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Paper Title: Super tensile ductility in an as-cast TiVNbTa refractory high-entropy alloy
Content :

Introduction

Owing to the fast development of advanced industrial equipment in various fields, structural materials with more and more excellent mechanical properties are in high demand. In the past decade, a great deal of efforts was devoted to achieving advanced alloys with high strength and plasticity. For instance, one of excellent approaches for achieving high performance steels is the microstructure design via regulating processing parameters based on thermodynamics and kinetics in phase transformation and the criterion of generalized stability [1,2]. In recent years, high-entropy alloy (HEA), a new concept in alloy design and development, has opened up new design paths for advanced materials [3]. Among HEAs, alloys constituted with refractory metal elements like Mo, Ti, V, Nb, Hf, Ta, Cr, W, etc., are called refractory high-entropy alloys (RHEAs) [[4], [5], [6], [7], [8]]. RHEAs usually have high melting points and body-centered cubic (BCC) structure, displaying excellent hardness and strength at room temperature (RT) and high strength and ductility at high temperatures [[9], [10], [11]]. Besides the promising mechanical properties, some RHEAs also exhibit good storage capacity of H and He, and high resistance to radiation damage [12,13], thus RHEAs are expected to show broad application prospects in high-temperature structural components in nuclear industry, aerospace and other fields [14].

Senkov et al. [15] first reported single-phase BCC NbMoTaW and VNbMoTaW RHEAs, which exhibit good phase stability up to 1400 °C, and also good high temperature strength. At 1600 °C, the yield strengths of NbMoTaW and VNbMoTaW are 405 MPa and 477 MPa, respectively, suggesting very good resistance to high-temperature softening. However, the two alloys are relatively brittle at RT. The compressive plasticity is less than 10 % [15,16]. Later, a ductile HfNbTaTiZr RHEA with single-phase BCC structure was developed [17]. Despite a decrease in yield strength, the RT compression plasticity exceeds 50 %, which significantly distinguishes it from the common brittle RHEAs. The successful development of HfNbTaTiZr provides ideas for the design of high temperature alloys with good RT mechanical properties.

Nonetheless, the vast majority of current REHA related researches are limited to compression properties, which usually cannot accurately reveal the fracture mechanisms under opening tensile loading, one of the most dangerous loading modes in engineering components [[18], [19], [20]]. The lack of studies on tensile properties is mainly due to the poor RT tensile plasticity of many RHEAs. Equiatomic TiVNbTa is one of the few single-phase BCC RHEAs with both excellent high-temperature strength and compressive ductility. Lee et al. performed the high-temperature compression tests and found that the TiVNbTa alloy displayed a high yield strength of 595 MPa at 900 °C [21], which demonstrates this alloy has great potentials for applications at high temperatures. However, the tensile properties of TiVNbTa RHEA have not received enough attentions, especially the deformation and fracture behaviors under tensile stress state, which is critical to the future structural applications as well as the processing of the material [22,23]. It is known that the plasticity of the material has a decisive influence on its molding ability and processing costs. Zhang et al. reported that the kink band deformation allows the $Hf_{15}Nb_{40}Ta_{25}Ti_{15}Zr_5$ alloy to be cold-rolled at RT by 91 % without cracking, which opens up new possibilities for room-temperature macro-plastic processing of RHEA [24]. Therefore, the development of RHEA with large plastic deformation capacity is of great engineering importance. In this work, we fabricated a super ductile TiVNbTa RHEA with large tensile ductility using a vacuum levitation melting (VLM) method. The deformation and fracture behaviors under tension at RT were also studied. The findings are of significance to reveal the great ductility potentials in RHEAs and may provide some insights for designing RHEAs with good RT ductility.

Results and discussion

The results of microstructure characterization of the as-cast VLM TiVNbTa are shown in Fig. 1. The SEM back scattered electron (BSE) image of the alloy displays a dendritic structure. Grain boundaries (GBs) were also observed in Fig. 1(a) and the enlarged figures of some regions in Fig. 1(b)–(d) suggested that the dendrite grew across the GBs. The EDS point scanning indicated that the dendrites are trace-enriched with the high melting-point (Tm) element Ta, and the interdendrites are trace-enriched with the relatively low Tm elements of Ti and V. The high-Tm Ta-rich material formed at the tip of the dendrite could act as heterogeneous nucleation sites for neighboring grains during solidification process. This causes the growth of dendrite tip in the nascent grains which may inherit some of the growth orientation, leading to the crossing of GBs for dendrites. From the EDS mapping results, the distributions of the four elements is rather uniform, which is better than the previous reported results for as-cast TiVNbTa [25]. The relatively homogeneous composition and microstructure is mainly due to the VLM process and the accompanying electromagnetic stirring treatment, in which the molten liquid alloy is thoroughly mixed to prepare alloys of uniform and accurate composition. Moreover, during the VLM process, the melt was not in contact with the crucible, thus the ingot is free from contaminations, resulting in minimized casting defects, which is obviously conducive to the improvement of performance. From the EBSD IPF-Z map (Fig. 1(f)), the as-cast VLM TiVNbTa alloy exhibits equiaxed grains with an average size of ~150 μm. The XRD patterns show that the TiVNbTa RHEA has a single-phase BCC structure (a ≈ 3.249 Å) before and after tension and no phase transition was found during plastic deformation process, which is in agreement with other observations of TiVNbTa in literature [25].

The typical tensile engineering stress-strain curves of the as-cast VLM TiVNbTa RHEA at RT are shown in Fig. 2(a). The samples exhibited Young's modulus of 117 GPa, yield strength (σy) of 804 ± 24 MPa, ultimate tensile strength (σuts) of 864 ± 12 MPa, a surprising 12.8 ± 0.6 % uniform elongation and 40.1 ± 2.1 % fracture elongation. These values are quite more superior than the previous study for the alloy with the same composition of TiVNbTa, e.g., the only tensile result reported by Xu et al. [26], who observed a yield strength of 720 MPa and a fracture elongation of only 14 %. Furthermore, it is noted that in Fig. 2(a), the fracture elongation is much larger than the uniform elongation, leading to a post-necking elongation of ~27 %. This high value suggests the sample is difficult to be broken after necking, which is also distinctive from traditional alloys, implying a high fracture resistance. To ensure the observation of super tensile ductility, several samples were tested and the results are similar. As shown in Fig. 2(a), engineering stress-strain curves of three samples were displayed, demonstrating the reproducibility of tensile results. Fig. 2(b) shows the true stress-strain curves and strain-hardening rate curves of the present VLM TiVNbTa alloy. Good strain-hardening ability can be observed; especially, after necking, the strain-hardening rate does not drop very quickly, which is consistent with the large post-necking strain and the slow fracture in the necking region. Besides the tensile tests, uniaxial compression tests were also conducted. The compression results at RT for the as-cast VLM TiVNbTa RHEA are shown in Fig. 2(c)–(d). The representative specimens exhibited compressive yield strength (σcy) of 800 ± 2.5 MPa and large compressive plasticity. The VLM TiVNbTa remained unfractured after compressive strain exceeded 30 %. The true stress-strain curve and strain-hardening rate curve under compression are similar to those under tension, suggesting a similar plastic deformation behavior and mechanism between two loading modes, which is common behavior for traditional ductile metals [27].

Although many RHEA compositions have been developed up to now, most of RHEAs exhibit small plasticity even under compressive loading, and fracture under tension usually occurs before yielding [28]. A few RHEAs display tensile ductility, but their RT tensile strains are limited to 20 % [29]. In the present work, the as-cast VLM TiVNbTa without any treatment exhibited a surprising 12.8 ± 0.6 % uniform elongation and 40.1 ± 2.1 % fracture elongation. The excellent RT elongation of the as-cast alloy indicates that TiVNbTa has brilliant processability and application prospects. Fig. 3 compares the present VLM TiVNBTa RHEA with the other reported RHEAs which exhibit certain tensile ductility [18,22,26,[30], [31], [32], [33], [34], [35], [36], [37], [38], [39], [40], [41], [42], [43], [44], [45], [46], [47], [48], [49]]. The RT tensile yield strength versus fracture elongation of the present TiVNbTa alloy and other RHEAs in the published references is shown in Fig. 3(a). It can be seen that among all the RHEAs with tensile ductility, the present alloy displays a quite high plasticity and also a good yield strength. The only RHEA that possesses the higher elongation is $Ti_{50}Zr_{18}Nb_{15}V_{12}Al_{5}$ [37], which shows a fracture elongation of ~46.7 %, the highest value reported so far. It can be seen that the alloy contains a large amount of Ti element, which may facilitate the large deformability. In this study, the equimolar as-cast TiVNbTa alloy prepared by VLM method has excellent fracture elongation and high strength, and it is expected also that the properties can be further enhanced by microstructure modulation and chemical composition adjustment at later stages.

RHEAs usually exhibit promising properties at elevated temperatures [28], thus are expected to be used as high-temperature structural materials for hot parts of aerospace power systems. In order to save the energy costs, a high demand for low density or high specific strength, is required. Therefore, we plotted the RT specific strength v.s. fracture elongation of the present VLM TiVNbTa and other RHEAs in literature, as shown in Fig. 3(b). The VLM TiVNbTa has a specific strength of 89 MPa g−1 cm3, which is in the middle of the range of Ti and/or Al containing RHEAs.

It is also worth to note that the TiVNbTa RHEA also shows good high-temperature properties. High temperature compression of the VLM TiVNbTa alloy was performed and the engineering stress-strain curve is shown in Fig. 4. It is found that the VLM TiVNbTa as-cast alloy exhibits a yield strength of 330 MPa at 1273 K, a compressive strength of 423 MPa, and a compressive plasticity larger than 30 %, as shown in Fig. 4, while no cracking was observed in the test process. The relatively high yield strength is consistent with the previous studies of TiVNbTa [20,49], in which strength values larger than 590 MPa were reported for testing temperature lower than 1200 K. The high-temperature strength of TiVNbTa is higher than those of conventional Inconel 718 and Haynes 230 superalloys in the temperature range with temperature higher than 800 °C [5]. Combined with the excellent fracture elongation at RT, which could facilitate the plastic forming and the processing of components with complex shapes, TiVNbTa RHEA shows promising potentials as future structural materials in high-temperature industry.

In order to reveal why the VLM TiVNbTa shows such a high ductility, we observed the fracture and deformation morphologies after tensile fracture. As shown in Fig. 5(a), the overall image of the fracture surface demonstrates a huge reduction of the sample cross-section area. By comparison with the undeformed section area, the area reduction ratio of the tensile sample is ~79.3 %. This large value is consistent with the fracture elongation of ~40 % observed from stress-strain curves, confirming the large tensile ductility. A number of dimples were observed on the fracture surface (Fig. 5(b)), while no cleavage planes and cracks were found, suggesting a typical ductile fracture mechanism [27]. Fig. 5(c) is the macroscopic appearance of the sample surface near the fracture position. Considerable plastic flow was happened and significant necking can be observed. Wavy pattern of slip band (slip offset) can be also found on the sample surface, as shown in Fig. 5(d). Usually, two types of slip band pattern on the sample surface are seen: planar pattern and wavy pattern, which are due to the planar glide and wavy glide of dislocation, respectively [50]. When the cross-slip of dislocation behavior is easy and thus popular during plastic deformation, the wavy glide will be dominated and a wavy pattern of slip bands can be seen. Therefore, in the present TiVNbTa alloy, dislocation cross-slip is expected to happen, which could improve the glide ability of dislocation and contribute to the good ductility [8].

We note that the dislocation density within the grains near the fracture surface seems to be not uniform (see Fig. 6(b)–(d)). This may be caused by the ununiform plastic deformation degrees among grains with different orientations. To examine this assumption, nanoindentation test was performed on different grains. EBSD was used to determine the orientation of each grain firstly, and the nanohardness values at 6 × 3 lattice positions were tested, as shown in Fig. 7(a). The resulted map of nanohardness display in Fig. 7(b) and the load-depth curves were plotted in Fig. 7(c). It if found that the nanohardness values of the two differently oriented grains #17 and #18 are 2.61 GPa and 4.55 GPa, respectively, with a relatively huge difference in hardness of 1.94 GPa. It is well known that the critical stress required for the dislocation slipping is highly dependent on the Schmidt factor, which leads to a large effect of grain orientation on plasticity. Orientation mismatch among different grains leads to inevitable differences in the order and degree of plastic deformation in the tension process, which may explain the difference in dislocation density observed by TEM in different grains (Fig. 6). However, this relatively large hardness difference, leading to the ununiform plastic strain distribution, may be harmful for the global plasticity. Therefore, the microstructure or chemical composition of the present alloy can be further modulated in the future. For example, homogenization treatment can lead to a more uniform element distribution and enhanced intrinsic lattice distortion effects, and grain refinement can reduce orientation mismatch and grain boundary stress concentrations, resulting in a significant increase in yield strength and elongation.