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Direct metal deposition of refractory high entropy alloy MoNbTaW

Henrik Dobbelstein[a,*], Magnus Thiele[a], Evgeny L. Gurevich[a], Easo P. George[b], Andreas Ostendorf[a]

[a]*Applied Laser Technologies, Ruhr-Universität Bochum, Universitätsstr.150, 44801 Bochum, Germany*
[b]*Institute for Materials, Ruhr-Universität Bochum, Universitätsstr.150, 44801 Bochum, Germany*

Abstract

Alloying of refractory high entropy alloys (HEAs) such as MoNbTaW is usually done by vacuum arc melting (VAM) or powder metallurgy (PM) due to the high melting points of the elements. Machining to produce the final shape of parts is often needed after the PM process. Casting processes, which are often used for aerospace components (turbine blades, vanes), are not possible. Direct metal deposition (DMD) is an additive manufacturing technique used for the refurbishment of superalloy components, but generating these components from the bottom up is also of current research interest. MoNbTaW possesses high yield strength at high temperatures and could be an alternative to state-of-the-art materials. In this study, DMD of an equimolar mixture of elemental powders was performed with a pulsed Nd:YAG laser. Single wall structures were built, deposition strategies developed and the microstructure of MoNbTaW was analyzed by back scattered electrons (BSE) and energy dispersive X-ray (EDX) spectroscopy in a scanning electron microscope. DMD enables the generation of composition gradients by using dynamic powder mixing instead of pre-alloyed powders. However, the simultaneous handling of several elemental or pre-alloyed powders brings new challenges to the deposition process. The influence of thermal properties, melting point and vapor pressure on the deposition process and chemical composition will be discussed.

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1. Introduction

Processing of refractory metals is difficult due to their high melting points and tendency to rapidly oxidize. To produce useful parts, subtractive machining has to be done after powder metallurgy or vacuum arc melting. But these materials have high hardness, especially tungsten and its alloys. Subtractive machining should be minimized to

* Corresponding author. Tel.: +49-234-3223931 .
E-mail address: dobbelstein@lat.rub.de

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reduce tool wear and time of production. Therefore, it is of great interest to build up functional structures by additive manufacturing. Commonly, pre-alloyed powders are used in additive manufacturing techniques like selective laser melting and DMD. The latter technique especially allows in-situ mixing of powders in order to build up composition gradients. However, the processing of a mixture of elements introduces new challenges in finding the best process parameters, since their thermal properties can be very different. Although molybdenum, niobium, tantalum and tungsten all have relatively high melting points, the difference in the melting points of niobium and tungsten is large, around 900 °C.

Research on HEAs is of topical interest, because they are very promising as advanced materials. Definition and properties can be found elsewhere, for instance Zhang et al. 2014 and Murty et al. 2014. Refractory metals are interesting because of their mechanical strength at high temperatures and possible applications can be found in aerospace (Doychak 1992) and nuclear science (Wu 2009). HEAs based on refractory metals, such as the equimolar alloy MoNbTaW, have been investigated, for example by Antonaglia et al. 2014, Senkov et al. 2010/2011 and others, but the alloys were always produced by vacuum arc melting. To avoid elaborate pre-alloying of refractory metals, which can only be done by vacuum arc melting, DMD can be considered for *in situ* alloying by dynamic powder mixing. Here we report results of preliminary investigations of the effects of process parameters on the chemical composition of material generated by DMD.

2. Experimental Procedure

Direct metal deposition was performed with a pulsed Nd:YAG laser with 300 W maximum average power, focusing optics with a focal length of 200 mm and a spot diameter of 800 µm. All samples were prepared on sintered molybdenum substrates with a thickness of 2 mm and a surface area of 12 x 15 mm². The surface was first ground (abrasive paper P1000) to remove its oxide layer and ultrasonically cleaned in acetone. It was then positioned on a 15 x 20 mm² (3 mm thick) stainless steel holder, which was welded to two heating elements. Temperature was measured with a thermocouple inserted through a pinhole and welded to the upper surface of the holder (see Figure 1). The refractory metals in our HEA have a body-centered cubic lattice and all except for Ta show a ductile-brittle transition whose temperature strongly depends on the microstructure. Therefore, the holder was preheated to 500 °C and the measured temperature reached 600 - 700 °C during DMD. To protect the refractory metals from oxidation the deposition process was performed in argon atmosphere. The process chamber was semi-closed with an outlet at the highest position to compensate for the incoming carrier and protection gas (also argon). During preheating, processing and cooling the chamber was constantly purged with argon gas.

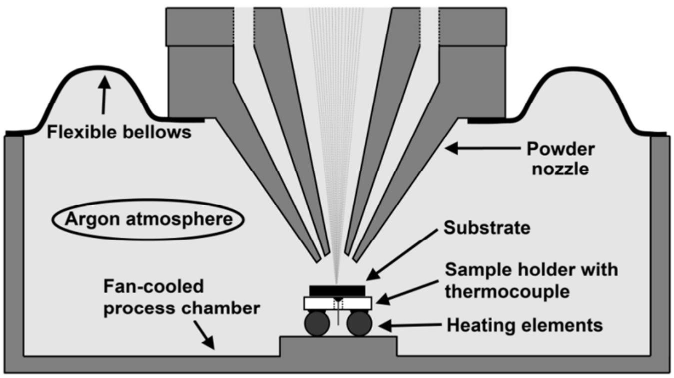

Fig. 1. Experimental setup of direct metal deposition in argon atmosphere.

Generated structures were cross-sectioned, polished and analyzed with the use of a scanning electron microscope (SEM) equipped with BSE and EDX detectors. Elemental Mo, Nb, Ta and W powders, provided by H.C. Starck, were carefully weighed using a high precision scale to produce equimolar mixture (sample size 150 g; $Mo_{25.00\ g}Nb_{25.17\ g}Ta_{49.02\ g}W_{49.81\ g}$).

Table 1. Physical properties of the refractory metals in our HEA.

Refractory element	Nb	Mo	Ta	W	Reference
Melting point [°C]	2468	2610	3000	3380	Savitskii 1970
Boiling point [°C]	4927	5560	5427	5900	Savitskii 1970
Density [g/cc]	8.6	10.2	16.6	19.3	Savitskii 1970
Standard atomic weight [u]	93	96	181	184	CIAAW 2015

3. Powder analysis

DMD process efficiency and stability strongly depends on powder properties. Controlled deposition can only be achieved with homogeneous welding seams, which in turn need a high quality powder focus. High quality powder focus can be achieved by well directed powder flow with low powder scattering and a powder focus size matched to the laser spot size. If the powder focus size is larger than the laser spot size, the powder catchment efficiency will decrease significantly. However, the overlap of powder flow and laser beam should be low to avoid overheating and evaporation of powder particles. Powder scattering not only enlarges the powder focus but also makes the powder flow more chaotic. Thereby particles can cross-penetrate the laser beam and cause welding spatter on the substrate or at the edges of generated structures. The powder flow quality depends on the geometries of the powder nozzle, carrier gas velocity, particle size and particle shape. Best powder flow can be achieved with spherically shaped particles and a size distribution of 50-100 µm (Kong et al. (2007)).

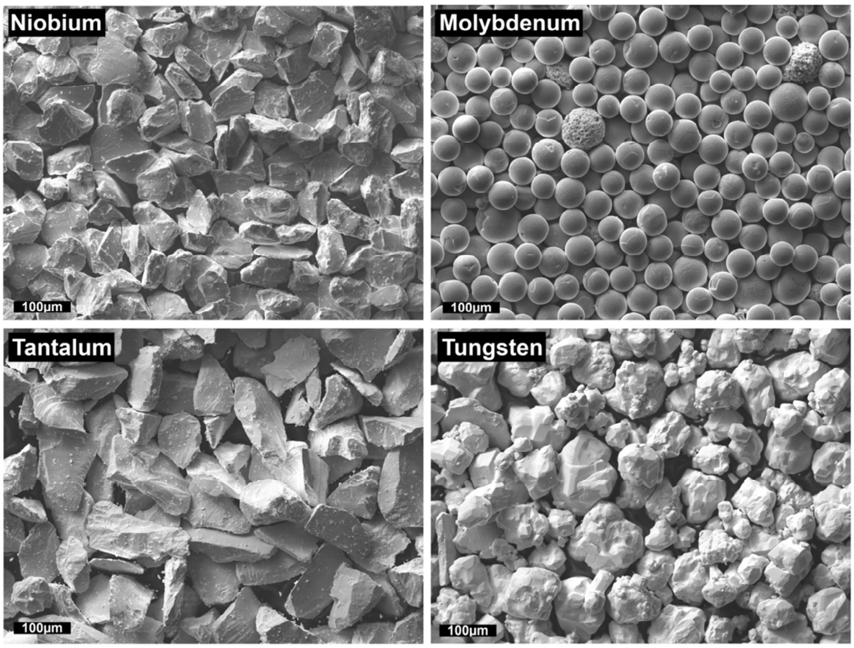

Fig. 2. SEM images of Mo, Nb, Ta and W powders (powders provided by *H.C.Starck).* Except for molybdenum, all elements show an irregular, crushed shape. Tantalum and tungsten have a slightly larger powder size distribution.

The particle size ranges of the elemental powders, as given by the manufacturer, were quite similar (see Table 2), but since they were measured by sieving, the size distribution can be different because of their different shapes. Figure 2 illustrates the particle shapes and it can be seen that only molybdenum particles exhibit a spherical shape. Additionally, they are somewhat smaller than the other powders, which have irregular, crushed shapes. Tantalum and tungsten show the largest size distribution, although the tungsten particles are a little bit more rounded. As will be shown later the irregular shaped particles cause powder flow scattering and have an influence on the deposition quality and process strategy.

Table 2. Flow properties and powder size distribution of elemental powders.

Refractory element	Nb	Mo	Ta	W
Particle size [µm]	45-75	45-90	45-90	45-106
Particle shape	crushed, irregular	spherical	crushed, irregular	crushed, rounded
Flow time of test sample [s]	66	54	59	65
Angle of repose [°]	38	25	37	36

To feed the powder a rotating disc with a groove was used. Due to gravity the powder falls from a storage container through a funnel into the groove. Thereby an inverse cone is formed in the remaining powder. Segregation typically occurs when powder mixtures of different sizes are exposed to vibration or motion. Since the powder was prepared as an equimolar mixture, segregation is not acceptable. Therefore, the flowability of the elemental powders was examined. Sample volumes of 10 cm³ were placed in a funnel (22° angle) with an aperture diameter of 1.5 mm. Flow time and angle of repose were measured with a video camera (see Table 2). Highest deviation can be seen for the spherical molybdenum powder, which has the lowest flow time and angle of repose. For the other powders the angle of repose was almost equal, although tantalum has a lower flow time. As segregation of molybdenum could not be excluded, further tests were conducted where several equal DMD samples were generated at different filling levels of the storage container. A significant difference in their chemical composition could not be measured. Consequently, segregation of the powders may be neglected in the following experiments of the current study, but it has to be mentioned that only a small amount of powder was used (max. 150 g in storage container). For process up-scaling segregation should be reconsidered.

4. Results and discussion

4.1. Single-track welds

In DMD, a laser is used to locally deposit energy into a material's surface. This generates a melt pool and powder is transported to the melt pool by a carrier gas. As the powder particles pass through the laser beam they are preheated and liquid metal droplets can be formed. If the transition time or laser energy is too high for a given particle size and material properties, particles will be evaporated. This has to be considered when a pre-alloyed powder, is used and the process parameters are set for high build-up rates and efficiency. Although small amounts of evaporation do not cause any problems, too much evaporation can cause serious pollution of the powder nozzle and processing chamber. Additionally, plasma formation will corrupt the deposition process. For *in situ* alloying several powders with different material properties and even different geometries are used. Therefore the selection of laser parameters becomes quite challenging. For the present powder mixture of refractory metals, the difference in melting points is highest between niobium and tungsten, around 900°C, with niobium having the lower melting point (Table 1). In the first experiments, single track welds were produced with constant pulse length of 2 ms and feed speed of 150 mm/min, while pulse power and pulse frequency were changed. Optimal pulse power was found to be 800 W (120 Hz pulse frequency); higher pulse power causes too much evaporation, while lower pulse power decreases deposition efficiency. Nevertheless, the resulting weld seam does not look smooth in comparison to known welding characteristics of pre-alloyed powders. As can be seen in Figure 3, the surface of the weld seam is dotted with adhering particles. The weld seam itself is quite inhomogeneous. This surface topography can be explained in terms of a low proportion of true deposition welding but a high proportion of thermal spraying. Consequently *in situ* alloying is not possible with a single track weld. For single wall structures many single track welds are placed on top of each other. However, it is not possible to build up wall structures with the described single track weld process, because a poor and porous connection will be formed. When the laser heats up the surface of this porous layers the heat cannot be transferred into the substrate as easily. Heat accumulation in these loosely connected particles and droplets leads to uncontrollable structure growth with absence of real welding.

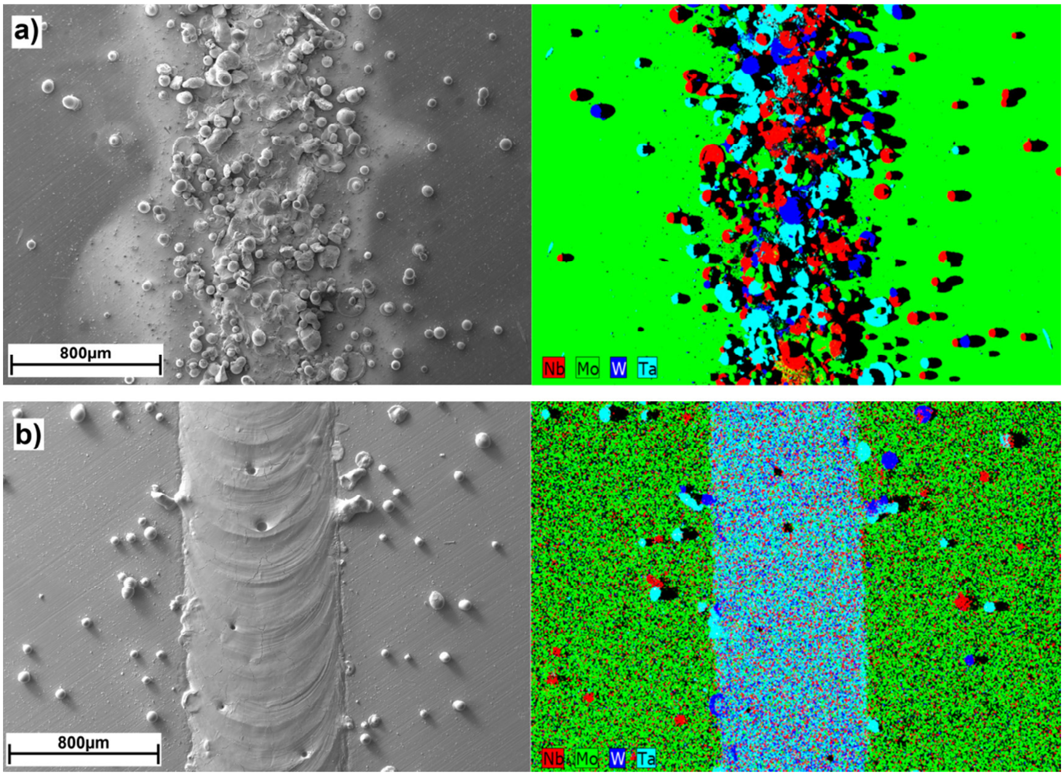

Fig. 3. SEM images (left) and EDX maps (right); (a) single weld seam with incomplete powder mixing and adhering droplets; (b) remolten weld seam with smooth surface and homogeneous distribution of the constituent elements.

In order to modify the loose and porous surface topography, laser remelting was added to the build-up strategy. For this second processing step, a significantly higher laser power has to be chosen to remelt and mix the adhering particles. Care must be taken that the track width of the remelted zone is wide enough to cover almost all the deposited powder material. The number of remaining, incompletely molten particles at the edge of the remolten area should be low, because during the generation of a wall structure more and more powder material will accumulate at the edges (compare with Fig 4) and can lead to a corrupted weld seam due to powder shadowing effects. As a consequence, it is of interest to reduce the spreading of the particles during deposition welding. Wide spreading can be explained by the irregular, crushed particle shape. In order to enlarge the track width of the remolten line the laser focus was shifted 3 mm above the surface. Pulse power was set to 4500 W for a pulse length of 1 ms, pulse frequency of 61 Hz and a feed speed of 500 mm/min. Lower feed speed, that is, higher pulse overlap, leads to evaporation of the deposited powder material. To get homogeneous alloying (by ensuring the melting and mixing of all tungsten particles) this remelting was repeated thrice. For multi-track welding the described procedure was repeated 30 times as described in Table 3.

Table 3. Deposition welding parameters and strategy .

	Pulse power [W]	Pulse frequency [Hz]	Pulse length [ms]	Feed speed [mm/min]
Step 1: Deposition	800	120	2	150
Step 2: Remelting (3 times)	4500	61	1	500
Both steps were repeated 30 times with 60 µm z-layer offset				

4.2. Multi-track welds with equimolar powder mixture

Multi-track welding was performed with the parameters given in Table 3 and the result is shown in Figure 4 (negative image of BSE picture). All multi-track deposits exhibit cracks with a high crack density close to the molybdenum substrate. Incidence of cracking could be reduced by grinding and cleaning of the substrate surface, but could not be entirely eliminated. Possible reasons for this include a mismatch of thermal expansion coefficients and contamination by oxidation. The oxygen content in the atmosphere was not measured and since there was no evacuation before purging, some residual oxygen has to be expected. In particular tungsten and molybdenum are known to be sensitive to embrittlement by oxidation. Apart from the inferior mechanical properties, cracking can critically affect the deposition process. Cracking at the substrate interface limits the heat conduction, which leads to heat accumulation and uncontrollable structure growth.

Back scattered electrons are sensitive to atomic number and elements like tungsten and tantalum scatter more and can be recognized by their darker colors in the negative of the BSE images shown in this paper. As already mentioned powder particles and droplets stick at the sides of the structure, where the elements with higher melting points are not molten but embedded in a matrix of niobium and molybdenum. In contrast the central sections of the weld seams are relatively well mixed, except for a few darker local areas. These can be explained by an imperfect powder delivery system. Although the remelting step is performed without powder flow, remaining powder inside the delivering tubes can come loose. High melting point particles can penetrate the melt pool and are only partly melted before solidification. The EDX analysis, also shown in Figure 4, revealed a non-equimolar composition in the center. Average atomic concentrations are given in Figure 5 and indicate a relation between melting point and concentration. Except for molybdenum, the lower the melting point of an element the higher its concentration. This may be related to the deposition characteristic of single weld tracks. Not only is the probability higher of the powder particles becoming molten while passing through the laser beam for low melting point particles but so is the probability of sticking and melting on the laser heated surface. Assuming a temperature gradient on the surface with a maximum higher than the highest melting point in the center of the laser spot, it is more likely for niobium particles than for tungsten particles to stick and melt outside of that center and even outside of the laser spot. Molybdenum is an exception and shows low concentration in the generated alloy, which cannot be explained at present and needs further study. Unfortunately, molybdenum is the only element with spherical particle shape and slightly lower size. As a consequence, these particles evaporate more easily while penetrating the laser beam (lower surface/volume ratio) and the probability of rebound is higher compared to irregular shaped particles due to a smaller contact area. In order to prove this assumption, molybdenum particles with irregular shape have to be tested or the other elements with spherical shapes should be used. Another factor could be that, relative to its melting point, molybdenum has a high vapor pressure compared to the other elements (see Figure 5).

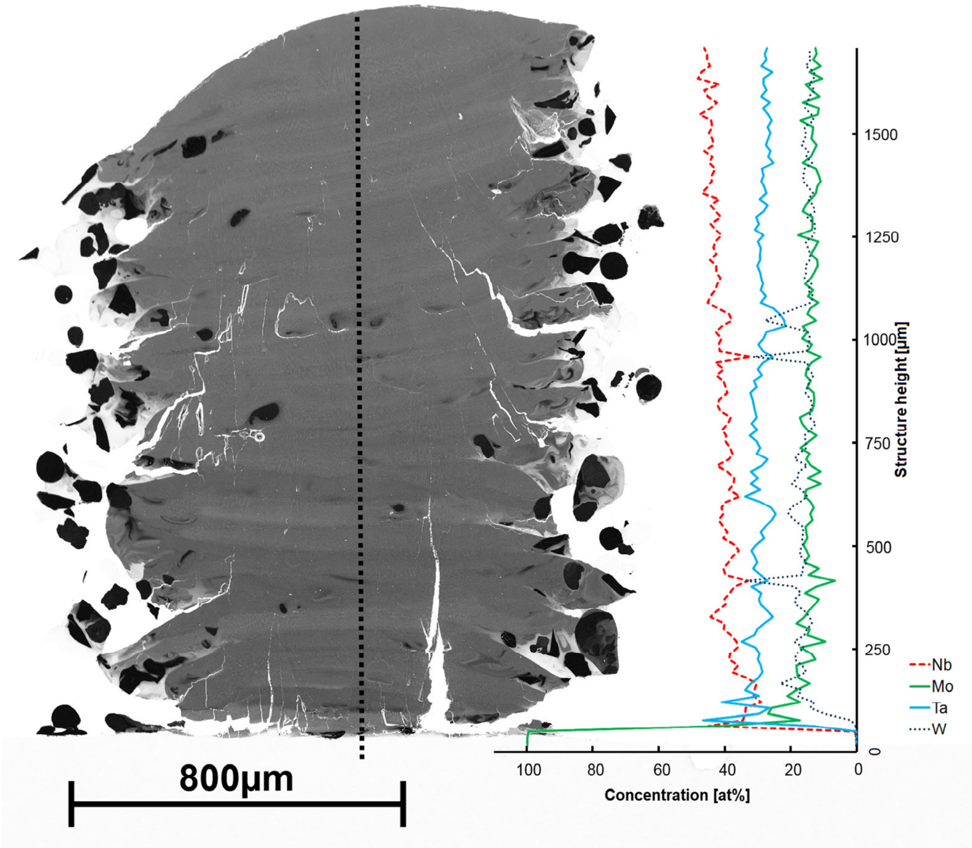

Fig. 4. Cross-section of a multi-track weld of $Mo_{25}Nb_{25}Ta_{25}W_{25}$ [at.%] powder mixture on molybdenum substrate. EDX along the dotted line shows non-equimolar composition. Negative image of BSD picture shows heavier elements (tungsten, tantalum) darker than light elements (niobium, molybdenum).

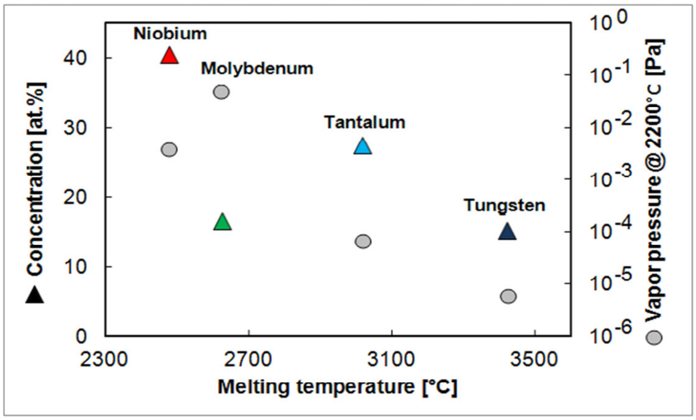

Fig. 5. Average concentrations of the constituent elements in the $Mo_{25}Nb_{25}Ta_{25}W_{25}$ [at.%] HEA deposited by multi-track welding as a function of melting point and vapor pressure. In general, concentration decreases with increasing melting point. Only molybdenum differs from this trend, but it has a relatively high vapor pressure (Plansee 2015) and it was the only powder with a spherical shape.

4.2. Multi-track welds with modified composition of powder mixture

The composition of the generated multi-track weld discussed above was used as a guide to change the composition of the pre-mixed powder from $Mo_{25}Nb_{25}Ta_{25}W_{25}$ [at.%] to $Mo_{32}Nb_{13}Ta_{19}W_{35}$ [at.%] (sample size ~100 g; $Mo_{21.56\ g}Nb_{8.53\ g}\ Ta_{24.51\ g}W_{45.11\ g}$). Deposition parameters were kept constant, only the z-layer offset was reduced from 60 µm to 40 µm. Results are shown in Figure 7 where both samples were prepared on the same substrate, but for the first sample (Fig. 7a) the deposition was started at a preheating temperature of 500 °C while the second sample (Fig. 7b) was started after preheating to 650 °C. The influence of preheating temperature can be easily seen, not only in the shape of the generated structure but also in the chemical composition. Lower preheating results in a small structure width, which is comparable to that of the single track weld, since the area in which the particles stick to the surface is simply smaller. Additionally, the number of incompletely mixed particles at the sides of the structure is reduced. This is due to the fact that the sides are cleaned during the remelting step, because of a larger laser spot size und higher laser power. From that point of view it would be of interest to reduce the preheating temperature, in order to improve the quality of the structure sides, but this behaviour has to be investigated for larger structures. Presumably, the number of incompletely mixed particles at the lower part of the structure will increase in that case. In addition to the observed geometrical modifications, the chemical composition was improved and approached the desired equimolar composition of the HEA (Fig. 7b). It can be seen that the content of niobium and molybdenum in particular is still too high, but there is also a drift to the equimolar composition from bottom to top. The second sample (Figure 7b) exhibits better geometrical consistency compared to the very first sample (Figure 4), which was the basis for the powder mixture modification, and therefore confirms a comparable deposition temperature history. That is why the chemical composition comes close to the equimolar composition. Thus it is possible to perform *in situ* alloying of elements with a high difference in melting points, but the results also stress the sensitivity to temperature.

In the first experiments, the laser parameters of the deposition step were selected based on deposition efficiency, low evaporation rate and process chamber pollution, but an additional series of experiments showed the influence on composition. Figure 6 illustrates the variation of concentration with pulse power. Pulse frequency was set to provide the maximum average power allowed by the laser system. Further parameters were kept constant as given in Table 3 and the chemical composition was averaged over the cross section. The results show the higher concentration of low melting point elements at lower pulse power.

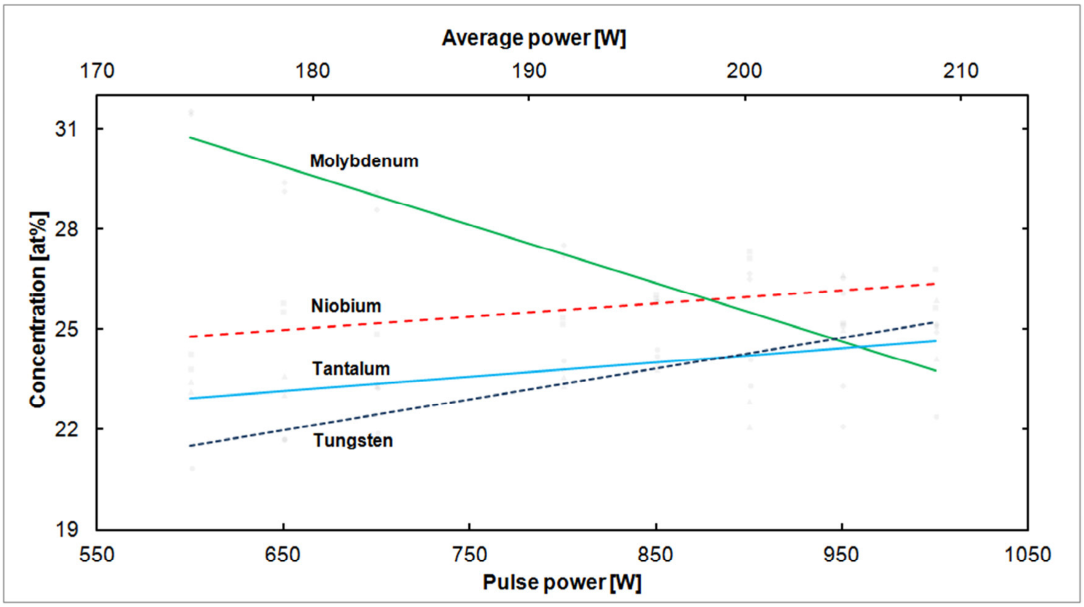

Fig. 6. Elemental concentrations in multi-track welds (modified powder mixture) as a function of pulse power. Pulse length was kept constant and pulse frequency was fixed at the maximum value. Resulting average power is shown.

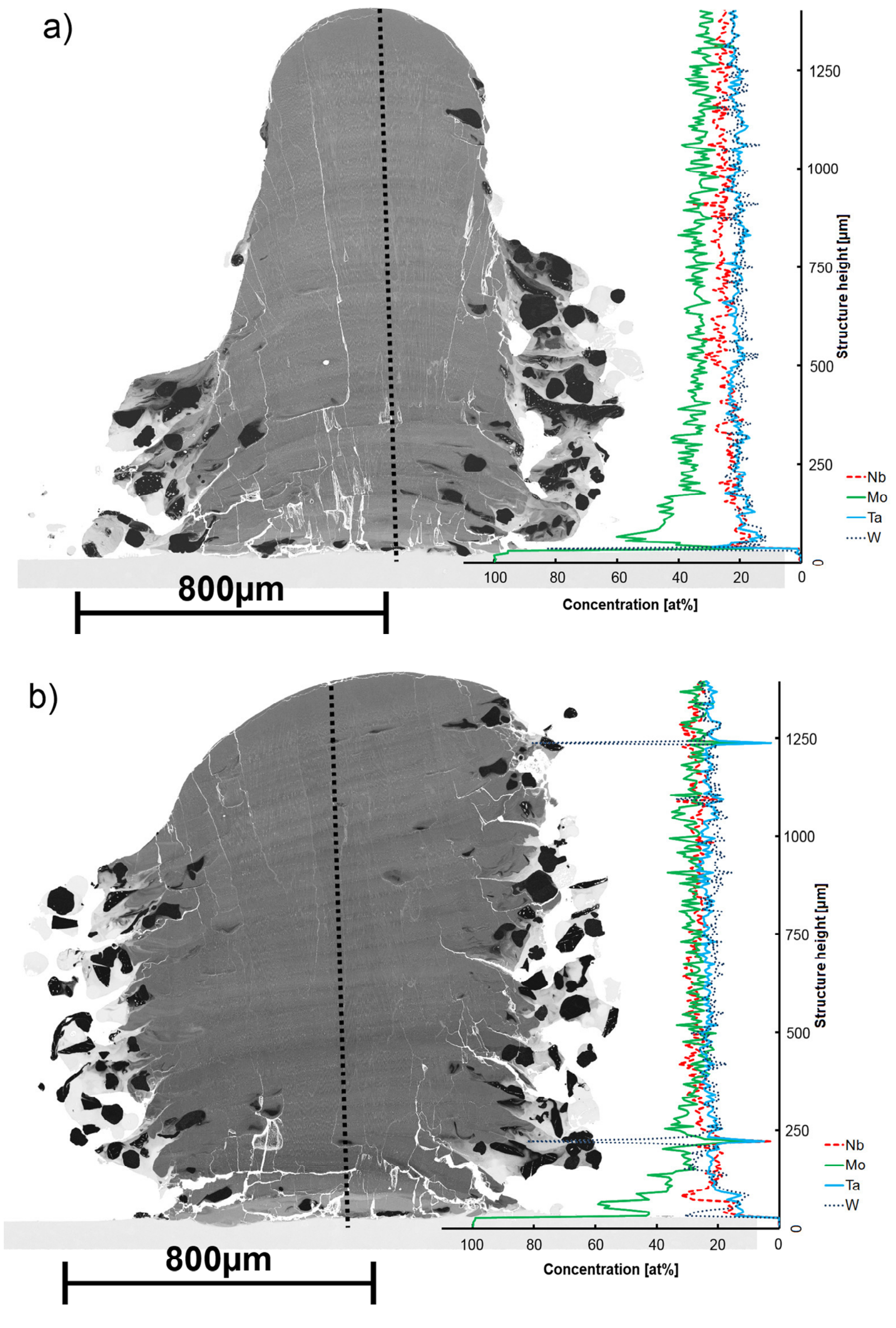

Fig. 7. Multi-track weld of modified $Mo_{32}Nb_{13}Ta_{19}W_{35}$ [at.%] powder mixture on molybdenum substrate. EDX analysis was performed along the dotted line and the resulting compositions are plotted on the right. Negative image of BSE picture shows heavier elements (tungsten, tantalum) darker than light elements (niobium, molybdenum). (a) Substrate was preheated to 500 °C. Structure shows non-equimolar concentrations. (b) Substrate was preheated to around 650 °C. Structure shows near equimolar composition.

5. Conclusion and outlook

Experiments have shown that it is possible to use pre-mixed powder and perform *in situ* alloying, but the generated chemical composition deviates from the starting powder composition. In general, the concentration of an element will be higher the lower its melting point. Using calibrating experiments it is possible to modify the powder composition and produce an equimolar HEA, but the results are very sensitive to laser parameters and in particular to the temperature during the deposition process. Despite the overall high, but also different, melting points of different refractory metals, DMD can be achieved, but it needs an additional remelting step between the powder deposition steps.

Since all refractory metals are sensitive to oxidation the amount of oxygen inside the purged process chamber has to be further decreased. The temperature of the structure depends on several factors such as preheating, laser parameters, geometries, heat conduction, etc. In order to control the composition in large structures, melt pool size and temperature should be measured and a loop control should be established. The powder focusing of irregular-shape particles is inferior and either spherical particles have to be used or the track width of the remelted zone has to be broadened to ensure a better quality of the sides of the structure. Compositional homogeneity inside the structure depends on remelting efficiency but also on the quality of the powder delivery system. Remelting efficiency could be increased by using longer laser pulses. However, since the laser system was used at power output limit, it could not be tested in this study. Introduction of powder particles during the remelting step should be avoided. Further research should be concentrated on DMD of graded structures. In that way the interface of the substrate and structure could be optimized and mechanical properties of different compositions studied.

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