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Doctoral Thesis - Reviewer Report

Title: Microstructural investigations of novel high entropy alloys

Candidate: Mgr. Tomáš Vlasák
Supervisor: prof. Mgr. Jakub Čížek, Ph.D.

Reviewer: prof. Conrado Ramos Moreira Afonso, Ph.D.

The Ph.D. thesis of the candidate presented a strong set of results of experimental investigations of BCC based high entropy alloys based in noble alloying elements: Hf, Nb, Ta, Ti, V, Zr. The main combinations studied: NbTaTiZr, HfNbTaTiZr, HfNbTiVZr and HfNbTaTiVZr were cast by arc melting. Microstructure characterization was very well done in as-cast and annealed states in order to compare phase (lattice parameters and possible phase transformations) and microstructure modifications.

After general characterization of the alloys, one specific HfNbTaTiZr alloy system was processed by high pressure torsion (HPT) applying severe plastic deformation, which lead to significative grain size refinement and reaching ultrafine/nanoscale grained material. In the optimal condition of HPT processing of equivalent strain in the range e = 20 to 30, maximum of yield and ultimate tensile strength were obtained together with maximum of elongation to failure (between 10 to 12%) for e = 10 to 20, mapping best processing parameters through HPT.

The thesis present novelty in the processing HEA of BCC refractory systems by HPT with significative contributions to the field in solid state physics and materials science areas, open possibility to new investigations in an very actual (hop topic) and highly relevant theme due to the used experimental alloys and the implementation of the methodology and the achieved results.

The candidate published in 7 papers regarding the thesis theme in Materials Science journals and participated of 8 papers as a co-author.

In the following comments the reviewer looks for some doubts and improve the discussion of some points in the literature, as a constructive criticism for a work that is already very good, and that can only have a few points improved.

- Page 15, Topic: 1.4.2 Types of microstructure, 1st Paragraph: …"The most common phases are disordered (solid solution) FCC phase (found 465 times in 410 alloys) and BCC phase (found 357 times in 306 alloys). Ordered IM phase B2 follows with 177 occurrences in 175 alloys".

It was not possible to understand, how a FCC phase can appear 465 time in 410 alloys, a greater number of appearing than alloys? In some alloys, there is two FCC phases coexisting in some of the alloys? Please explain in more detail.

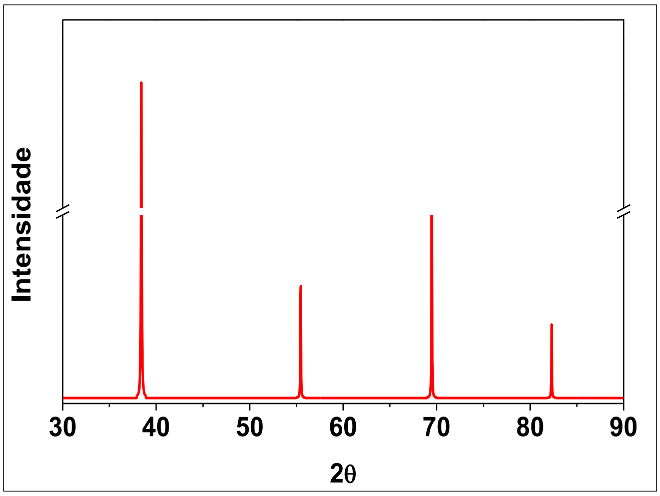
- Page 15, Topic: 1.4.2 Types of microstructure, 3rd Paragraph: …"which resultn", should be corrected to …"which result".

- Page 37, Topic: 3.1 Vacuum arc melting, All the Paragraphs: …"vacuum arc remelting process, the alloy is formed into a cylinder electrode. The electrode is put into a cylindrical crucible made of copper…" It is not mentioned the dimensions of cylindrical cast sample, diameter and hight, the candidate should provide the dimensions in this Section.

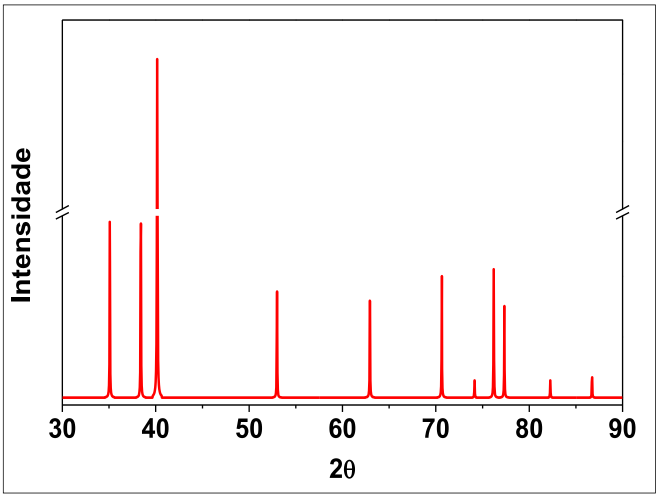
- Pages 41 to 43, Figures: 4.1 to 4.5, All the Paragraphs: …" The NbTaTiZr alloy microstructure at as-cast and annealed state, the microstructure characterization of SEM micrographs is correct, but due to the fluctuation of composition between solute rejection upon dendritic solidification might be generated a Nb-Ta-rich phase and another Ti-Zr-rich phase, which is correct.

As references in the literature (ISCD) for X-ray diffraction data, the following X-ray data can indicate the main peaks of α-Ti (hcp) and β-Ti (bcc) phases.

β				
H	K	L	2θ	Intensidade relativa
1	1	0	38,417	100,00
2	0	0	55,457	15,43
2	1	1	69,48	28,81
2	2	0	82,296	8,63



α				
H	K	L	2θ	Intensidade relativa
1	0	0	35,084	24,89
0	0	2	38,402	25,44
1	0	1	40,161	100,00
1	0	2	52,988	13,70
1	1	0	62,939	15,30
1	0	3	70,636	15,61
2	0	0	74,142	2,23
1	1	2	76,195	16,39
2	0	1	77,339	11,75
0	0	4	82,260	2,19
2	0	2	86,736	2,89



Comparing with the X-ray patterns of Figure 4.3 for NbTaTiZr alloy in the as-cast and annealing state, peaks around 2θ ~34° (red curve of Figure 4.3, NbTaTiZr annealed) is more related to α-Ti phase (hcp) than β-Ti (bcc) one. The candidate should review that point for the other set of α-Ti possible peaks as well: 2θ = 62 - 66° at least of one the peaks is probably of α-Ti phase to. For 2θ ~37° it is coherent that it would be a β-Ti (bcc) or a β′ separated phase.

- Page 45, Figure 4.9: SEM image of HfNbTaTiZr alloy after annealing at 1200 ◦C. The same for the XRD peaks and possible phases formed. The peak around 2θ ~31° is typical of metastable nanoscale omega (ω) phase. And after annealing 1000 ◦C for one hour and slowly cooled (furnace), peak around 2θ ~34° (red curve of Figure 4.9, HfNbTaTiZr annealed) can be related to α-Ti phase (hcp), as confirmed in the Fig. 4.11(b) in detail of microstructure with α-Ti precipitated in the grain boundaries.

- Page 51, Figure 4.18: XRD patterns of HfNbTaTiVZr alloy, the same of mentioned above.

- Page 55, Figure 5.3: EBSD map of HPT processed samples with equivalent strain a) e = 1, b) e = 2, c) e = 5.
It is very interesting result, and a question would be the histogram of grain sizes distribution similar to Fig. 5.2, and the average grain size after equivalent strains of e = 1, e = 2, e = 5.

- Page 62, Figure 5.9: Tensile stress-strain curves for as-cast sample and HPT processed samples with different equivalent strain measured on miniature samples.
Just to mention, was it possible to determine the Young modulus, E (GPa)? Because it is usually interesting evaluate it for Beta Ti alloys. Since there was a significative increase in the Vickers microhardness (very nice graphic in Fig. 5.7), it would be interesting to check possible modulus variation.

- Pages 66/67, Figures 5.14 and 5.15: It is not mentioned the possibility of metastable nanoscale omega (ω) phase formation during cooling after annealing ($\omega_{athermal}$ for water quenching and $\omega_{isothermal}$ for furnace cooling), because ω phase precipitation is usually responsible for significant hardness increasing in Beta Ti alloys, even in high entropy alloys such phase could be formed besides solid solution and grain coarsening.

Although there is some questions and suggestions of improve discussion of the Thesis, which can be incorporated in a future paper publication of the candidate and the respective research group. The Ph.D. thesis in general is very great, with a high quality of the results presented, such as XRD patterns, microstructure characterization images, SEM and EBSD analysis. The candidate has a very good English writing, and presented a clear writing, easy to read and understand. Regarding bibliographic references, significative papers in the theme of high entropy alloys and related themes of the thesis were stated and mentioned during discussions, increasing the coherence of results obtained. High entropy BCC solid solution alloys of the systems studied NbTaTiZr, HfNbTaTiZr, HfNbTiVZr and HfNbTaTiVZr tend more to refractory alloy systems with increased mechanical properties when compared with more common Beta Ti alloys, and can open perspective of applications as advanced alloys for high temperature environments with high thermal stability, which could be evaluated in future studies.

I recommend the thesis for acceptance and Tomáš Vlasák to get a Ph.D. degree after the successful defense.

São Carlos, January 6th, 2023.

Conrado Ramos Moreira Afonso, Ph.D.

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