the \(\beta\)-transus temperature of the alloy whilst sintering at 1000 °C and 1100 °C was above the \(\beta\)-transus temperature. This implies that Mo as a strong \(\beta\)-stabiliser was able to retain the \(\beta\)-phase as the sample cools to room temperature.

4. Conclusion
The Ti-5Al-1Mo alloy was successfully produced by SPS technique. The sintering temperature effect on density, microstructure evolution, hardness and phase transformation of the alloys were explored. The following deductions can be drawn:

- The density of sintered samples increased with increase in temperature, and fully densified samples were obtained at temperature of 1000 °C and 1100 °C.
- Densification has direct impact on the hardness of the material as it increases as porosity reduces with the highest hardness value of 290.35HV.
- The microstructures of the alloy sintered at temperature of 1000 °C and 1100 °C consisted of a Widmanstatten lath-like morphology with a lamellar \(\alpha\) and small ‘basketweave’ retained \(\beta\) phase.
• The presence of Mo (β-stabiliser) assisted in retaining small portion of β-phase within the microstructure. The development of dispersed basketweave microstructures at the grain boundaries would increase the strength and fatigue resistant of the alloy.

• The obtained results show that the 800 °C SPS temperature regime for near alpha titanium alloy should be avoided.

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