Bi-modally grained Ti-based alloys fabricated by semi-solid sintering based on the hypoeutectic transformation

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Abstract—We present a fundamentally different approach to process the bimodal Ti-based alloy (Ti-Nb-Fe-Co-Al) by semi-solid sintering stemmed from hypoeutectic reaction, aiming at achieving ultrafine eutectic structure, $\beta$-Ti and micron-sized dispersed phase with strengthening effect. As expected, the microstructure of the processed Ti-Nb-Fe-Co-Al alloy contains local ultrafine eutectic structure ($\beta$-Ti and TiFe), residual equiaxed $\beta$-Ti and micron-sized dispersed phase TiCo. This alloy possesses excellent properties, the yield strength is $1620\text{MPa}$ and large plastic strain is $20\%$, superior to those of the previous fully eutectic alloy by casting. The novel idea is helpful to fabricate high-performance alloys and metals, which belonging to high temperature alloy systems.

1. Introduction
For the past few years, in order to obtain high strength alloys without sacrificing plasticity, scientific workers have developed various strategies to fabricate so-called multiscale microstructures \cite{1}. Among these strategies, it makes this topic climaxing that bimodal microstructure containing nanostructured intermetallic compound matrix and micron-sized ductile $\beta$-Ti dendrites, which was fabricated in titanium alloys by semi-solid processing based on casting \cite{2}. In addition, the plastic deformation and heat treatment-induced recrystallization \cite{1}, the solidification of powders with different particle sizes, and the recrystallization behavior of powder sintering, the above three treatments can produce multi-scale structure alloys with different scale grains coexisting.

As a typical phase transformation behavior, eutectic transformation is often used by researchers to adjust the microstructure and macroscopic properties of alloys, mainly due to the excellent yield strength of the lamellar eutectic structure \cite{2}. For the traditional semi-solid processing technology, the eutectic structure is very common. Especially, aluminum alloys and magnesium alloys prepared by traditional semi-solid processing techniques often exhibit typical lamellar eutectics in the microscopic field. Fortunately, after years of hard work by our research group, expectant lamellar eutectic has been raised in powder metallurgy formed titanium alloys, which were fabricated by spark plasma sintering (SPS) based on semi-solid processing \cite{3}. However, previous studies have found that the presence of a large amount of eutectic structure in the alloy will deteriorate the properties of the alloy.

In this study, we implement the methodology of semi-solid sintering through hypoeutectic transformation, to develop bimodal microstructure containing few lamellar eutectic structures in titanium alloy by optimize processing technology based on hypoeutectic reaction. The resultant bimodal
alloy contains local ultrafine lamellar eutectic β-Ti phase and TiFe phase, residual equiaxed β-Ti and micron-sized dispersed Ti$_2$Co phase, exhibiting simultaneous high yield strength (1620MPa) and large plastic strain (20%), the plasticity of this alloy is significantly higher than that of the previous fully eutectic alloy by casting.

2. Materials and methods

On basis of hypoeutectic compositions in Ti-Fe phase diagram, marked by red lines in Fig. 1, the quinary ((Ti$_{75.5}$Fe$_{6.3}$Co$_{18.2}$)$_{82}$Nb$_{12.2}$Al$_{5.8}$) (at.%) (i.e. Ti$_{62}$Nb$_{12.2}$Fe$_{5}$Co$_{15}$Al$_{5.8}$) alloy with solid solvent Co, β-stabilizer Nb and α-stabilizer Al was designed to facilitate occurrence of the hypoeutectic reaction between strengthening phase β-Ti and intermetallic compound TiFe, and invalid eutectic transformation between β-Ti and Ti$_2$Co [3]. Thus, the alloy powder particles would enter a semi-solid state containing the hypoeutectic liquid phase and remaining solid phases β-Ti and Ti$_2$Co, when heated to a moderate temperature interval above the eutectic temperature.

![Fig. 1 Phase diagram of Ti and Fe](image)

The alloy powder was prepared by ball milling of blended elemental powders in a stainless-steel jar with a weight ratio of stainless-steel balls to alloy powder 5:1 at a rotation rate of 248 rpm under protection of purified Ar atmosphere. Appropriate as-milled powder was taken out every 5h and examined via differential scanning calorimetry (DSC) at 10°C/min under a purified Ar atmosphere, to ensure maximizing content of glassy phase after 45 h milling. Also, in order to determine the sintering temperature of semi-solid sintering, that is, the eutectic temperature of the five-component Ti-Nb-Fe-Co-Al alloy, as-milled powder after 45 h milling was examined by DSC. The DSC curve in Fig. 2 indicates that as-milled alloys powders exhibit two endothermic peaks, the temperatures are 1080 °C and 1200 °C, respectively. According to the key temperature values of the phase diagram of Ti and Fe in Fig. 1, we can preliminarily determine that the eutectic transformation temperature of this constituent alloy is 1080°C, the temperature of the Ti$_2$Co phase melting is 1200°C. Therefore, the semi-solid sintering temperature was determined to be 1080°C in this study.

Subsequently, the as-milled alloy powders sealed by a piece of tantalum foil were inserted into graphite molds and semi-solid sintered at 30 MPa by a Dr. Sintering SPS-825 system under an Ar atmosphere. The sintering procedure was set up as first heating to 1050°C (below the eutectic temperature between the β-Ti and TiFe) by 100°C/min, followed by continuously heated to the semi-solid temperature (1080°C herein) at 15°C/min and held for 2min. Applied load was removed when cooled rapidly to 600°C to eliminate thermal residual stress. The XRD, scanning electron microscopy (SEM) and transmission electron microscopy (TEM) were employed for studying microstructure and phase constitution of the semi-solid sintered samples. Cylindrical specimens (Φ3mm×6mm) were compressed in MTS testing system at the strain rate of 1×10$^{-3}$ s$^{-1}$ by using a gauge to measure and calculate the strain.
3. Test Results and Discussions

3.1. Microstructure

Fig. 3 shows XRD patterns of the solid and semi-solid sintered Ti$_{62}$Nb$_{12.2}$Fe$_5$Co$_{15}$Al$_{5.8}$ bulk alloys. XRD patterns indicate that both the semi-solid sintered and solid sintered bulk alloys have three constituted phases of solid solutions, bcc β-Ti and TiFe, and fcc Ti$_2$Co.

Fig. 3 XRD patterns of the solid (900°C) and semi-solid (1080°C) sintered bulk alloys

Fig. 4 shows SEM images of the solid and semi-solid sintered Ti$_{62}$Nb$_{12.2}$Fe$_5$Co$_{15}$Al$_{5.8}$ bulk alloys. SEM microstructure analysis indicates that compared with the typical ultrafine equiaxed structure in the solid sintered alloy (Fig. 4a), the semi-solid sintered one has a bimodal microstructure of residual phase Ti$_2$Co embedded into micron-sized β-Ti and ultrafine lamellar eutectic matrix (β-Ti and TiFe), as marked by white circles in Fig. 4b. This bimodal microstructure differs distinctly from other bimodal or multimodal microstructures fabricated by rapid solidification.

Fig. 5 shows TEM images of the solid and semi-solid sintered Ti$_{62}$Nb$_{12.2}$Fe$_5$Co$_{15}$Al$_{5.8}$ bulk alloys. Consistent with previous results [4,5], the solid sintered sample has equiaxed grain structure consisting of the bcc TiFe, the bcc β-Ti and the fcc Ti$_2$Co. As marked by white circles in Fig. 5b, the semi-solid sintered bimodal specimen possesses three characteristic areas, including micron-sized equiaxed fcc Ti$_2$Co, local lamellar structure (marked by white circles in Fig. 5b) with the interleaving lamellae of β-Ti and TiFe phases, and residual β-Ti.
3.2. Mechanical property

Fig. 6 presents compressive engineering stress-strain curves of the solid and semi-solid sintered Ti₆₂Nb₁₂.₂Fe₅Co₁₅Al₅.₈ bulk alloys. Corresponding mechanical properties were average values of three counterparts. The solid sintered sample consistently suffers from poor plastic deformation, partly due to limited work hardening [4,5]. Surprisingly, the semi-solid sintered bimodal alloy exhibits ultra-high yield and ultimate strength of 1620 MPa and 2115 MPa together with large plastic strain of 20%, superior to those of the previous fully eutectic alloy by casting [3]. Obviously, the excellent properties originate from its special bimodal microstructure, especially in our case with local lamellar eutectic and β-Ti matrix surrounding micron-sized fcc Ti₂Co. Again, this proves the importance of our innovative idea in fabricating fascinating combination of better strength and ductility in a metallic alloy.
Fig. 6 Engineering stress-strain curves of the solid and semi-solid sintered alloys during compression test

Fig. 7 shows the fracture cross section of two as-fabricated alloys after compression test. It can be seen that for the solid sintered titanium alloy, the fracture cross section shows a large number of brittle fractures. For the semi-solid sintered alloy, the fracture cross section shows a composite feature of a main ductile characteristics and local brittle characteristics. Plastic characteristics is obvious, especially in the eutectic structure and spherical β-Ti phase areas, many small dimples and light tearing edges are clearly visible. Moreover, it can also be found that there are many lamellar eutectics at the bottom of the dimple. It can be inferred that the dimple is caused by the crushing and movement of hard Ti₂Co particles in the matrix. The previous studies of our team [3] has also confirmed the strengthening mechanism and failure mechanism of Ti₂Co particles. The tearing characteristic of eutectic structure is the most direct embodiment of the high strength and toughness of the alloy. In addition, the residual β-Ti phase region can prevent crack propagation, indicating that the crack did not expand and fail immediately after its initiation here.

Fig. 7 Fracture morphologies of the solid (a) and semi-solid (b) sintered alloys after compression test

4. Conclusion
1) For the designed same component alloy, which can experience hypoeutectic reaction, at the different sintering temperature (900 °C and 1080 °C), only semi-solid sintering can successfully prepare multi-scale structured Ti-based alloy, which consists of local eutectic, residual β-Ti and dispersed Ti₂Co phase.
2) The yield and ultimate strength, and plasticity of the semi-solid sintered alloy are significantly better than those indexes of solid sintered alloy. Specifically, semi-solid sintered titanium alloy possesses a higher yield strength (1620±10 MPa) and higher ultimate compressive strength (2115±8 MPa), and larger plastic strain (20±0.6 %).

3) The plasticity of the semi-solid sintered alloy containing the local lamellar eutectic is significantly better than that index of the previous fully eutectic structured alloy by cast, but the strength is degenerated slightly. It implies that eutectic structure is more conducive to strength strengthening than plastic plasticity improvement. However, the residual β-Ti have a disposition to profit to the plasticity of the alloy.

Acknowledgments
This work was financially supported by the University Scientific Research Project of Guangzhou Education Bureau (No. 202032783), Special Project in Key-Area of the Colleges and Universities in Guangdong Province (No. 2020ZDZX2072), Guangzhou Basic and Applied Basic Research Foundation (No. 202102080259), GuangDong Basic and Applied Basic Research Foundation (No. 2020A1515110629), National Natural Science Foundation of China (No. 52101039).

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