



Research Article

Microstructures in a Nb-Cr-V-W-Ta high entropy alloy during annealing

S.K. Varma^{1,*}, Francelia Sanchez¹, C.V. Ramana²¹ Department of Metallurgical, Materials and Biomaterials Engineering, The University of Texas at El Paso, El Paso, TX 79968-0520, USA² Mechanical Engineering Department, The University of Texas at El Paso, El Paso, TX 79968-0520, USA

ARTICLE INFO

Article history:

Received 27 February 2020

Accepted 26 March 2020

Available online 6 May 2020

ABSTRACT

A Nb-Cr-V-W-Ta high entropy alloy has been subjected to annealing treatment at 600, 700 and 800 °C in air for 6 hours. Five different phases have been identified based on their composition in the as received condition. The annealing treatment does not alter the phase analysis and compositions except for the W-rich phase where minor changes in the composition have been observed. This is considered as an experimental evidence of sluggish diffusivity associated with HEAs. Absence of phase transformation during the heating and the minimal changes in observed compositions of the phases is an indication of the resistance to diffusion offered by the elements of the high entropy alloy. Scanning electron microscopy (SEM), energy dispersive spectroscopy (EDS) and color X-ray elemental mapping have been used to conduct this research.

© 2020 Published by Elsevier Ltd on behalf of The editorial office of Journal of Materials Science & Technology.

Introduction

The oxidation resistance of high entropy Nb-Cr-V-W-Ta alloy was reported recently [1] in a range of temperature from 600 to 1400 °C for 12 or 24 hours in air. Similar oxidation studies have been conducted by the authors on Nb-15Re-15Si-10Cr-20Mo and Nb-Cr-Mo-Si-B alloys [2–5]. Present high entropy alloy (HEA) exhibits adequate oxidation resistance up to 800 °C while extensive oxide cracking results in very high rate of oxidation at temperatures beyond this. The microstructural stability was determined at 600, 700 and 800 °C by annealing in air for 6 hours.

Several excellent reviews on HEAs have been published recently [6–9]. There are four important factors that can be common to all the HEAs: (1) inclusion of a minimum of 5 elements in the alloy, in equiatomic proportion, increases the entropy, (2) the unit cell must be highly distorted to accommodate so many atoms from these elements, (3) due to these two factors the diffusion is believed to be highly sluggish, and (4) properties are totally dependent on a given element in the system. Each one of these factors may be attributed to the uniqueness for the development of new alloys. Although the initial attempts were made using BCC metals, the concept has been extended to beyond this self-imposed restriction. In fact, the concept of medium entropy alloys is based on the study of alloys

composed of 3 or 4 elements [10–14]. A more general discussion on HEA can be found in many, already published, review articles [8,15].

It must be noted that if high temperature HEA has to be developed for high temperature application, like refractory metals and alloys, then the alloy must show high resistance to microstructural changes. Thus the microstructural stability during service temperatures must be established carefully. It has been found that Inconel 718 softens at 800 °C and SKH51 and SUJ2 soften at 600 and 200 °C respectively [16,17]. Both sluggish diffusivity and defects can be the contributing factor for the microstructural stability issue. For example, grain growth may be considered more difficult in HEA as has been shown for CoCrFeMnNi alloy. Activation energy for grain growth was found to be 321 kJ/mole [18] while AISI 304 L N steel exhibited only, approximately, half of this value. Similarly, other microstructural parameters such as precipitate coarsening resistance is expected to be high due to the high entropy [19,20]. It can be concluded that driving force and sluggish diffusion of HEAs make significant contribution.

The purpose of this paper is to report experimental results on the microstructural stability for a Nb-Cr-V-W-Ta HEA during static annealing for 6 hours in air at 600, 700, and 800 °C. Special attention was paid to estimate the features of microstructures such as phase transformations, formation or suppression of phases, microstructure coarsening and changes in the compositions of the existing phases.

* Corresponding author.

E-mail address: skvarma@utep.edu (S.K. Varma).

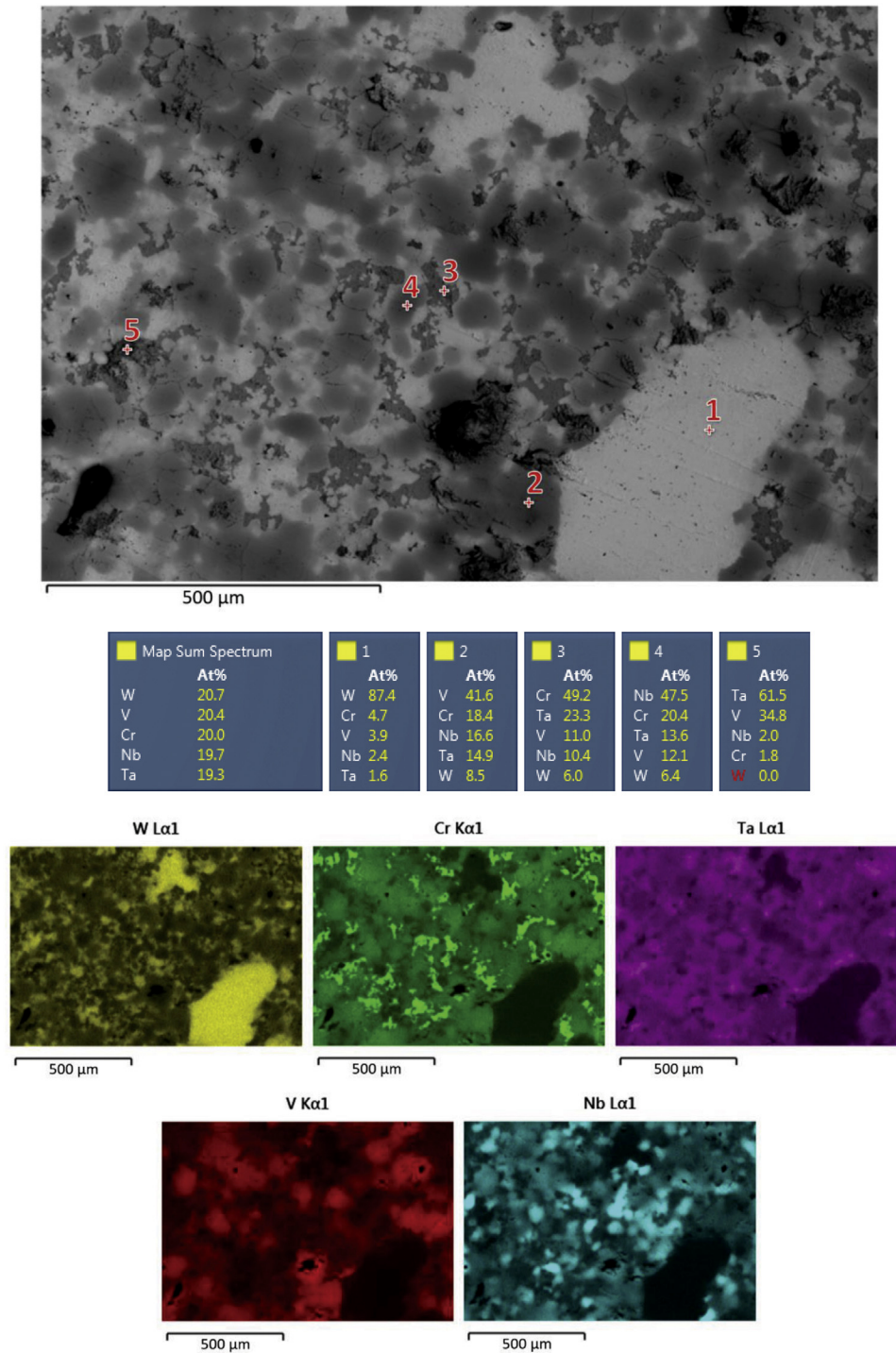


Fig. 1. Microstructure of as received Nb-Cr-V-W-Ta HEA.

Experimental details

An equiatomic Nb-Cr-V-W-Ta alloy was fabricated by the Plasma Materials in California (USA) by arc melting using metals of at least 3 nines purity. As received samples were cubes of 5 mm edges prepared by the electrical discharge machining (EDM). Composition of the trace elements in the alloy is indicated in Table 1 (as supplied by the fabricating unit). A SentroTech furnace with computer controlled heating and cooling cycles was used for static annealing. Heating rate of 10 °C per minute was used up to the pre-

Table 1

Composition of the trace elements in Nb-Cr-V-W-Ta.

Element	PPM	Element	PPM	Element	PPM
Fe	89.8	Si	15.1	Ni	12.6
Mo	13	Ti	<10	Mn	<10
Cu	15.6	Ca	<10	Sn	10
Al	13.4	Mg	10	P	15
Pb	<10	As	<10	Bi	<10
Sb	<10	K	28.3	Na	78.9

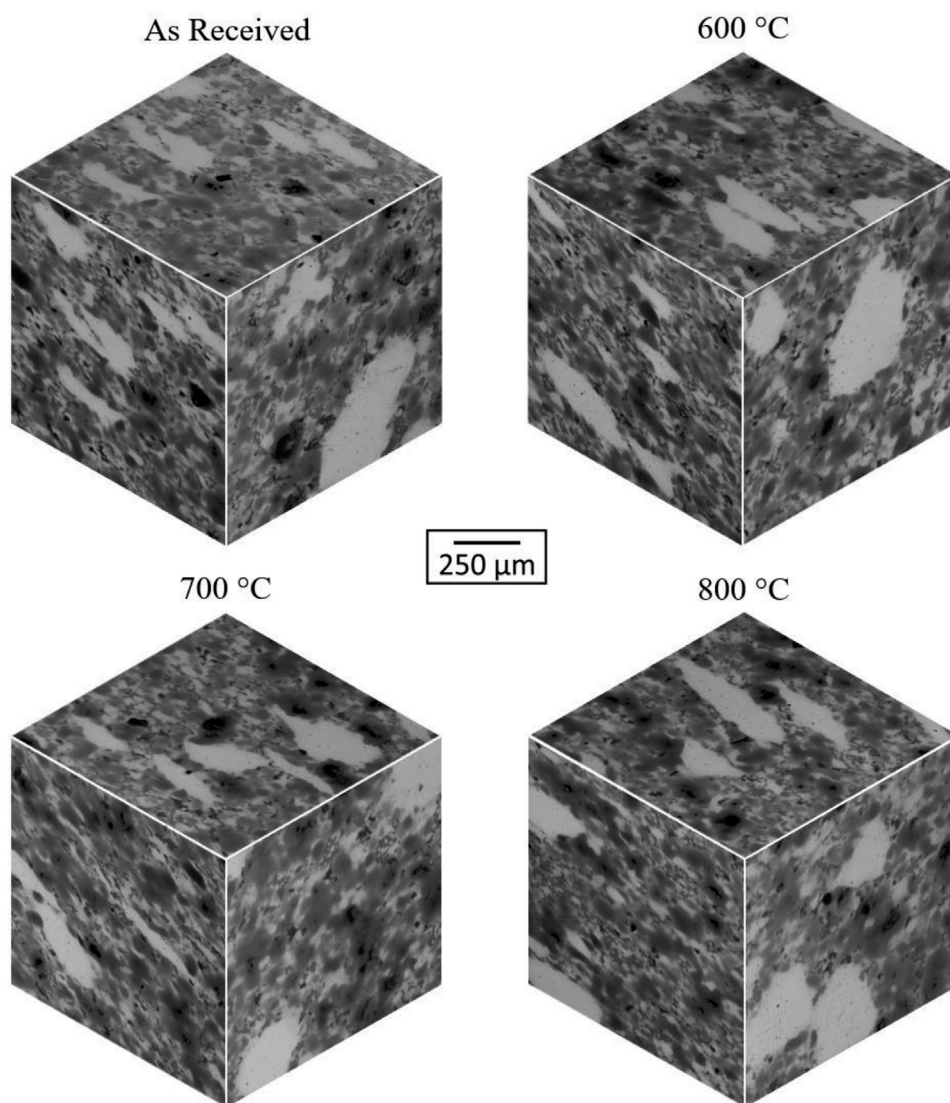


Fig. 2. 3D section of the samples indicating both elongated and equiaxed grains even after annealing.

selected annealing temperature. The samples were cooled to room temperature in the furnace.

Microstructures were observed by scanning electron microscopy (SEM) under a Hitachi SU 3500 using back-scattered electron mode after polishing the surface on a 600 grit paper. The compositions of the phases were determined by energy dispersive spectroscopy (EDS) while X-ray color mapping allowed the determination of the distribution/locations of elements in the microstructures.

Results and discussion

Fig. 1 shows the microstructure of the alloy prior to the annealing treatment. EDS analysis of the overall composition confirms the equiatomic proportion of the metals in the alloy. In contrast to the fewer number of phases, generally, found in HEAs, the alloy of present study has been found to contain 5 different phases. It must be noted that phase identification has been performed by contrast and compositional differences. Fig. 1 vividly shows large white areas marked as phase 1. The compositions have been reported in atomic percent throughout this study. The EDS shows that phase 1 is rich in W (87.4%) along with trace elements Cr (4.7%) and V (3.9%). This phase is easily identified in the x-ray

color mapping of Fig. 1. The microstructure is also composed of phases that are visible as clouds. However, there are light and dark clouds that are marked with numbers 2 and 4. The dark cloudy phase is V rich (41.6%) while its counterpart, the light phase is Nb rich (54.5%). The important features of these cloudy phases, 2 and 4, are: (a) small amounts of W and (b) other elements such as V, Nb, Cr and Ta are all within a range of 10 to 18%. Phase 5 is black areas which have been identified as Laves phase VTa_2 . Another phase, marked as 3, is the grainy structure which is Cr rich containing a mixture of Laves phase and a Ta-Cr solid solution.

Another interesting aspect of the microstructures, both prior to and after annealing is the morphology of the phases. Fig. 2 represents the microstructures along the 3 cross sections. The front and top faces of the cubes clearly show the elongated grains while side face is more or less equiaxed. It can be speculated that since both as received and annealed structures show identical morphologies, the structure has not undergone recrystallization although our annealing temperatures are below the conventionally defined recrystallization temperature (i.e., $T = 0.57T_m$). In other words, the microstructure is thermally stable under the experimental conditions in the range of annealing temperatures from 600 to 800 °C for 6 hours.

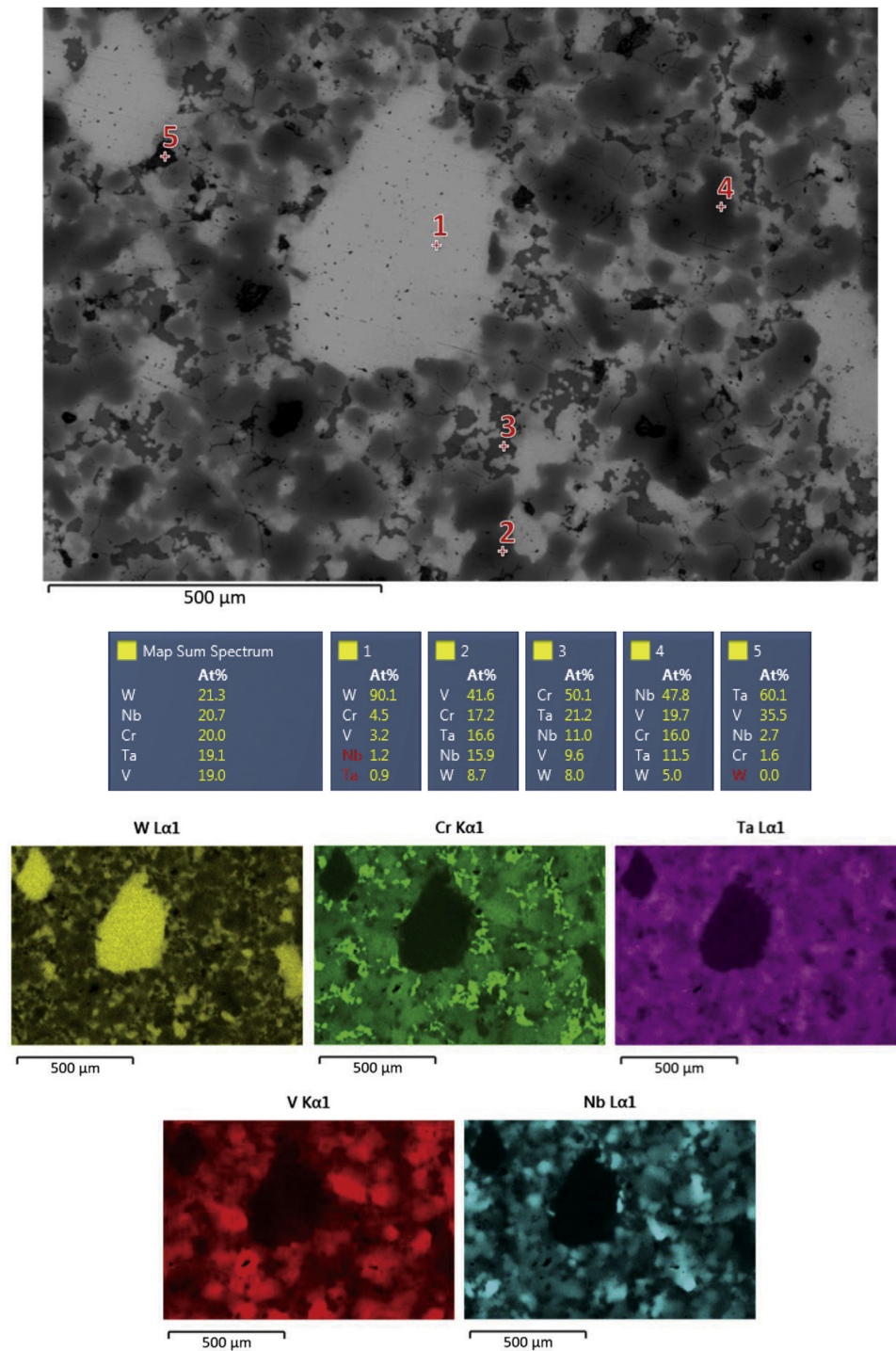


Fig. 3. Microstructure of Nb-Cr-V-W-Ta HEA annealed at 600 °C

Although Fig. 2 can be considered as an experimental proof for the thermal (microstructural) stability in terms of morphology, it does not prove that there are no (a) addition/elimination of phases, phase transformations, and (b) compositional changes due to diffusion. Such hypothesis is verified by the microstructures of the alloy after annealing (along with their respective EDS analysis) at different temperatures.

Annealing at 600 °C

Fig. 3 shows annealed microstructure at 600 °C for 6 hours along with the EDS analysis indicating the locations of various elements and their approximate compositions. First, the equiatomic composition of the alloy has been verified by EDS as well. W is present as while globules (phase 1) and it contains 90.1% W. It contains,

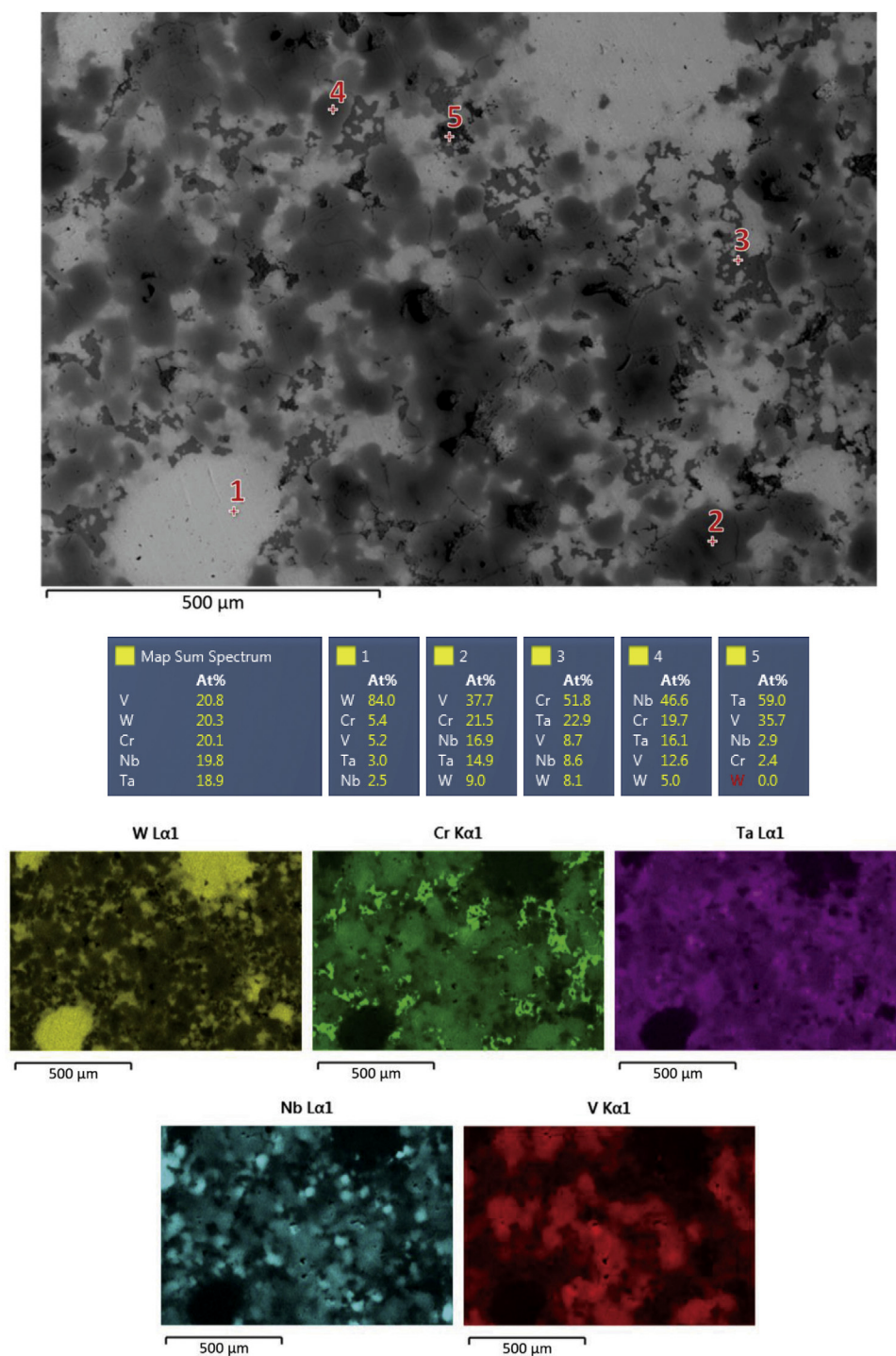


Fig. 4. Microstructure of Nb-Cr-V-W-Ta HEA annealed at 700 °C

approximately, 3.2 and 4.5% of Cr and V (respectively) while Nb and Ta are present in minor amounts. Phase 2 is V rich with Cr, Nb, ranging from 15.9 to 16.2%. Another phase (4) is contained in the cloudy areas which has been found to be Nb rich (47.8%) as opposed to V rich phase 2. This phase also contains Cr, Ta, and V in a 11.5 to 19.7% range with W at 5.0%. Phase 3 is a grainy Cr rich solid solution with 50.1% Cr and 21.2% Ta and rest of the elements are below 11%. The black phase marked as 5 is essentially Ta rich (60.1%) but contains 35.5% V and rest of the elements are below 2.7%.

Annealing at 700 °C

Microstructures developed during annealing at 700 °C for 6 hours are shown in Fig. 4. Some of the notable and comparable features include the composition of the W rich phase 1 is 84% with similar compositions of the rest of the elements as was observed at 600 °C. Although the cloudy phases 2 and 4 still remain V and Nb rich at 37.7 and 46.6% respectively, Cr rich Phase 3 shows only 0.7% jump in Cr compared to this phase observed at 600 °C. Black phase 5 has been observed to be 59.0% Ta with only 1.1% change from its value at 600 °C.

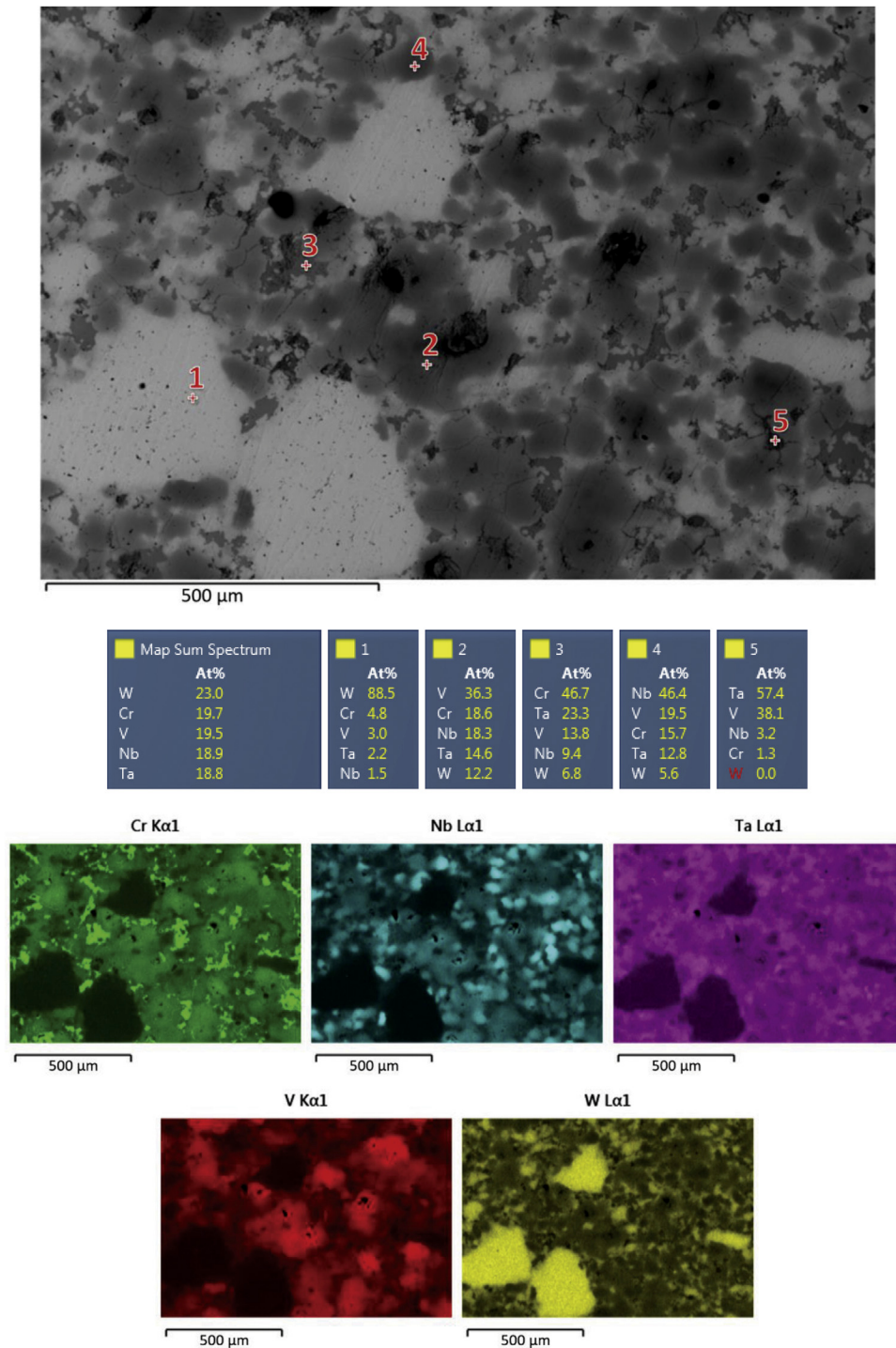


Fig. 5. Microstructure of Nb-Cr-V-W-Ta HEA annealed at 800 °C

Annealing at 800 °C

Fig. 5 shows a micrograph for the microstructure observed at 800 °C. Phase 1 remains W rich at 88.5%W with all other elements at below 4.8% and are quite comparable to compositions at other two annealing temperatures. Cloudy phases 2 and 4 are both V and Nb rich and contain other elements in a 19.5 to 12.0% range. On the other hand, phase 3 is maintained at 46.7%Cr along with 23.3%Ta and 13.8%V. Phase 5 is with black contrast containing 57.4% Ta and 38.1%V rest of the elements fall below 3.2% level.

Summary of Results

- 1 No new phases were observed in this study after annealing at 600, 700, and 800 °C for 6 hours in the HEA of this study.
- 2 There is no significant amount of coarsening of the microstructure.
- 3 There are 5 identical phases present after annealing consistent with the microstructure observed prior to annealing treatment.
- 4 Table 2 summarizes the details of the compositions of all the 5 phases in the as received and after annealing at 600, 700, and 800 °C for 6 hours.

Table 2
Summary of composition of the phases.

Overall Composition					Phase 1				
	AR	600 °C	700 °C	800 °C		AR	600 °C	700 °C	800 °C
W	20.7	21.3	20.3	23.0	W	87.4	90.1	84.0	88.5
V	20.4	19.0	20.8	19.5	Cr	4.7	4.5	5.4	4.8
Cr	20.0	20.0	20.1	19.7	V	3.9	3.2	5.2	3.0
Nb	19.7	20.7	19.8	18.9	Nb	2.4	1.2	2.5	1.5
Ta	19.3	19.1	18.9	18.8	Ta	1.6	0.9	3.0	2.2
Phase 2					Phase 3				
	AR	600 °C	700 °C	800 °C		AR	600 °C	700 °C	800 °C
V	41.6	41.6	37.7	36.3	Cr	49.2	50.1	51.8	46.7
Cr	18.4	17.2	21.5	18.6	Ta	23.3	21.2	22.9	23.3
Nb	16.6	15.9	16.9	18.3	V	11.0	9.6	8.7	13.8
Ta	14.9	16.6	14.9	14.6	Nb	10.4	11.0	8.6	9.4
W	8.5	8.7	9.0	12.2	W	6.0	8.0	8.1	6.8
Phase 4					Phase 5				
	AR	600 °C	700 °C	800 °C		AR	600 °C	700 °C	800 °C
Nb	47.5	47.8	46.6	46.4	Ta	61.5	60.1	59.0	57.4
V	12.1	19.7	12.6	19.5	V	34.8	35.5	35.7	38.1
Cr	20.4	16.0	19.7	15.7	Nb	2.0	2.7	2.9	3.2
Ta	13.6	11.5	16.1	12.8	Cr	1.8	1.6	2.4	1.3
W	6.4	5.0	5.0	5.6	W	0.0	0.0	0.0	0.0

Phase 1It contains 90.1, 84.0 and 88.5%W after annealing compared to 87.4%W in the as received condition. All other elements in this phase are at below 5% level under the conditions of present experiments.

Phase 2It is V rich (36.3 – 41.6%) phase, perhaps a solid solution with Cr, Nb and Ta and they fall in the 14.9 to 21.5% range.

Phase 3The composition varies from 46.7 to 50.1%Cr but forms a solid solution with Ta varying in composition from 21.2 to 23.3%. This phase also contains V in significant amount ranging from 8.7 to 13.8% and Nb from 8.6 to 11.0%.

Phase 4It is a phase contained in the cloudy area which is Nb rich but is solid solution with V, Cr, and Ta (varying from 11.5 to 20.4%). W is below 6%.

Phase 5 Ta rich (57.4 to 61.5%) phase is a solid solution with V and the rest of the elements present are in minor amounts (less than 3.2%).

5 Summary of compositions shown in Table 2 clearly indicates that compositions of the phases do not change significantly and demonstrates no systematic variation with annealing temperatures.

6 The results of this study supports the general concept of HEAs for the sluggish diffusivity due to the presence of 5 elements. This is one concept which has been mentioned in the literature at numerous locations.

Conclusions

Microstructure thermal stability study for the Nb-Cr-V-W-Ta alloy in a range of temperature from 600 to 800 °C for 6 hours in air shows

- No addition or deletion of phases after annealing (absence of phase transformations).
- No coarsening of the microstructures.
- Minimal changes in the composition of the phases after annealing.

- No systematic variation in compositional changes, if there are any.

- Experimental observations are, perhaps, the result of sluggish diffusivity, characteristic of high entropy alloys.

Acknowledgments

This research was conducted at the Center for Advanced Materials Research (CMR) at The University of Texas at El Paso, El Paso, TX. The funding for research was provided by the National Science Foundation with NSF-PREM grant #DMR-1827745.

References

- [1] S.K. Varma, F. Sanchez, C.V. Ramana, J. Mater. Sci. Technol. 38 (2020) 189–196.
- [2] D.M. Dosary, S.K. Varma, J. Mater. Res. Technol. 3 (1) (2014) 25–34.
- [3] Kathryn S. Thomas, S.K. Varma, Metall. Mater. Trans. A 45 (2014) 1124–1135.
- [4] K.S. Thomas, S.K. Varma, Corros. Sci. 99 (2015) 145–153.
- [5] N. Esparza, V. Rangel, A. Gutierrez, B. Arellano, S.K. Varma, Mater. High Temp. 33 (2016) 106–114.
- [6] Y. Zhong, T.T. Zuo, Z. Tang, M.C. Gao, K.A. Dahmen, P.K. Liaw, Prog. Mater. Sci. 61 (2014) 1–93.
- [7] M.H. Tsai, J.W. Yeh, Mater. Res. Lett. 2 (2014) 107–123.
- [8] D.B. Miracle, O.N. Senkov, Acta Mater. 122 (2017) 448–511.
- [9] Y.P. Lu, Y. Dong, S. Guo, L. Jiang, H. Kang, T.M. Wang, B. Wen, Z.J. Wang, J.C. Jie, Z.Q. Cao, H. Ruan, Sci. Rep. 4 (2014) 6200.
- [10] J. Zyka, J. Malek, J. Vesley, F. Lukac, K. Cizek, J. Melikhova, Entropy 21 (2019) 114.
- [11] L. Santodonato, F. Zang, M. Feygenson, C.M. Parish, M.C. Gao, R.J.K. Weber, J.C. Neufeld, Z. Tang, P.K. Liaw, Nat. Commun. 6 (2015) 5964.
- [12] M.F. del Grosso, G. Bozzolo, H.O. Mosca, J. Alloys Compd. 534 (2012) 25–31.
- [13] C.J. Tong, M.R. Chen, S.K. Chen, J.W. Yeh, T.T. Sun, C.H. Tsau, S.J. Lin, S.Y. Chang, Metall. Mater. Trans. A 36 (2005) 1263–1271.
- [14] Y. Zhang, T.T. Zuo, T. Tang, M.C. Gao, K.A. Dahmen, P.K. Liaw, Z.P. Lu, Prog. Mater. Sci. 61 (2014) 1–93.
- [15] Y.F. Ye, Q. Wang, J. Lu, C.T. Liu, Y. Yang, Mater. Today 6 (2016) 349–362.
- [16] C.Y. Hsu, C.C. Juan, W.R. Wang, T.S. Sheu, J.W. Yeh, S.K. Chen, Mater. Sci. Eng. A 528 (2011) 3581–3588.
- [17] M.H. Chuang, M.H. Tsai, W.R. Wang, S.J. Lin, J.W. Yeh, Acta Mater. 59 (2011) 6308–6317.
- [18] W.H. Lin, Y. Wu, J.Y. He, T.G. Nieh, G.P. Lu, Scripta Mater. 68 (2013) 526–529.
- [19] M.H. Tsai, H. Hang, G. Cheng, W. Xu, W.W. Jian, M.H. Chuang, C.C. Juan, A.C. Yeh, S.J. Lin, Y. Shiu, Intermetallics 33 (2013) 81–86.
- [20] T.T. Shun, C.H. Hung, C.F. Lee, J. Alloys Compd. 495 (2010) 55–58.