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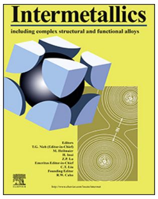

Accelerated oxidation in ductile refractory high-entropy alloys

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ABSTRACT

Refractory high-entropy alloys (RHEAs) are promising candidates for new-generation high temperature materials, but they generally suffer from room temperature brittleness and unsatisfactory high-temperature oxidation resistance. There currently lack efforts to address to these two critical issues for RHEAs at the same time. In this work, the high temperature oxidation resistance of a previously identified ductile $Hf_{0.5}Nb_{0.5}Ta_{0.5}Ti_{1.5}Zr$ RHEA is studied. An accelerated oxidation or more specifically, pesting, in the temperature range of 600–1000 °C is observed for the target RHEA, where the oxidation leads the material to catastrophically disintegrate into powders. The pesting mechanism is studied here, and is attributed to the failure in forming protective oxide scales accompanied by the accelerated internal oxidation. The simultaneous removal of zirconium and hafnium can eliminate the pesting phenomenon in the alloy. It is believed that pesting can also occur to other equiatomic and non-equiatomic quinary Hf-Nb-Ta-Ti-Zr or quaternary Hf-Nb-Ti-Zr and Hf-Ta-Ti-Zr RHEAs, where all currently available ductile RHEAs are identified. Therefore, the results from this work will provide crucial perspectives to the further development of RHEAs as novel high-temperature materials, with balanced room-temperature ductility and high-temperature oxidation resistance.

1. Introduction

Refractory metals and alloys have gained quite some interest due to their potential of becoming ultrahigh temperature materials, which is derived from their higher melting points and the ability to achieve high temperature strength [1,2]. Despite numerous efforts, the use of refractory alloys in high-temperature applications is still limited mainly due to their poor oxidation resistance, which becomes worse with increasing temperature [3,4]. In the past, plenty of work has been done to enhance the oxidation resistance of refractory alloys through alloying additions which include elements such as Al, Cr and Si. These elements can enable the formation of protective oxide layers, i.e., Al_2O_3, Cr_2O_3 and SiO_2, if present in sufficient amounts [5–8]. The addition of oxide forming elements comes with a compromise though, since Al, Cr and Si are chemically active and have very negative heats of formation with other metallic elements, and therefore tend to promote the formation of brittle intermetallic compounds such as Nb_3Al, $NbCr_2$, Nb_5Si_3, and $MoSi_2$, leading to the poor room temperature ductility/toughness [9]. The development of refractory alloys with enhanced oxidation resistance, while at the same time with optimal mechanical properties, has been proved to be a formidable challenge [10]. New alloy design strategies have to be developed, to formulate new alloy systems and to advance the development of novel high-temperature materials. The concept of high-entropy alloys (HEAs), or multi-principal-element alloys, is believed to hold the promise in this regard. HEAs are alloys consisting of four or more metallic elements in equiatomic or near-equiatomic proportions [11–13]. The high configurational entropy in HEAs can help to stabilize the formation of simple solid solution phases while inhibiting the formation of detrimental intermetallic compounds [14–16]. Since their early development, HEAs have been considered as promising candidates for new high-temperature materials, due to their claimed slow diffusion kinetics and softening resistance at elevated temperatures [17–20]. Particularly, refractory HEAs (RHEAs), HEAs that are made of refractory metals, have attracted most attention since

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they already exhibit superior high-temperature performance compared to some commercial nickel-base superalloys at elevated temperatures [21–24].

Nevertheless, there is still a long way to go before RHEAs can be really used for high-temperature applications. Initially, most RHEAs suffered from room-temperature brittleness [21–26], but recent efforts utilizing strategies like electron theory or phase transformation clearly indicate that the ductilization of RHEAs is possible [27–29]. Based on the known facts for refractory alloys, the oxidation resistance could also be problematic for RHEAs, but there exists only limited work towards the study of high-temperature oxidation of RHEAs [30–39]. Furthermore, since the intentional ductilization of RHEAs was made possible only very recently, previous efforts on studying and improving the oxidation resistance of RHEAs basically did not address to the room-temperature ductility at the same time. To name a few examples, $CrMo_{0.5}NbTa_{0.5}TiZr$ was reported to form a protective oxide scale at 1000 °C after 100 h of exposure, but the material lacked room-temperature ductility because of the presence of brittle Laves phase [32,36]; AlCrMoTaTi RHEAs seemed to form a protective and dense alumina scale below the rutile layer after air exposure at 1000 °C for 48 h, with a low mass gain and its oxidation kinetics adhering to the parabolic rate law, but there is no report on its mechanical properties [39]; AlCrMoNbTi, upon alloying with Si, showed some improved oxidation behavior, but its mechanical properties were poor and it showed no evidence of plastic deformation at room temperature [37,38]. In other words, there lacks clear information on the oxidation resistance for ductile RHEAs, which motivates the current work.

Here in this work, we studied the oxidation resistance of a previously developed ductile $Hf_{0.5}Nb_{0.5}Ta_{0.5}Ti_{1.5}Zr$ RHEA with a single-phase bcc structure, having a fracture stress of ~ 1 GPa and an elongation of ~20% [27]. Apparently, $Hf_{0.5}Nb_{0.5}Ta_{0.5}Ti_{1.5}Zr$ does not contain any protective oxide layer forming elements like Al, Cr or Si, therefore, its oxidation resistance at elevated temperature is open to question. However, previous studies showed that a substantial improvement in oxidation resistance for RHEAs can still be expected even without the formation of continuous/protective Al_2O_3, Cr_2O_3 and/or SiO_2 [35]. On the other hand alloying of Al, Cr and Si to RHEAs has the high chance of forming unwanted intermetallic compounds and causing embrittlement in the material [40]. Therefore, it is reasonable to investigate the inherent oxidation behavior of the ductile $Hf_{0.5}Nb_{0.5}Ta_{0.5}Ti_{1.5}Zr$ RHEA, considering the fact that group IV elements Ti, Zr, and Hf have the highest thermodynamic activity towards oxygen, and group V elements Nb and Ta are also subject to strong oxidation at temperatures above 400 °C [41]. More importantly, our preliminary results indicated that the bulk $Hf_{0.5}Nb_{0.5}Ta_{0.5}Ti_{1.5}Zr$ alloy exhibits accelerated oxidation at some particular temperatures, which has not previously been reported for RHEAs [42].[1] The similar behavior is expected to also occur to other currently available RHEAs. It is therefore crucial and timely to provide a clear understanding on the oxidation resistance of ductile RHEAs, revealing the temperature range and underlying mechanism for the accelerated oxidation. The ultimate goal of the current work is certainly to address to the balance of mechanical properties and oxidation resistance for RHEAs, for the optimal development of RHEAs aiming at high-temperature applications, but the focus here is limited to investigating the accelerated oxidation for the ductile $Hf_{0.5}Nb_{0.5}Ta_{0.5}Ti_{1.5}Zr$ alloy.

2. Experimental

Alloy preparation for $Hf_{0.5}Nb_{0.5}Ta_{0.5}Ti_{1.5}Zr$ was carried out using high purity (> 99.9%) elemental metals by arc melting on a water-cooled copper plate, and in a Ti-gettered Ar atmosphere to avoid contamination from any residual oxygen and nitrogen. Arc-melted ingots were flipped and re-melted at least five times to ensure thorough chemical homogeneity. The finally drop-cast ingots had dimensions of 60 mm (length) × 10 mm (width) × 10 mm (thickness). Specimens with dimensions of 5 mm × 10 mm × 10 mm were extracted from the ingots for the isothermal oxidation test, and they were oxidized at 600, 700, 750, 800, 850, 900, 950, 1000 and 1100 °C in air with the exposure time of 1, 2, 3, 4 and 5 h for each temperature, the heating rate being ~10 °C/min. The oxidation of alloys was monitored by the weight change per unit area as a function of time, and by visual observation. Oxidation tests were carried out in a horizontal tube furnace that is opened on both ends and can achieve the maximum working temperature of around 1400 °C. During the oxidation tests, specimens were placed in alumina boats and positioned in the heating zone when the target temperatures were reached, and taken out immediately from the furnace to cool in air when the supposed oxidation tests were completed. One specimen was used for each oxidation test. After each oxidation test, the sample was weighed using an analytical balance with the accuracy of 0.1 mg. It is emphasized that only the bulk specimen was weighed, not including the spalled-off powders, which is different to conventional oxidation studies as we are mainly interested at knowing the severity of powder spallation here. Therefore, essentially we did not do strictly speaking oxidation study in this work. The phase constitution of oxidation products was characterized by X-ray diffraction (XRD, MiniFlex 600, Rigaku) using Cu-K_α radiation. Microstructure and chemical compositions were studied using a LEO Gemini 1550 scanning electron microscope (SEM) equipped with energy dispersive spectrometer (EDS) and Oxford Nordlys electron backscatter diffraction (EBSD) detector. For both XRD and SEM, cross-sections of specimens were subject to mechanical polishing but not etching, and top surfaces were untreated.

3. Results

3.1. Oxidation resistance of ductile RHEAs

Fig. 1 shows the weight change per unit area versus time curves for the RHEA that was oxidized in the temperature range of 600–1100 °C. Two distinctive oxidation responses can be observed. At temperatures from 600 to 1000 °C, the RHEA displays accelerated oxidation evidenced by material gradually disintegrating into powders, while at temperatures higher than 1000 °C, the alloy retains its shape without any noticeable powder formation. For the first case, almost at all temperatures continuous weight loss (again, it is emphasized that only the bulk specimen was weighed, not including the spalled-off powders) is observed, and the spallation from the sample surface continuously exposes fresh surfaces to oxidation and eventually leads the alloy to disintegrate into powders. Similar behavior has been seen in conventional refractory intermetallics such as $NbAl_3$ and $MoSi_2$, where accelerated oxidation leads to total disintegration of the material into powders, and the phenomenon is referred to as *pesting* or *pest disintegration* [43–49]. However, pesting has not been reported for RHEAs previously. Pesting is most severe for the current RHEA oxidized at 800 °C, with a drastic weight change of $-6.022\ mg/mm^2$ after 5 h as showcased in Fig. 1(a), while Fig. 1(b) clearly shows the remaining bulk material and spalled-off powders. Above and below 800 °C, i.e., at 700 and 750 °C, and 850 and 900 °C, pesting is also found but is less severe compared to at 800 °C, seen from Fig. 1(c) for example, on the specimen oxidized at 900 °C for 5 h, where less amount of powders are spalled off from the bulk alloy. Noticeably, the weight changes at 600 and 1000 °C are much less significant compared to those at other temperatures, and there is even an initial positive weight change for oxidation at 600 °C up to 3 h, but further exposure at this temperature results in negative weight change, despite the weight change is at a level of $-0.150\ mg/mm^2$ after 5 h. Although no positive weight change is seen for 1000 °C, the weight

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[1] It is noted that shortly before this work is submitted for publication, Chang et al. published a work on the ductile equiatomic HfNbTaTiZr RHEA, where they also reported the similar phenomenon, i.e., accelerated oxidation, but they did not analyze the mechanism, which is however the focus of the current work.