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Mechanical properties and impact energy release characteristics of Al<sub>0.5</sub>NbZrTi<sub>1.5</sub>Ta<sub>0.8</sub>Ce<sub>0.85</sub> high-entropy alloy

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Abstract

To explore the potential of high-entropy alloys (HEAs) as energetic structural materials (ESMs), Al<sub>0.5</sub>NbZrTi<sub>1.5</sub>Ta<sub>0.8</sub>Ce<sub>0.85</sub> high-entropy alloys were prepared by vacuum arc melting. XRD and TEM indicated the coexistence of BCC and FCC structures. SEM images illustrated element segregation in HEA. HEA exhibited excellent mechanical properties and impact energy release characteristics. When the strain rate increased from 10<sup>−3</sup> s<sup>−1</sup> to 4500 s<sup>−1</sup>, the yield strength increased by 56.2% from 909 MPa to 1420 MPa. Under impact, the threshold of strain rate of HEA was about 1200 s<sup>−1</sup>. Ballistic gun tests were performed to investigate the penetration behaviour and energy release characteristics. Al<sub>0.5</sub>NbZrTi<sub>1.5</sub>Ta<sub>0.8</sub>Ce<sub>0.85</sub> could penetrate 6 mm A3 plate at the speed of 712 m s<sup>−1</sup> and ignite the cotton behind the target, combining excellent mechanical properties and impact energy release characteristics.

1. Introduction

Energetic structural materials (ESMs) are a special category of material that combine mechanical properties and energy release characteristics. ESMs can not only destroy the target through kinetic energy penetration, but also cause secondary damage such as arson, overpressure etc. through energy release reaction [1, 2]. It is of great significance to improve the mechanical properties and energy release characteristics of ESMs for improving the damage effect of fragmentation warhead. Generally, based on the composition, ESMs can be divided into metal-polymer [3, 4], metal-metal oxide [5], metal-metal [6, 7] etc. They can not meet the requirements for limited mechanical properties or energy release characteristics.

There are two methods to design ESMs. One is to improve the mechanical properties of materials with excellent energy release characteristics and the other is to improve the energy release characteristics of materials with excellent mechanical properties. High-entropy alloys provide a solution for their flexibility in composition design. Some explorations have been done on high-entropy alloys in the field of energetic structural materials. Tang [8–10] etc investigated high-entropy alloys based on Al, Hf, Nb, Zr, V, Ti and Ta element systems. By regulating the components and processes, they obtained high-entropy alloys with combinations of different strength and plasticity and pointed out their application as energetic structural materials. Dai’s team analyzed the energy release process and overpressure of two types of high-entropy alloy fragments WFeNiMo [11] and FeNiCoCr [12] in the velocity range of 500–1800 m s<sup>−1</sup> and found that the energy release characteristics of WFeNiMo high-entropy alloy fragments were better than those of tungsten alloy. Tang [13] investigated the mechanical properties of TiZrHfTa<sub>0.7</sub>W<sub>0.3</sub> high-entropy alloys in terms of microstructural evolution and energy release characteristics in terms of chemical composition of the combustion products at different strain rate, indicating that the addition of tungsten could promote combustion.

Based on Nb, Zr, Ti and Ta element, Al was introduced to regulate the intensity and density and Ce was introduced to regulate its energy release characteristics. We investigated the mechanical properties and impact energy release characteristics of Al<sub>0.5</sub>NbZrTi<sub>1.5</sub>Ta<sub>0.8</sub>Ce<sub>0.85</sub> high-entropy alloy using a material testing machine/
split Hopkinson pressure bars and the ballistic gun. Al_{0.5}NbZrTi_{1.5}Ta_{0.8}Ce_{0.85} showed both excellent mechanical properties and energetic characteristics.

2. Materials and methods

2.1. Materials and instruments
Al, Nb, Zr, Ti, Ta particles have a particle size of 3–6 mm and purity over 99.95%, Beijing Yijin New Material Technology Co., Ltd. Ce is a block with purity over 99.95%, Beijing Yijin New Material Technology Co., Ltd.

The following instruments were used: a vacuum arc furnace (WK-II A, Beijing Physicence Opto-electronics Co., Ltd., Beijing, China), an x-ray diffractometer (Bruker D8 Focus, Bruker, Karlsruhe, Germany), a scanning electron microscope (SEM, JEOL JSM 7200F, JEOL Ltd., Tokyo, Japan), a transmission electron microscope (TEM, FEI Tecnai G2 F20, FEI Company, Hillsboro, America), an energy dispersive spectroscopy (EDS, Oxford X-Max, Oxford Instruments, Abingdon, Britain), an universal testing machine (MTS E43.504, Mechanical Testing & Simulation, Minnesota, America), a Split Hopkinson pressure bar (SHPB, ATL1500, Archimedes Industry Technology Co., LTD., Beijing, China), a high-speed camera (Phantom, Vision Resesarch, Inc. New Jersey, America), a 14.5 mm ballistic gun (Nanjing University of Science and Technology, Nanjing, China).

2.2. Preparation of Al_{0.5}NbZrTi_{1.5}Ta_{0.8}Ce_{0.85} high-entropy alloy
Al_{0.5}NbZrTi_{1.5}Ta_{0.8}Ce_{0.85} alloys (abbreviation for HEA) were prepared by vacuum arc furnace. The prepared raw materials were placed in the water-cooled copper crucible in the order of low melting point to high melting point and were melted in a Ti-gettered argon atmosphere to prevent the alloy from being oxidized during the melting process. To achieve a homogeneous distribution of the elements in the alloy, the ingots were flipped and remelted for 12 times. The as-cast alloys were like a button and cut into three different types of cylindrical specimens of Φ3 × 7 mm, Φ5 × 4 mm and Φ10 × 11 mm using a wire cutting method.

2.3. Performance test
Crystal structure of the Al_{0.5}NbZrTi_{1.5}Ta_{0.8}Ce_{0.85} alloy was analyzed by x-ray diffraction using Cu Kα1 target with 2θ between 20°–80° and a scan step of 0.05° min^{-1}. The microstructure was examined by scanning electron microscopy equipped with energy-dispersive detectors. Fine structure observations were conducted by transmission electron microscope equipped with energy-dispersive detectors.

The quasi-static compressive mechanical property at room temperature was tested using a universal testing machine with a specimen size of Φ3 × 7 mm and an initial strain rate of 10^{-3} s^{-1}.

The dynamic compressive mechanical properties at different strain rates were tested using a Split Hopkinson pressure bar with the specimen dimension of Φ5 × 4 mm. A high-speed camera was used to record the progress of compression. Strain, stress and strain rate can be obtained from the following equations:

\[
\sigma = \frac{AE}{A_0} \varepsilon_t
\]
\[
\varepsilon = -\frac{2c_0}{l_0} \int_0^t \varepsilon_rdr
\]
\[
\dot{\varepsilon} = -\frac{2c_0}{l_0} \varepsilon_r
\]

where E is the modulus of elasticity of the rod; c_0 is the wave velocity of the stress wave. A and A_0 are the cross-sectional area of the rod and the specimen; l_0 is the length of the specimen; \varepsilon_t and \varepsilon_r are the strain of the incident rod and transmitted rod.

Ballistic gun tests were used to investigate the penetration behaviour and energy release characteristics of high-entropy alloy. The specimen dimension is Φ10 × 11 mm. During the test, the velocity of fragments was controlled in the range of 600–1000 m s^{-1} by changing the amount of propellant. The target was 6 mm A3 plate with cotton placed behind it. At the same time, a high-speed camera was used to record the penetration and damage process of the fragments.

3. Results and discussion

3.1. Microstructures
As depicted by the XRD pattern (figure 1), there are two sets of diffraction peaks corresponding to body-centered cubic (BCC) and face-centered cubic (FCC) structure in HEA, which could be also confirmed by the diffraction spots in TEM images (figure 3(b)). Figure 2 is the SEM-EDS image of HEA. It could be seen that HEA has a
dendritic morphology. EDS map shows clearly elemental segregation. Al, Nb, Ti and Ta are prone to segregate in intra-dendritic regions. Zr and Ce are prone to segregate in inter-dendritic regions. This phenomenon is a little different from existing research [14]. It is assumed that the addition of cerium could promote the formation of element segregation [15, 16]. TEM images (figure 3) show the presence of three different regions (region I, II and III) with different structures. According to the EDS and SAED results, region I with BCC structure is rich in Al, Nb, Ti, Ta but less in Ce. Region II with FCC phase is rich in Zr and region III is rich in Ce. Interestingly, Zr-rich regions exist in the form of needle (figure 3(a)) and island (figure 3(b)). Ce-rich regions tend to form another phase and exist in the forms of dots (figure 3(c)), corresponding to exiting researches [17, 18].

3.2. Mechanical properties

Compressive engineering stress versus engineering strain curves of HEA at strain rates ranging from $10^{-3}$ s$^{-1}$ to 4500 s$^{-1}$ are shown in figure 4(a). HEA exhibits different characteristics under quasi-static and dynamic conditions. Under quasi-static compression (at the strain rate of $10^{-3}$ s$^{-1}$), the yield stage of HEA is obvious. The yield strength, ultimate compressive strength and fracture strain are 909 MPa, 1259 MPa and 13.6%, respectively. Under dynamic compression, when the strain rate is over 2400 s$^{-1}$, the yield stage is not obvious.
Instead, it is slowly unloaded in the form of strain softening after the stress reached the ultimate compressive strength. HEA exhibits high compressive strength. Because in the alloy, the interaction between atoms with different sizes causes elastic deformation in the lattice. Local stress field hinders the movement of dislocations. Besides, solid solution strengthening effect will also improve the strength of HEA. Figure 4(b) shows the ultimate compressive strength and fracture strain at different strain rates. HEA shows obvious strain-rate effect. When the strain rate increases from $10^{-3}$ s$^{-1}$ to 4500 s$^{-1}$, the yield strength increases by 56.2% from 909 MPa to 1420 MPa and the ultimate compressive strength increases from 1259 MPa to 1594 MPa. The fracture strain decreases by 53% from 13.6% to 6.4%, which indicates the decrease of plasticity and the increase of brittleness under dynamic compression. This can be explained by shear compensation theory [19]. Under quasi-static conditions, the strain rate is low. The alloy is in equilibrium at any time and has sufficient time to form and propagate secondary shear bands. However, at high strain rates, the stress state inside the specimen is not consistent all the time. The stress wave is transmitted along the incident rod, specimen and transmission rod. Due to the high strain rate, deformation will occur on the end impacted by the incident rod. Then the other parts will generate dynamic response. Besides, the alloy does not have enough time to complete shear compensation, resulting in the reduction of secondary shear bands and a significant increase in brittleness.

According to the SEM images of HEA after compressed at 2400 s$^{-1}$ as shown in figure 5, a large amount of cracks appear on the surface of HEA. The cracks are mainly generated at the grain boundary and the interface of different phases. TEM images (figure 6) of HEA after compressed at 2400 s$^{-1}$ show that there are plenty of dislocations at the grain boundary and the interface between the Zr-rich regions and the matrix. The results indicate that the fracture mechanism is intergranular fracture and interphase fracture.

### 3.3. Energetic characteristics

#### 3.3.1. Dynamic compression process

The dynamic compressive progress of HEA at 1200 s$^{-1}$ and 4500 s$^{-1}$ were recorded by a high-speed camera as shown in figure 7. At low strain rate (1200 s$^{-1}$), HEA broke into two main large pieces and several small fragments under impact. Small amount of flame was generated and disappeared quickly. It could be considered that the threshold of strain rate of HEA was about 1200 s$^{-1}$. When the strain rate increased to 4500 s$^{-1}$, HEA broke obviously and reacted violently with the air, releasing bright light. HEA was compressed flat and there was melting trace on its surface. This was caused by the heat generated by the redox reactions between HEA and the oxygen, which made the local temperature reach the melting point of HEA.

Figure 8 shows the XRD pattern of HEA after compressed at 2400 s$^{-1}$ and the peaks of the major oxides produced are indicated. It can be concluded that complex oxidation reaction has taken place on HEA under impact. Under impact, the energy release mechanism of the alloy is the reaction between the active element and HEA.
the oxygen. Redox reaction will occur only when the adiabatic temperature rise generated by the impact reaches the ignition point of the constituent element [20]. Cerium is the most active and is oxidized first, and the heat released promotes the reaction with oxygen of other components in the alloy.

The degree of oxidation is related to the size of the fragment. The more fully the alloy is broken, the more fully the energy release reaction is. For large piece of HEA, the redox reaction only occurs on the surface.
3.3.2. Ballistic performance

To better investigate the penetration behaviour and energy release characteristics, ballistic gun tests were performed. The target was 6 mm A3 plate and cotton was placed behind the target to evaluate the post-target damage effect. As shown in figure 9(a), under impact, HEA fragment broke into pieces and reacted violently with the oxygen, releasing a large amount of energy. At the impact location, flame generated gave off a dazzling light. The target was penetrated and the cotton behind the target was ignited (figure 9(b)) With the increase of speed, HEA fragment broke more fully and more energy was released.

As shown in figures 9(c) and (d), there were holes in the plate. Around the holes, we can see melting trace, indicating a large amount of energy was released and the rise of temperature exceeded the melting point of A3 plate. On the back of the target, a rolled edge occurs around the hole. It is supposed to be caused by the overpressure generated by the deflagration reaction of the fragment, which makes the surrounding air expand rapidly and thus tear the edge of the hole, indicating excellent impact energy release characteristics of HEA.

4. Conclusions

In conclusion, Al0.5NbZrTi1.5Ta0.8Ce0.85 high-entropy alloys prepared by vacuum arc melting showed excellent compressive mechanical properties and impact energy release characteristics. The result of XRD and TEM indicate the coexistence of BCC and FCC structures. SEM images illustrate element segregation in HEA. HEA shows obvious strain-rate effect. When the strain rate increases from $10^{-3}$ s$^{-1}$ to 4500 s$^{-1}$, the yield strength increases by 56.2% from 909 MPa to 1420 MPa. SEM images indicate that the fracture mechanism is intergranular fracture and interphase fracture.

Under impact, the threshold of strain rate of HEA was about 1200 s$^{-1}$. By investigating the samples after compression, XRD shows that complex oxidation reaction has taken place on HEA under impact. Ballistic gun tests were used to further investigate the penetration behaviour and energy release characteristics. Al0.5NbZrTi1.5Ta0.8Ce0.85 can penetrate 6 mm A3 plate at the speed of 712 m s$^{-1}$ and ignite the cotton behind the target, pointing out its potential as an ideal energetic structural material.

Data availability statement

The data that support the findings of this study are available upon reasonable request from the authors.

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Conflicts of interest
The authors declare no conflict of interest.

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