Development of Oxidation Resistant Refractory High Entropy Alloys for High Temperature Applications: Recent Results and Development Strategy

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Abstract Refractory High Entropy Alloys (HEAs) can be considered as promising materials for high temperature applications because of their high melting point and outstanding high temperature strength. The microstructure of the equimolar alloy Nb-Mo-Cr-Ti-Al consists of a disordered body centered cubic (BCC) phase and a small amount of the Laves phase, while the equimolar alloy Ta-Mo-Cr-Ti-Al exhibits the ordered B2 and several Laves phases in addition to the BCC phase. The experimental studies reveal that these alloys possess a beneficial combination of

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high temperature strength and corrosion protectiveness. The compressive yield stress of the alloy Nb-Mo-Cr-Ti-Al and Ta-Mo-Cr-Ti-Al at 1200 °C is determined to 100 MPa and 200 MPa, respectively. The oxidation resistance of the alloy Ta-Mo-Cr-Ti-Al in the temperature range between 900 and 1100 °C is comparable to that of multi-phase Ni-based alloys. The main drawback of both alloys is their low ductility at room temperature. Strategies for the future alloy development are discussed.

Keywords High entropy alloys • Refractory metals • Microstructure
Mechanical properties • Oxidation resistance

Introduction

The development of high entropy alloys (HEAs) with at least 5 components based on refractory elements has been motivated by high temperature structural applications, particularly aerospace applications. Research on these alloy systems has been mainly driven by Senkov and co-workers [1, 2]. The main incentive has been to develop new materials exhibiting outstanding combination of properties such as high temperature strength, fracture toughness, ductility at room temperature (RT) as well as fatigue and oxidation resistance. Fervent research activities conducted in the field of HEAs during recent years indeed show substantial potential to exceed the service temperature and/or strength of Ni-based superalloys.

Two refractory HEAs, Mo-Nb-Ta-W and Mo-Nb-Ta-V-W, show exceptionally high values of strength that retain reasonable up to around 1700 °C [1]. The compressive yield strength of the alloy Mo-Nb-Ta-V-W, for example, has been determined to 842 MPa at 1000 °C, while the superalloy MAR-M 247® yields a value of only about 350 MPa at the same temperature and applied strain rate [1]. Both refractory HEAs alloys possess a single phase BCC crystal structure. Unfortunately, these materials show a brittle to ductile transition temperature of around 600 °C and their densities are rather high, 12.36 and 13.75 g/cm^3 for the alloys Mo-Nb-Ta-W and Mo-Nb-Ta-V-W, respectively [1]. Thus, in the next series of alloy development, the heavy elements W, Mo and Ta were substituted by the lighter Ti, Hf, and Zr [3]. Though these alloys, retaining still the single BCC phase, became significantly lighter and more ductile, their high temperature strength also decayed substantially. For example, the alloy Hf-Nb-Ta Ti-Zr exhibited a yield strength of only 295 MPa at 1000 °C [3]. Remarkable ductility in compression ($\varepsilon > 50\%$) and even RT tensile ductility values ($\varepsilon \sim 9.7\%$) were detected for the alloy Hf-Nb-Ta Ti-Zr [4]. The addition of Cr to these refractory HEAs with reduced density positively increases the yield strength, being e.g. 546 MPa for the alloy Cr-$Mo_{0.5}$-Nb-$Ta_{0.5}$-Ti-Zr at 1000 °C, however, this was accompanied with a simultaneous loss of ductility [5]. These converse effects of the Cr additions on strength/ductility were attributed by the authors to the formation of the Laves phase that is expected from the thermodynamic point of view [6, 7]. Several studies have clearly proven that the Laves phase is inherently brittle at lower temperatures [8, 9]. In a very recent study, Senkov et al. investigated the microstructure and mechanical properties of the alloy Al-$Mo_{0.5}$-Nb-$Ta_{0.5}$-Ti-Zr [10]. This alloy consists of a nano-scale two-phase microstructure of disordered BCC and coherent, ordered B2 phase. The alloy has an exceptionally high yield strength being superior to the strength of Ni-based superalloys over the whole temperature range from 20 to 1200 °C. It was concluded that the two-phase BCC/B2 nano-structure of the alloy is responsible for its high strength [10]. Furthermore, this alloy possesses sufficient RT ductility in compression ($\varepsilon \sim 10\%$) [11]. Though RT tensile ductility data are completely missing up to date, this alloy represents the first refractory HEA that exhibits simultaneously high strength up to high temperatures and reasonable ductility at RT.

Based on above literature survey, it can be stated that tensile ductility at ambient temperatures of refractory HEAs seems to be the critical challenge rather than sufficient high temperature strength. Low ductility and damage tolerance at RT as well as poor oxidation resistance are well-known shortcomings of refractory metals and their solid solutions in general [12]. It seems therefore a reasonable strategy to search the available literature for potentially ductilizing elements that enhance the RT ductility of refractory elements and refractory metal-based alloys. A first remarkable effect of Re addition on mechanical properties of Mo and W was presented at the Second Plansee Seminar in 1955 already. Geach and Hughes reported that Mo alloyed with 35 at.% Re could be directly cold-rolled in the as-cast condition to reductions of 90% without cracking. The authors explained this behavior by the fact that (coarse) twinning substantially contributed to the overall amount of deformation [13]. Later, Jaffe et al. investigated the effect of Re on the mechanical properties of Mo at room and elevated temperatures. They found that up to 20 at.% Re increased the strength but decreased the (tensile) ductility, while higher Re concentration up to 35 at.% increase both, the tensile strength and the ductility of the alloy at RT [14]. Leichtfried et al. investigated in the most recent study the mechanical properties of powder-metallurgically processed binary Mo-Re-alloys ranging from 5 to 47.5 wt% and concluded that the mechanical properties as determined by impact and low-temperature bend testing were improved essentially in a monotonic way with increasing Re concentration [15].

Similar findings can be stated for the effect of Re in W-based alloys [16]. Klopp et al. found that the W-Re-alloys with high Re contents (Re addition up to 25.6 at.%), which deform initially by twinning, were only slightly more ductile than the dilute alloys (up to 9.05 at.%) which deform entirely by dislocation slip [16]. It should however be noted that the alloy chemistry, in particular the purity, and the microstructure, e.g. the grain size, also have an important impact on alloy ductility [16]. Further, the mechanical properties of Cr have been found to be affected extremely sensitively by Re additions. Generally, Re additions induce solid-solution strengthening of Cr involving a significant increase in the ductile-brittle transition temperature at Re concentrations up to about 10 at.%. This was followed, though, by a dramatic decrease of the ductile-brittle transition temperature at higher Re concentrations [17].

In this paper, the most relevant experimental results on microstructure, mechanical properties and high temperature oxidation behavior of the alloys Nb-Mo-Cr-Ti-Al and Ta-Mo-Cr-Ti-Al will be summarized and discussed in terms of their perspectives and shortcomings. Based on the current experimental observations, the strategy for the future alloy development will be presented.

Experimental Procedures

The alloys Nb-Mo-Cr-Ti-Al and Ta-Mo-Cr-Ti-Al were produced from elemental bulk materials by arc-melting in ~0.6 atm of argon (arc-melter AM 0.5 by Edmund Bühler GmbH). The purities of the starting materials Ta, Mo, Nb, Al were all 99.9%, whereas Cr and Ti had a purity of 99% and 99.8%, respectively. In the alloys, nitrogen impurities were found to be below the detection limit of 5 10 wt. ppm, oxygen content was measured being between 50 and 100 wt. ppm. The prepared buttons were flipped over and remelted more than five times in a water-chilled copper mold to facilitate alloy homogenization. The analysis of nitrogen and oxygen impurities was carried out after the remelting. The alloy microstructure was analyzed by means of a dual beam system Scanning Electron Microscope and Focused Ion Beam (SEM/FIB) of type FEI Helios Nanolab 600 as well a Zeiss Auriga. X-ray diffraction (XRD) measurements were carried out using the X'Pert Pro MPD diffractometer operating in Bragg-Brentano geometry. In order to characterize the microstructures of the alloy Ta-Mo-Cr-Ti-Al, an aberration-corrected (image) transmission electron microscopy (TEM) FEI Titan 80 300 (FEI, Eindhoven) operated at 300 kV and equipped with field emission gun and a Gatan Ultrascan CCD camera (Gatan Inc., Pleasanton, CA) was employed. Quasistatic compression tests were performed at an initial engineering strain rate of 10^{-3} s^{-1} utilizing a Zwick Z100 electromechanical universal testing machine equipped with a vacuum furnace by Maytec. The details of the compression test performance are given in Ref. [18]. Oxidation experiments were carried out in static laboratory air in the temperature range between 900 and 1100 °C. Detailed sample preparation procedures as well as detailed description of oxidation tests can be found elsewhere [19].

Experimental Results: Microstructure, Mechanical Properties and Oxidation Behavior of the Alloy System X-Mo-Cr-Ti-Al (X = Nb, Ta)

A new equimolar alloy system X-Mo-Cr-Ti-Al (X = Nb, Ta) has been proposed as a promising HEA candidate for applications at high temperatures. The alloys should possess the following property combination: (i) a melting point exceeding those of

Ni-based superalloys by at least 200 K, (ii) superior long-term high temperature strength, (iii) oxidation protectiveness at temperatures of at least 1100 °C, and (iv) a density of less than 9 g/cm^3. With respect to the first and second requirements, it seems reasonable that Mo, Nb and Ta can be considered as prime candidates for the new alloy system. Unfortunately, all these refractory elements show a very poor high temperature oxidation resistance, being prone to so-called catastrophic oxidation due to the formation of volatile or solid, non-protective oxides [20]. In order to potentially enable the formation of a protective oxide scale on the metallic surface and, consequently, to ensure the alloy protectiveness, Al and Cr have been added to refractory elements. Both elements, Al and Cr, are essential in promoting the formation of an alumina layer that maintains its protective properties also at temperatures above 1000 °C [21]. In terms of high temperature oxidation, Cr effectively supports the formation of a continuous alumina scale in many alumina-former high temperature alloys [21]. The high density, which is typical of most refractory metals, is undesirable for many practical applications. In order to reduce the density of the new alloy system, Ti has also been added (besides the already mentioned Al).

Figures 1a, b show the microstructures of the alloys Nb-Mo-Cr-Ti-Al and Ta-Mo-Cr-Ti-Al after heat treatment at 1300 °C for 20 h. Experimental results reveal that the alloy Nb-Mo-Cr-Ti-Al after heat treatment (designated as 0 h in Fig. 2a) consists of a disordered BCC-matrix, and a small amount of the Laves-phase Cr_2Nb (C14, hexagonal, <0.5% by volume) located predominantly at grain boundaries (see Fig. 1a). A subsequent heat treatment at 1000 °C for 24 and 72 h leads to the formation of an additional (minor) intermetallic phase $Al(Mo, Nb)_3$ (A15, cubic), see XRD pattern in Fig. 2a designated as 24 and 72 h. Instead, the alloy Ta-Mo-Cr-Ti-Al seems to consist of a phase mixture of a BCC-matrix and its ordered B2-counterpart after heat treatment at 1300 °C for 20 h. However, three Laves-phases, C14, C15 and C36, were also identified (see Fig. 1b and XRD pattern designated as 0 h in Fig. 2b). A subsequent heat treatment of the alloy Ta-Mo-Cr-Ti-Al at 1000 °C does not cause formation of any new phases (XRD, cf. the patterns designated as 24 and 72 h in Fig. 2b). Heat treatment of the alloy Ta-Mo-Cr-Ti-Al performed at 1500 °C reveals, in contrast, only a negligibly small amount of Laves phase precipitated at grain boundaries whereas the grain interior showed no phase contrast (see Fig. 1c).

In order to identify which phases form in the matrix of the alloy Ta-Mo-Cr-Ti-Al at 1500 °C for 20 h, TEM analysis was carried out. Obviously, the heat treatment at 1500 °C amplifies the formation of the ordered B2 phase which seems to precipitate at nano-scale in the BCC matrix, see the respective TEM diffraction pattern (left) and dark field micrograph (right) in Fig. 3. The sample was prepared by FIB subsequent to orientation determination by electron backscatter diffraction (EBSD) in order to adjust a [110] zone axis. B2 super lattice reflections can be easily recognized additional spots at higher reflection orders are attributed to the Pt protection layer which was deposited prior to the FIB lift-out. Dark field imaging using one of the super lattice reflections, namely (300), reveals spatial irregularities of the ordering. Quantitative analysis of these irregularities is yet difficult to be

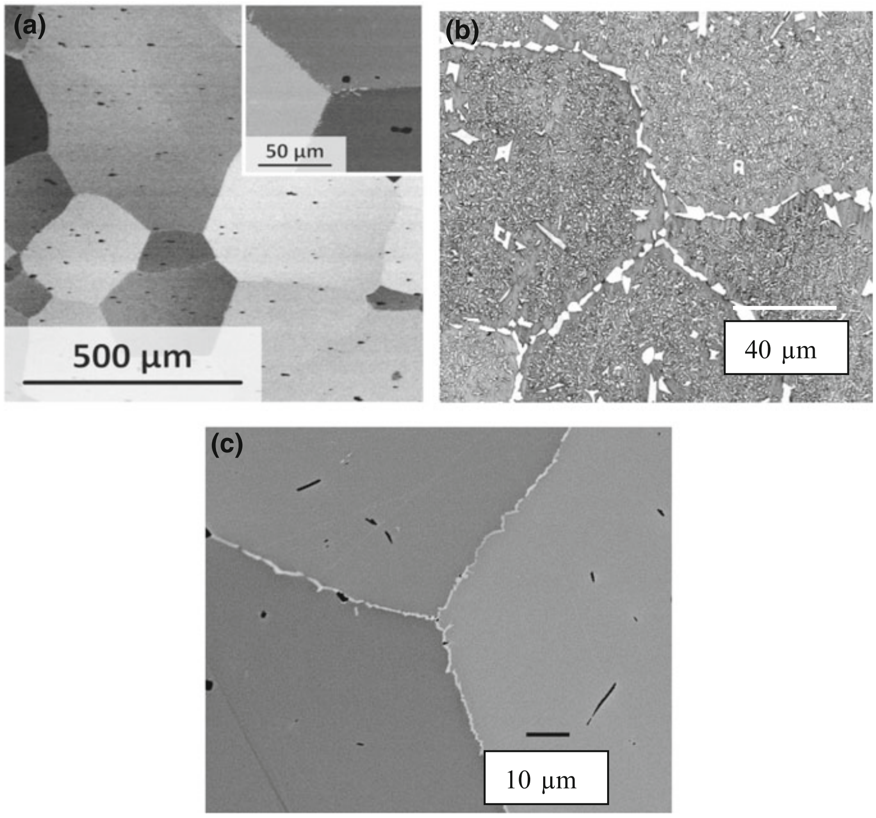

Fig. 1 BSE image of the microstructure of the refractory HEAs, **a** Nb Mo Cr Ti Al after heat treatment at 1300 °C for 20 h [18], **b** Ta Mo Cr Ti Al (heat treatment at 1300 °C for 20 h) and **c** Ta Mo Cr Ti Al (heat treatment at 1500 °C for 20 h)

performed due to massive internal stress and distortion of the TEM lamella, but the micrograph is clearly indicative for a large amount of nano-scaled B2 phase inherent in the microstructure.

In order to evaluate the potential of the alloys Nb-Mo-Cr-Ti-Al and Ta-Mo-Cr-Ti-Al regarding mechanical properties at temperatures ranging from RT to 1200 °C, compression tests were performed on bulk samples at a strain rate of 10^{-3} s^{-1}. At room temperature, linear elastic behavior without significant plastic deformation was observed for the alloy Nb-Mo-Cr-Ti-Al. In order to clarify whether the matrix, i.e. BCC-phase in the alloy Nb-Mo-Cr-Ti-Al, yields inherently brittle behavior, nanoindentation measurements were carried out at room and elevated temperature. Figures 4a, b show exemplarily SEM-micrographs of a hardness indentation conducted on the BCC-matrix at RT, but essentially the same behavior was also observed for temperatures up to 400 °C. Obviously, the BCC-matrix develops no cracks on indentation independent of the grain orientation which was

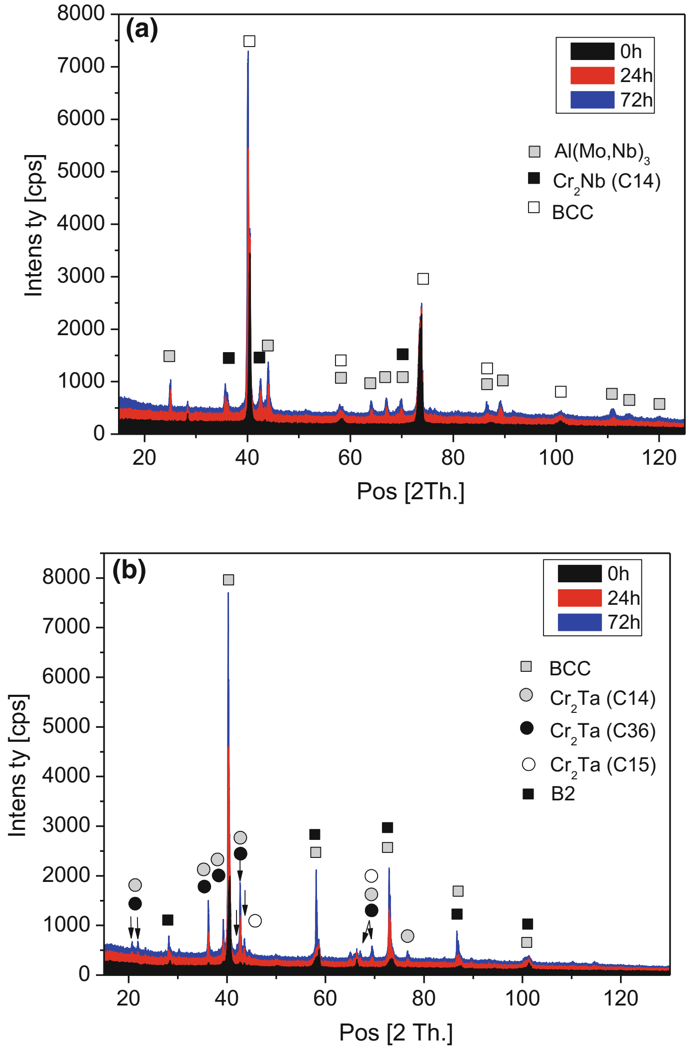

Fig. 2 XRD patterns of the HEAs Nb Mo Cr Ti Al and Ta Mo Cr Ti Al after heat treatment at 1300 °C for 20 h (designated as 0 h) and additional heat treatment at 1000 °C for 24 and 72 h (designated as 24 and 72 h); **a** Nb Mo Cr Ti Al and **b** Ta Mo Cr Ti Al

probed. Rather, pronounced slip bands are clearly visible near the indent suggesting a potentially ductile dislocation mediated plastic deformation of the BCC-matrix. It is, thus, more likely that the brittle behavior of the bulk samples can be attributed to the presence of the $Al(Nb, Mo)_3$ and Laves-phase at the grain boundaries. Figure 4c shows the compressive stress-strain diagram for the alloy Nb-Mo-Cr-Ti-Al at 800, 1000 and 1200 °C. First indications of plastic deformation were noted for the alloy Nb-Mo-Cr-Ti-Al at 400 °C (not shown here). At 800 °C, yield stress of 980 MPa

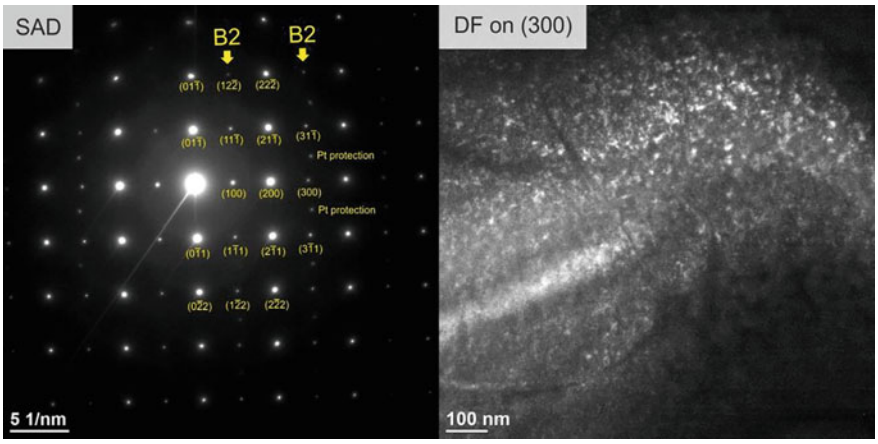

Fig. 3 TEM diffraction pattern and dark field micrograph of the alloy Ta Mo Cr Ti Al after annealing at 1500 °C for 20 h

was detected and significant plastic deformability with a clear indication of strain hardening was observed before eventual failure at around 13%. At even higher temperatures, dislocation-driven plasticity without indication of internal cracking was reached; at 1200 °C the yield stress drops to 100 MPa [18]. Generally, yield stresses are found to be lower as compared to Senkov's Al-containing HEAs [10]. As discussed above, the combination of BCC/B2-phases building a coherent or semi-coherent nano-scale microstructure shows promise for a higher strength at elevated temperatures [10]. Hence, the alloy Ta-Mo-Cr-Ti-Al in the condition after a heat treatment after 1500 °C for 20 h (see Figs. 1c and 3) may be considered as a proof of concept with a yield stress value of nearly 200 MPa at 1200 °C (not shown here). Even at 1400 °C, the alloy Ta-Mo-Cr-Ti-Al shows notable yield stress of 70 MPa. At RT, the alloy Ta-Mo-Cr-Ti-Al exhibits, however, brittle behavior.

In general, alloys containing a relatively high amount of refractory metals possess poor oxidation resistance as elements such as Mo, Nb or Ta tend to form volatile oxides often causing a fast disintegration of the alloy [20]. The results on the oxidation resistance of the alloy Nb-Mo-Cr-Ti-Al at high temperature have been published in [19, 22]. The alloy oxidizes according to the linear rate law, however, the oxidation rates are rather low. For example, after 48 h of oxidation at 1100 °C, a mass gain of only 8 mg/cm^2 was measured. A discontinuous alumina layer was detected on the alloy substrate. The addition of minor amounts of Si seems to improve the oxidation resistance of the alloy by further lowering the oxidation rates and by supporting the formation of a continuous protective alumina scale [19].

Figure 5a shows thermogravimetric curves of the alloy Ta-Mo-Cr-Ti-Al during exposure to air at high temperatures. Obviously, this alloy oxidizes according to the parabolic rate law indicating the formation of a fully protective oxide layer. This is

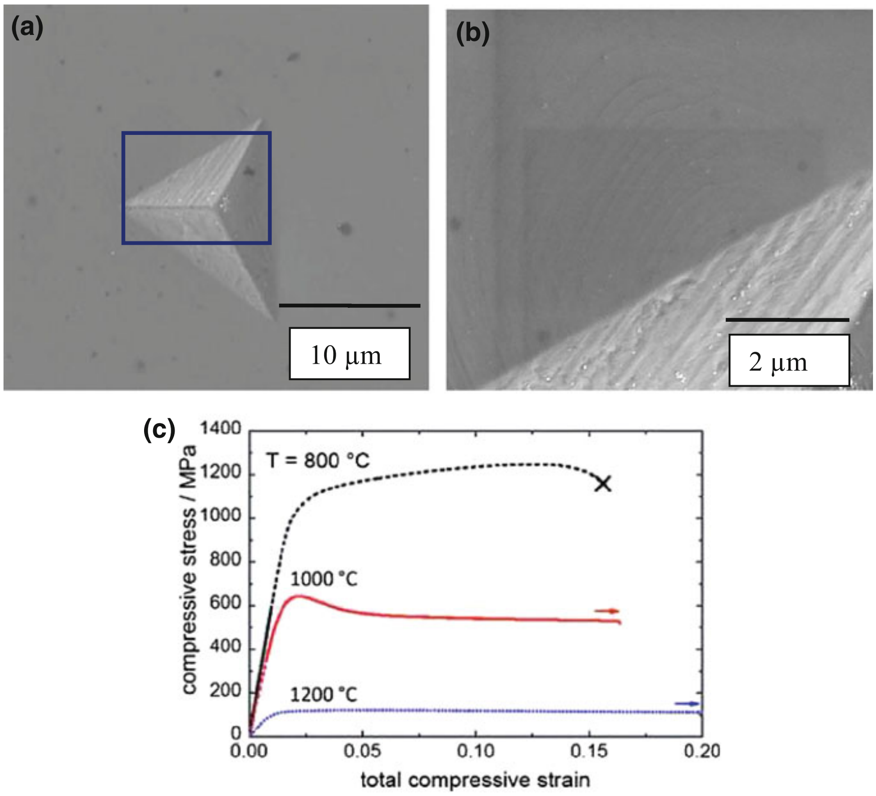

Fig. 4 **a** Hardness indentation in the BCC matrix of the alloy Nb Mo Cr Ti Al at RT, **b** Enlarged view of the box shown in **a**, **c** stress strain dependence of quasistatic compression tests with a strain rate of 10^{-3} s^{-1} of the alloy Nb Mo Cr Ti Al at 800, 1000 and 1200 °C [18]. Fracture is highlighted by "X". Arrows indicate tests deliberately stopped (without failure)

because underneath coarse particles of rutile, a thin and continuous alumina scale (see Fig. 5b) was observed. Despite the high amount of refractory metals, the alloy Ta-Mo-Cr-Ti-Al exhibits oxidation rates that are comparable to those of Ni-based alloys (see Fig. 5c) [23]. The very good oxidation resistance of the alloy Ta-Mo-Cr-Ti-Al can apparently be attributed to the presence of both elements Cr and Al.

Development Strategy

The relevant properties of two refractory equimolar HEAs, Nb-Mo-Cr-Ti-Al and Ta-Mo-Cr-Ti-Al, have been screened and it can be concluded that these materials show substantial potential for high temperature applications. The first preliminary

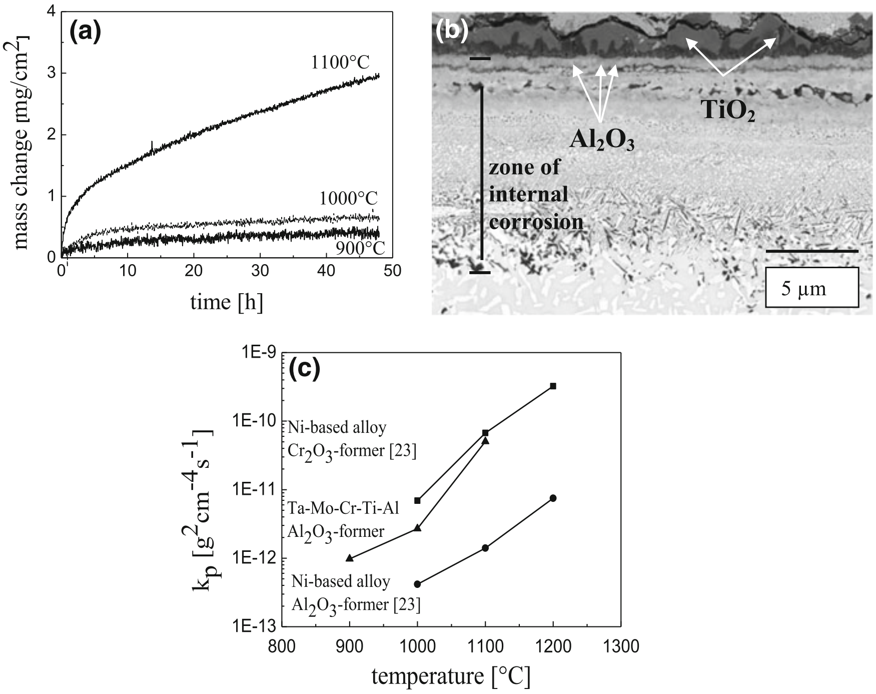

Fig. 5 Oxidation behavior of the alloy Ta Mo Cr Ti Al in air at high temperatures; **a** Thermo gravimetric curves, **b** Cross section after 48 h oxidation at 1000 °C and **c** Oxidation constants of the alloy Ta Mo Cr Ti Al compared to those of Ni base alloys after [23]

results on the mechanical properties of the alloys at room and elevated temperatures show potentials with respect to the high temperature strength, while the low-temperature ductility should be significantly improved. In terms of high temperature oxidation behavior, both refractory metal-based alloys, Nb-Mo-Cr-Ti-Al and Ta-Mo-Cr-Ti-Al, exhibit good to even excellent oxidation resistance. The prime aim of the further alloy development is the successive improvement of mechanical properties of these alloys. The alloy development will be particularly focused on the improvement of low-temperature ductility and high temperature strength while keeping the oxidation resistance on the level already established for the Ta-system (Fig. 5). To improve mechanical properties, three strategies will be pursued in three subsequent steps: (i) the formation of the inherently brittle phases should be suppressed, (ii) a two-phase microstructure with a substantial amount of the second strengthening phase should be established and (iii) the alloy matrix should provide sufficient intrinsic RT ductility.

The first approach primarily aims at the increase of the alloy's intrinsic ductility. This goal will be realized by suppressing the formation of the Laves-phase. Starting from the equimolar alloy composition, the chromium concentration will be progressively reduced related to the concentration of other elements. As mentioned above, to eliminate Cr entirely seems to be not reasonable because Cr facilitates the formation of the protective alumina scale. The aim is, therefore, to find a suitable balance in the Cr concentration which ensures that Laves-phase will not form on the one hand and the formation of the alumina scale is still possible on the other hand.

The second strategy focuses on an enhancement of the high temperature strength to achieve the level of other refractory HEAs exhibiting two-phase microstructures [10]. Following this approach, the formation of BCC and B2 two-phase microstructure with (preferentially) coherent phase boundaries will be aimed. As shown above, BCC is the major phase in the alloy Nb-Mo-Cr-Ti-Al, while the alloy Ta-Mo-Cr-Ti-Al contains a significant amount of the B2 phase. Through varying the Nb/Ta ratio in a new alloy series Nb-Ta-Mo-Cr-Ti-Al, the formation of both, BCC and B2 phases, is to be expected. Due to different Nb/Ta ratios, the fraction of the B2 phase should be controlled.

The third concept aims at further ductilizing the alloy matrix, i.e. the BCC phase, at RT. This will be done by Re addition. The positive impact of Re on ductility of refractory elements was confirmed for several alloy systems as discussed in *Introduction*. To explore the effect of Re on alloy ductility fundamentally, we will start with alloys Nb-Mo-Cr-Ti-Al and Ta-Mo-Cr-Ti-Al with decreased Cr concentrations, i.e. without Laves phases. Initially, the Re-concentration will be set equal to those of Nb/Ta, Mo, Ti and Al and then gradually decreased to identify the minimal Re-content required to reasonably improve the RT ductility.

In order to establish the fundamental understanding of the alloy behavior, the main attention in our future investigations will be paid on the establishment of the correlation between the alloy chemical composition and its microstructure as well as between the alloy composition/microstructure and its mechanical properties.

Summary

Based on recent experimental results, the following conclusions can be drawn in terms of a potential use of the alloy system X-Mo-Cr-Ti-Al (X = Nb, Ta) for high temperature structural applications:

- The microstructure of the alloy Nb-Mo-Cr-Ti-Al consists of a disordered BCC-matrix, and a small amount of minor phases, Cr_2Nb (C14, hexagonal) and $Al(Mo, Nb)_3$ (A15, cubic). The alloy Ta-Mo-Cr-Ti-Al consists of a mixture of BCC phase, the ordered B2 phase and three Laves-phases.
- The mechanical properties of the alloys Nb-Mo-Cr-Ti-Al and Ta-Mo-Cr-Ti-Al show perspectives, however, they should be significantly improved to satisfy requirements of high temperature applications. In particular, the alloys show reasonable values of high temperature strength, while the low-temperature ductility has to be enhanced significantly. It seems that the Laves-phase(s) contribute(s) to the unacceptable brittleness of the alloys at low-temperatures;

the B2-phase may have, in contrary, a positive effect on high temperature strength.

- Both alloys, Ta-Mo-Cr-Ti-Al in particular, show a surprisingly high level of oxidation resistance at high temperatures due to the formation of a protective alumina scale.

To improve the RT ductiliy, following strategies will be pursued: (i) the formation of the brittle Laves phase will be suppressed by lowering the Cr concentration, (ii) a two-phase microstructure with the second strengthening phase B2 should be established and (iii) a sufficient ductility at room temperature will be provided by addition of potentially ductilizing elements such as Re.

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