

Titanium Alloys for Rapid Solidification Processing

Rapid solidification ($\Delta T \approx 10$ to 10^{10} K/s) of metallic melt occurs in many technical processes, such as powder atomization, welding, Additive Manufacturing (AM), casting, arc or plasma melting etc. The gradient causes non-equilibrium phases, segregation effects and residual stresses, which confines the choice of processable alloys. It is therefore an objective of the present invention to disclose two alloy systems, which surprisingly show an outstanding rapid solidification behavior.

In some applications fine grained powder ($<1\text{mm}$) is needed. In other applications granular matter (comprising grains sizes $\geq 1\text{mm}$) is required. This might even be bulk goods. These are all powders in the sense of this specification.

The metal systems which the inventor found to show the best properties in terms of rapid solidification processability are Titanium (Ti) +Tantalum (Ta) + Iron (Fe) + Niobium (Nb) + Zirconium (Zr) and Ti + Ta + Fe + Tin (Sn).

In the following abbreviated as TTFNZ and TIFS:

Composition, wt. %: TTFNZ										
Element	Ti	Ta	Nb	Fe	Zr	Preferably Sn	Si	O	N	C
Target	Balance	6	8	4	6	-	-	-	-	-
Range A Min.	Balance	0,01	0,01	0,01	0,01	Preferably 0,01	0.001	0.001	0.001	0.001
Range A Max.	Balance	15	25	15	15	Preferably 10	3	0.3	0.2	0.9
Range B Min.	Balance	3	4	2	3, preferably 2	Preferably 0	0.001	0.001	0.001	0.001
Range B Max.	Balance	10	12	6, preferably 10	9, preferably 10	Preferably 10	3	0.3	0.2	0.9
Property		Unit								
Elastic modulus		<120 GPa, preferably < 100 GPa,								
Indent hardness		> 300 HV								
Density		< 7 g/cm ³								

TTFNZ comprises only optionally Sn.

Composition, wt. %: TTFS								
Element	Ti	Ta	Fe	Sn	Si	O	N	C
Target	Balance	7	5	3	-	-	-	-
Range A Min.	Balance	0,01	0,01	0,01	0.008	0.001	0.001	0.001
Range A Max.	Balance	20	15	10	3	0.3	0.2	0.9
Range B Min.	Balance	3	2	0,1	0.008	0.001	0.001	0.001
Range B Max.	Balance	10	10	9	3	0.3	0.2	0.9
Property	Unit							
Elastic modulus	<120 GPa, preferably < 115 GPa,							
Indent hardness	> 300 HV							
Density	< 7 g/cm ³							

The thermodynamic equilibrium of TTFNZ and TTFS is shown in figure 1, 1b and 2, 2b. The α/β Microstructure and phase composition of TTFNZ and TTFS after a **rapid solidification** process, (similar to 3D printing) is shown in figure 3, 3b and 4, 4b. And the β dominated microstructure of TTFNZ and TTFS after arc melting conditions is shown in figure 5 and 6.

The thermodynamic equilibrium of TTFNZ is shown in figure 1, 1b. The α/β microstructure of the alloy was confirmed using electron backscatter detector (EBSD) analysis for various conditions after rapid solidification (non-equilibrium) and/or finally accompanied by heat-treatment to achieve a near-equilibrium microstructure. The different microstructure produced by these processes are illustrated in figure 2, 2b, with the heat-treatment achieving a microstructure closer to the thermodynamic calculation.

This alloy shows, in the investigated processed windows, high compatibility with additive manufacturing processes, highlighted by the absence of cracks after processing.

The simulated thermodynamic equilibrium phase diagram of TTFS is shown in figure 2, 2b. The simulation was performed with a step size of 1 K. The alloy is in the liquid state at TS =

1922 K (Matrix Formation Temperature) and transforms to 100% phase mole fraction of the solid cubic BCC_B2 phase at TS = 1821 K. That leads to an equilibrium solidification interval of about TLS = 101 K. After cooling to 1027 K, the hexagonal HCP phase nucleates (Beta-Alpha Transition Temperature) and is stabilized to a simulated temperature of 300 K to 92,88 % phase mole fraction. At this temperature, the remaining phases are the rhombohedral μ -Phase (Fe₇Ta₆) with a 4,3 % phase mole fraction and the ordered intermetallic compound FeTi (BCC_B2#2, cubic B2-type) with a solution of Ta. The precipitation of intermetallic phases, such as the μ -phase, or secondary phases such as the HCP_A3 (α -Phase) leads to an increase in the electrical resistance of the material; this leads to higher absorption of laser radiation, which can lead to a reduction in production costs of laser-based manufacturing processes.

The α/β microstructure of the alloy was confirmed using an electron backscatter detector (EBSD) analysis for various conditions after rapid solidification (non-equilibrium) and/or finally accompanied by heat-treatment to achieve a near-equilibrium microstructure. The different microstructure produced by these processes are illustrated in Figure 6, with the heat-treatment achieving a microstructure closer to the thermodynamic calculation.

This alloy shows, in the investigated processed windows, high compatibility with additive manufacturing processes, highlighted by the absence of cracks after processing.

According to another aspect of the present invention, the novel materials could be interesting for aerospace, automotive, tooling or medical applications due to its high specific strength > 200 kN · m/kg.

According to another aspect of the present invention, the novel materials could be interesting for aerospace, automotive, tooling, or medical applications, due to their low density, high toughness, excellent corrosion properties and their resistance against hot or cold cracking.

The metal systems TTFNZ and TTFS are especially suitable for medical applications. The most common implant materials (Ti64, CoCr, 316L) [1] have a relatively high corrosion resistance, but within human body fluid they are exposed to a very aggressive environment of dissolved oxygen, chlorides and proteins, which promote the release of Al-, Co-, Cr-, Ni-, V-, ions into the human body. The dissolved ions can disturb the cellular metabolism and lead to lethal tumorous diseases if trace amounts are exceeded. The best properties in terms of corrosion resistance and biocompatibility are achieved for Ti, Ta, Nb, Zr and their alloys. A further critical parameter of the alloys currently used for medical application is the mismatch of

the elastic properties between the implant materials and the hard tissue. On this matter the presented metal systems TTFNZ and TTFS show a biocompatibility which is superior to established ISO [1] and ASTM standardized alloys. In particular, due to biocompatible alloying elements and the comparatively low elastic modulus ($E < 100\text{GPa}$, preferably $< 120\text{GPa}$), the presented metal system TTFNZ should be preferred in clinical use; compared to established ISO [1] and ASTM standardized alloys. In particular due to the biocompatible alloying elements and the comparatively low elastic modulus ($E < 115\text{GPa}$, preferably $< 120\text{GPa}$), the presented metal system TTFS should be preferred in clinical use; compared to established ISO [1] and ASTM standardized alloys.

Furthermore, common AM rapid solidification processing of TTFNZ and TTFS could empower tissue-engineered open porous, bone-mimicking lattice structures (scaffolds), which would allow the oxygenation and nutrition of bone cells, enabling osseointegration and a strong implant fixation.

According to another aspect of the present invention and regarding TTFS, it may be considered to add Tin (Sn; preferably 0.01 – 10wt.%) to all existing titanium alloys in order to improve the common additive (AM) processability, in particular weldability or printability (AM). Because Sn can reduce the high surface tension and high melt viscosity, which could cause the balling effect during rapid solidification. In particular Sn can at the same time increase the absorption of laser radiation, which can lead to more cost-effective processing of titanium alloys.

In this case, Sn can be added as elemental powder to the pre-alloyed powder mixture or Sn can be alloyed directly to the pre-alloyed powder.

This specification was written focusing on powders. However, the one skilled in the art understands that there are additive manufacturing methods not based on powders but rather on wires or for example metal powder mixtures in liquid polymers. The materials as presented in the present specification may be used in such methods as well, which is as well an aspect of the present invention.

According to another aspect of the present invention, it may be considered to add Oxygen O, and/or Carbon C, and/or Nitrogen to TTFNZ and/or TTFS to create a hard, wear-resistant material.

In this invention an additive manufacturing method for the production of components is claimed comprising the steps of

(a) providing and melting a metal based powder

(b) merging the molten particles with each other and with their underground thereby forming merged material

(c) cooling and thereby solidifying the merged material

characterized in that the metal based powder is a Ti based powder comprising at least Ta, Fe and i) Sn and/or ii) Nb and Zr

Preferably the method is characterized in that the Ti based powder comprises as well Si.

Preferably the method is characterized in that the Ti-based powder comprises C and/or N, and/or O.

In this invention a Ti based powder for additive manufacturing is claimed that is characterized in that the powder comprises:

- Ta in the range of 0.01wt% and 15wt%, preferably in the range of 3wt% and 10wt% and most preferably is comprised with 6wt% and

- Nb in the range of 0.01wt% and 25wt%, preferably in the range of 4wt% and 12wt% and most preferably is comprised with 8wt%

- Fe in the range of 0.01wt% and 15wt%, preferably in the range of 2wt% and 6wt% and most preferably is comprised with 4wt%

- Zr in the range of 0.01wt% and 25wt%, preferably in the range of 3wt% and 9wt% and most preferably is comprised with 6wt%.

In this invention a Ti based powder for additive manufacturing is claimed that is characterized in that the powder comprises:

- Ta in the range of 0.01wt% and 20wt%, preferably in the range of 3wt% and 10wt% and most preferably is comprised with 7wt% and

- Fe in the range of 0.01wt% and 15wt% preferably in the range of 2wt% and 10wt% and most preferably is comprised with 5wt%
- Sn in the range of 0.01wt% and 10wt% preferably in the range of 0.1wt% and 9wt% and most preferably is comprised with 3wt%
- Si in the range of 0.001wt% and 3wt%.

Preferably the Ti based powder is characterized in that the powder comprises:

- Oxygen, preferably in the range of 0.001wt% and 0.3wt%, and/or
- Nitrogen, preferably in the range of 0.001wt% and 0.2wt%, and/or
- Carbon, preferably in the range of 0.001wt% and 0.9wt%.

For some of the Ti based powders as described above the metals added to Ti lead to a faster solidification of the merged material the powder compared to the solidification of Ti based powder comprising only Ti as metallic element. In some of these cases this can be explained by an increase of the melting point of the merged material as compared to pure Ti. A higher melting point leads to a larger temperature gradient between the solidifying melt and the surrounding medium during cooling, which leads to faster solidification. Faster in this context means that the solidification is at least 1K/s faster.

Key literature

- [1] ISO 5832, Implants for surgery – Metallic materials

Claims

1. Additive manufacturing method for the production of components comprising the steps of:

- a) providing and melting a metal based powder,
- b) merging the molten particles with each other and with their underground thereby forming merged material,
- c) cooling and thereby solidifying the merged material,

characterized in that

the metal based powder is a Ti based powder comprising at least Ta, Fe and i) Sn or ii) Nb and Zr,

wherein for i) the powder comprises:

- Ta in the range of 3wt% and 10wt%,
- Fe in the range of 2wt% and 10wt%,
- Sn in the range of 0.1wt% and 9wt%, and
- Si in the range of 0.001wt% and 3wt%,

wherein Ti is used as a balance of the composition, and

wherein for ii) the powder comprises:

- Ta in the range of 3wt% and 10wt%,
- Fe in the range of 2wt% and 10wt%, and
- Nb in the range of 4wt% and 12wt%,
- Zr in the range of 3wt% and 9wt%,

wherein Ti is used as a balance of the composition.

2. Method according to claim 1, characterized in that the Ti based powder comprises as well Si.

3. Method according to one of the previous claims, characterized in that the Ti based powder comprises C and/or N and/or O.

4. Ti based powder for additive manufacturing, characterized in that the powder comprises:

- Ta in the range of 3wt% and 10wt%,
- Nb in the range of 4wt% and 12wt%,
- Fe in the range of 2wt% and 10wt%,
- Zr in the range of 3wt% and 9wt%,

wherein Ti is used as a balance of the composition.

5. Ti based powder for additive manufacturing, characterized in that the powder comprises:

- Ta in the range of 3wt% and 10wt%,
- Fe in the range of 2wt% and 10wt%,
- Sn in the range of 0.1wt% and 9wt%, and
- Si in the range of 0.001wt% and 3wt%,

wherein Ti is used as a balance of the composition.

6. Ti based powder according to claim 4 or 5, characterized in that the powder comprises:

- Oxygen, preferably in the range of 0.001wt% and 0.3wt% and/or
- Nitrogen, preferably in the range of 0.001wt% and 0.2wt% and/or
- Carbon, preferably in the range of 0.001wt% and 0.9wt%.