Effect of Cr on microstructures and properties of AlTiVZr0.2Crₓ light weight high entropy alloys

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Abstract: AlTiVZr0.2Crₓ (x=0,0.4,1) high entropy alloys have been prepared by powder metallurgy technology, and the effects of Cr content on the microstructures and properties of the alloys have been studied. The results show that the AlTiVZr0.2Crₓ alloys are mainly composed of body-centered cubic solid solution (BCC), face-centered cubic solid solution (FCC), and Al₂Zr, AlTi₂ and Cr₂Ti intermetallic compounds. The addition of Cr promotes the transformation of the alloys from FCC structure to BCC structure and generate new phase Cr₂Ti. The microstructure of the alloys are mainly massive or granulate. The hardness, compressive strength and elastic modulus of AlTiVZr0.2Crₓ alloys increase with the increase of atomic ratio of Cr content, the maximum hardness of AlTiVZr 0.2Cr alloy is 685.3 HV , and the maximum compressive strength and elastic modulus are 1180.36 MPa and 30221.36 MPa respectively. The addition of Cr content also affects the friction coefficient and wear resistance of the alloys. With the addition of Cr, the friction coefficient and wear resistance increase first and then decrease. The wear resistance of the AlTiVZr 0.2Cr0.4 alloy is the best in this experiment.

1. Introduction

There are usually accidental factors in the development of science, such as Oster's discovery that electricity can generate magnetism, Faraday's current magnetism can generate electricity, and in the field of material science, there are accidental factors in its development. Metals have become widely used materials for thousands of years. Due to the rapid development of human science and technology in recent years, the traditional metal materials based on Fe, Al, Cu can not meet the demand in some fields. In 1994, Professor Jien-Wei Yeh prepared a new system of alloys by mixing several metals with equimolar ratio and named them high entropy alloys in 2004[1~3].

The high entropy alloys (HEAs) are composed of 5-13 elements mixed with equal molar ratio or approximate equal molar ratio. Transition metal elements with similar radius and electronegativity are usually selected as the main raw materials for the preparation of HEAs[4]. For example, the
Cu-Co-Ni-Cr-Al-Fe HEA was first reported\[5\], later studies are based on this by adding or changing elements. Although HEAs have more elements, the number of phases is smaller than the phase law, and they even form a single solid solution. Elements commonly used to prepare HEAs are: Al, Ti, V, Cr, Mn, Fe, Co, Ni, Cu and other metal elements\[6,7\]. HEAs often have excellent properties and relatively simple structure. Taking CoCrFeMnNi alloy as an example, the structure of this series of HEAs is usually simple FCC structure, and its plasticity is usually higher than that of general steel materials\[8\]. In addition, the HEAs have excellent corrosion resistance and wear resistance. There are many methods to prepare HEAs, the most common methods are vacuum melting, powder metallurgy and magnetic levitation melting\[9~12\]. The powder metallurgy method can prepare metal materials with high hardness and good wear resistance. Due to powder metallurgy is usually below the melting point of metals, it is usually the first choice for the preparation of refractory metals.

With the increasing requirements of aviation technology and environmental protection, higher requirements are put forward for the preparation and production of low pollution, high performance and low density metals, and light weight high entropy alloys (LWHEAs) are in line with the development of the current situation. LWHEAs are developed on the basis of HEAs, its density is less than 6 g/cm\(^3\), often selected Al, Ti, Mg, V and other elements to prepare\[13\]. Metal materials with low density, high hardness and compressive strength are prepared by powder metallurgy. LWHEAs have great application prospect in aerospace field. In this paper, a new type of LWHEAs was designed and prepared, mainly composed of Al, Ti, V and Zr. By changing the content of Cr, the effects of different Cr content on the microstructures and properties of AlTiVZr\(_{0.2}\)Crx alloys were explored.

2. Materials and Methods

2.1 Alloy Composition Design

The metal elements with density less than 6 g/cm\(^3\) are: Be, Mg, Al, Ca, Sc, Ti, V, Zr, Ba, since the elements of the second family are active and difficult to process and prepare, the relatively stable Al, Ti, V, Zr four lightweight elements are selected and the Cr element with good corrosion resistance are added. According to empirical design criterion: \(\Omega \geq 1.1, \delta < 6.6\%\), the atomic ratio of the alloy was calculated and designed, shown as in formula (1) and (2)\[14\]:

\[
\Omega = \frac{T_m \Delta S_{mix}}{\Delta H_{mix}}
\]

\[
\delta = \sqrt{\sum_{i=1}^{m} c_i (1 - \frac{r_i}{f})}
\]

\(\Omega\) is entropy enthalpy ratio of the alloy, \(\delta\) is atomic radius difference, \(T_m\) is theoretical melting point of the alloy, \(\Delta S_{mix}\) is entropy of alloy mixing, \(\Delta H_{mix}\) is enthalpy of alloy mixing. The results are shown in Table 1 and the enthalpy of mixing of each element is shown in Table 2.

### Table 1 Entropy enthalpy ratio and atomic radius difference of AlTiVZr\(_{0.2}\)Crx LWHEAs

| Alloy      | \(T_m\) (K) | \(\Delta S_{mix}\) (J/K) | \(\Delta H_{mix}\) (KJ/mol) | \(\Omega\) | \(\delta\) (%) |
|------------|-------------|--------------------------|-----------------------------|-----------|---------------|
| AlTiVZr\(_{0.2}\) | 1710.63     | 10.51                    | -22.50                      | 0.80      | 5.17          |
| AlTiVZr\(_{0.2}\)Cr\(_{0.4}\) | 1757.22     | 12.24                    | -20.42                      | 1.05      | 5.59          |
| AlTiVZr\(_{0.2}\)Cr | 1812.30     | 12.57                    | -17.91                      | 1.27      | 6.51          |

### Table 2 Enthalpy of mixing of elements\[15\]

| Enthalpy of mixing (kJ/mol\(^{-1}\)) | Al | Ti | V | Zr | Cr |
|-------------------------------------|----|----|---|----|----|
| Al                                  | -  | -30| -16| -44| -10|
| Ti                                  | -  | -  | -2 | 0  | -7 |
| V                                   | -  | -  | -  | -4 | -2 |
| Zr                                  | -  | -  | -  | -  | -12|
2.2 Experimental scheme
Selecting Al, T, V, Zr, Cr metal powder (purity > 99%, diameter < 48μm), after the powder was fully mixed, powder consolidation of AlTiVZr0.2, AlTiVZr0.2Cr0.4, AlTiVZr0.2Cr LWHEAs were achieved by SMVB80 vacuum hot press sintering machine (sintering temperature: 950℃, pressure: 25 MPa, holding time: 5 min). For simplicity, the LWHEAs mentioned above are correspondingly shortened to the following names as Cr0, Cr0.4, Cr1. The phase structure was characterized by X ray diffractometer (D/max 2500V), the scanning speed was 6°/min, 20°~80° for 2θ. Density of the alloys were measured by Archimedes drainage method. The morphology of the samples after corroded by aqua regia and the compression fractures were analyzed by scanning electron microscope (SEM) (Hitachi S-3400N, with energy dispersive spectrometer). The hardness and compression properties of the alloys were tested by HVS-1000 microhardness tester and Instron 8801 universal testing machine respectively. The friction coefficient and wear resistance of the alloys were measured by HSR-2M high speed reciprocating friction and wear tester, and the wear morphology were analyzed.

3. Results & Discussion
3.1 Density and microstructure analysis
The alloys are processed into 10mm×10mm×10mm samples, and their density values are measured by the drainage method, and their computational formula is shown as formula (3). Table 3 shows the actual densities, theoretical densities and relative densities of Cr0, Cr0.4 and Cr1 alloys. It can be concluded from the Table 3 that the density increases gradually with the increase of Cr content, which is caused by the density of Cr element is larger than that of other elements.

$$\rho_s = \frac{m_1\rho_l}{m_1-m_2}$$  

(3)

where $\rho_s$ is actual density of alloys, $m_1$ is quality of alloys in air, $m_2$ is mass of alloys suspended in water, $\rho_l$ is density of water, $\rho_l=0.9958$ g/cm$^3$.

| Alloys | Actual densities (g/cm$^3$) | Theoretical densities (g/cm$^3$) | Relative densities |
|--------|-----------------------------|-------------------------------|-------------------|
| Cr0    | 4.221                       | 4.517                         | 0.934             |
| Cr0.4  | 4.610                       | 4.737                         | 0.973             |
| Cr1    | 4.786                       | 5.001                         | 0.957             |

Fig. 1 shows the XRD patterns of Cr0, Cr0.4, and Cr1 LWHEAs, the microstructures of the alloys are mainly composed of body-centered cubic solid solution (BCC) and face-centered cubic solid solution (FCC), and Al$_2$Zr, AlTi$_2$ and Cr$_2$Ti intermetallic compounds are formed. When the alloy doesn't contain Cr, the alloy is mainly FCC structure, and with the addition of Cr content, the alloys gradually change into BCC structure, the main diffraction peak change from 39° to 43°. At the same time, the Cr addition makes the peak at 2θ=45° in the alloys disappear and form a new phase Cr$_2$Ti. The addition of Cr has little effect on the content of Al$_2$Zr and AlTi$_2$. During the heating process, chemical reactions occur between the elements, which tends to produce compounds with lower mixing enthalpy to reduce their own energy. Because the mixing enthalpy values of (Al, Zr) and (Al, Ti) are relatively low, and they are stable relatively, the content of Al$_2$Zr and AlTi$_2$ don't change greatly.

Fig. 2 shows SEM images of the AlTiVZr$_{0.2}$Cr$_x$ alloys. The microstructure of AlTiVZr$_{0.2}$Cr$_x$ alloys are mainly massive and granulate, and the distribution of the microstructures is relatively uniform, with the increase of Cr content, the pits of the material are gradually less, which may be caused by the preparation process or the corrosion pit caused during metallographic sample preparation process. The compositions of each area measured by EDS are listed in Table 4. The elemental analysis of Fig. 2(a1) shows that the region A is rich in Al and V elements, while the content of Ti elements is less, there are only Al and Ti elements in region D, which may be AlTi$_2$ phase; From the elemental analysis of Fig. 2(b1) the contents of Cr and V in B region are low, and the contents of other elements are similar, there are only Al and Ti elements in the C region, D regions are rich in Al and Zr, the other three
elements are less abundant, the region may be a Al<sub>2</sub>Zr phase; The B and D regions of Fig. 2(c1) contain a large number of Cr elements, the E regions are rich in Al and Zr phases, which may be Al<sub>2</sub>Zr phase. The above analyses show that when the content of Cr is 0.4, the distribution of elements is more uniform, but when the content of Cr increases to 1, the aggregation of Cr elements occurs more seriously.

Fig. 1 X-ray diffraction patterns of AlTiVZr<sub>0.2</sub>Cr<sub>x</sub> HEAs
Fig. 2 SEM micrographs of the bulk AlTiVZr0.2Crx HEAs

Table 4 EDS analysis results of AlTiVZr0.2Crx HEAs (At%)

| Alloys Phase&Regional | Al   | Ti   | V    | Zr   | Cr   |
|-----------------------|------|------|------|------|------|
| Cr0                   |      |      |      |      |      |
| A                     | 31.58| 6.05 | 50.22| 12.14| 0    |
| B                     | 27.25| 50.49| 6.51 | 15.75| 0    |
| C                     | 3.86 | 0    | 96.14| 0    | 0    |
| D                     | 13.14| 86.86| 0    | 0    | 0    |
| Cr0.4                 |      |      |      |      |      |
| A                     | 25.12| 9.26 | 51.79| 7.91 | 5.92 |
| B                     | 32.17| 21.56| 15.87| 26.69| 3.7  |
| C                     | 17.6 | 82.4 | 0    | 0    | 0    |
| D                     | 34.88| 5.1  | 1.54 | 57.2 | 1.28 |
| Cr1                   |      |      |      |      |      |
| A                     | 19.4 | 35.65| 6.32 | 0    | 38.62|
| B                     | 24.12| 0.94 | 0    | 0    | 74.95|
| C                     | 23.77| 8.01 | 28   | 17.89| 22.33|
| D                     | 0.61 | 1.28 | 0    | 0    | 98.11|
| E                     | 34.9 | 1.98 | 3.3  | 58.86| 0.96 |

3.2 Analysis of hardness and compression properties

Hardness of the alloys are mainly related to preparation process, crystal structure, solution strengthening and intermetallic compounds. The hardness of AlTiVZr0.2Crx alloys are shown in Table 5. For Cr0, the minimum hardness is 458.3 HV, and for Cr1, the maximum hardness is 685.3 HV. Initially reported the hardness of CuCoNiCrFe HEAs as-cast were below 500 HV, after adding Al and V, and the hardness of CuCoNiCrAlFeTiV alloy quenched reaches 666 HV[I6]. It can be seen that powder metallurgy process can significantly improve the hardness of the alloy. It can be found in the Table 5 that the increase of Cr can improve the hardness of the alloys, which is consistent with the XRD test results. On the one hand, because of the addition of Cr gradually increases the volume fraction of BCC phase in the alloys, which increases the hardness of the alloys. On the other hand, the addition of Cr also gives birth to a new second phase Cr2Ti, and brittle and hard intermetallic compounds play the role of second phase strengthening, which makes the hardness of the alloys increase.

Table 5 Hardness of AlTiVZr0.2Crx alloys

| Alloys | AlTiVZr0.2 | AlTiVZr0.2Cr0.4 | AlTiVZr0.2Cr |
|--------|------------|-----------------|-------------|
| Hardness (HV) | 458.3 | 549.9 | 685.3 |

The compression stress-strain curves of AlTiVZr0.2Crx alloys at room temperature are shown in Fig. 3. The compression yield strength ($\sigma_y$), fracture strength ($\sigma_f$), strain ($\delta$) and elastic modulus (E) data

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obtained from the diagram are listed in Table 6. The compressive yield strength, fracture yield strength and elastic modulus of the alloys increase with the increase of Cr content. When the molar ratio of Cr is 1, the maximum compressive yield strength, fracture yield strength and elastic modulus of the alloy are 920.18 MPa, 1180.36 MPa and 30221.36 MPa respectively. With the increase of Cr content, the strain of the alloys increases first and then decreases, all the three alloys have lower strain and higher fracture strength.

The mechanical properties of metal materials have a great relationship with the type and content of phases. When the Cr element isn't included, the alloy is mainly FCC structure, and the compression yield strength and fracture strength are lower because of its more slip systems; When the molar ratio of Cr is 0.4, the alloy transforms from FCC structure to BCC structure, and the slip system of BCC structure is less, and the resistance to external deformation is stronger. In addition, the addition of Cr element promotes the alloys to form a brittle and hard Cr$_2$Ti phase, and the formation of the second phase produces pinning effect on the dislocation during the deformation of the alloys and improves the fracture strength of the alloys.

![Stress-strain Curve of Compression Engineering](image)

**Fig. 3 Stress-strain Curve of Compression Engineering**

| Alloys | $\sigma_{ys}$ (MPa) | $\sigma_p$ (MPa) | $\delta$ (%) | E (MPa) |
|--------|---------------------|-----------------|--------------|---------|
| Cr0    | 754.59              | 910.25          | 5.84         | 18540.29|
| Cr0.4  | 825.11              | 1011.73         | 6.31         | 21113.42|
| Cr1    | 920.18              | 1180.36         | 5.11         | 30221.36|

**Table 6 Compression mechanical properties**

Fig. 4 is characteristic diagram of compression fracture surface of AlTiVZ$_{0.2}$Cr$_x$ alloys at room temperature. It can be seen from the diagram that the compression fracture surface obtained by different alloys are relatively flat, with obvious cleavage steps, showing brittle fracture. Relatively speaking, with the increase of Cr content, the fracture morphology becomes smoother, while the alloy without Cr element produces certain cracks, which is related to the more FCC structural phase in the alloy. The more FCC structural phase, the better plasticity. In the compression process, the plastic deformation leads to dislocation stacking. When the dislocation stacking reaches a certain extent, the alloy will be destroyed, resulting in cracks.
3.3 Analysis of friction and wear performance

Fig. 5 shows the friction coefficient diagram of AlTiVZr0.2Crx alloys. It can be seen from the diagram that the friction coefficient of alloy Cr0 increases gradually with the increase of friction time, while the friction coefficient of Cr0.4 and Cr1 alloys increases first and then decreases. The average friction coefficients of the Cr0, Cr0.4 and Cr1 calculated from the figure are 0.781, 0.931 and 0.823 respectively, with the increase of the Cr content, the average friction coefficient of the alloys show the phenomenon of increase first and then decreasing.

The wear amount are measured by displacement sensor, the measured results are shown in Fig. 6, and the calculated wear amount are listed in Table 7. It can be seen from the figure that the addition of Cr reduces the wear amount of the alloys, and the wear amount decreases first and then increases with the increase of Cr. the wear resistance of Cr0.4 alloy is the best, and the wear amount is 0.264 mm³. Compared with the friction coefficient, The wear decreases with the increase of friction coefficient, and vice versa.
Fig. 6 Wear measurement curve of AlTiVZr0.2Crₓ

| Alloys | Wear width (mm) | Wear depth (µm) | Wear amount (mm³) |
|--------|-----------------|-----------------|-------------------|
| Cr0    | 1.523           | 85.508          | 0.765             |
| Cr0.4  | 1.155           | 49.174          | 0.264             |
| Cr1    | 1.332           | 43.537          | 0.331             |

The friction and wear morphology of the alloys is shown in Fig. 7. From Fig. 7(a), it can be seen that there are obvious ploughs and a large number of spalling of the alloys. The spalling is due to the cold welding phenomenon in the friction and wear process of the alloys, which makes the alloys produce scratch, a lot of scratches will lead to the increase of the friction coefficient of the alloys. The above phenomena show that the wear resistance of Cr0 alloy is poor, which is consistent with the measurement results of friction coefficient and wear amount, the main wear forms of materials are abrasive wear and adhesive wear. The main reason for the poor wear resistance of the material is that when there are no Cr element in the alloy, the alloy is mainly FCC structure, its structure is soft, and the hardness of the alloy is low, so the wear resistance of the alloy is poor. From Fig. 7(b), it can be seen that the wear morphology is dominated by ploughing deformation, and there is basically no spalling phenomenon, which indicates that the wear resistance of Cr0.4 alloy is better. This is because the addition of Cr content makes the alloys change from FCC to BCC structure, and the wear resistance of the BCC structure is better. When the hardness of the alloy (Hₘ) and abrasive hardness (Hₐ) exist, \( \frac{Hₘ}{Hₐ} > 0.8 \), wear resistance of the material increases with the increase of hardness. Because the addition of Cr increases the hardness of the alloys, the wear resistance is also improved. It can see from Fig. 7(c) that the friction morphology of the alloy has a small amount of spalling and a certain furrow deformation, so its wear resistance is located between the alloy Cr0 alloy and the Cr0.4 alloy, and the results are consistent with the measurement results of wear.
4. Conclusions

AlTiVZr0.2Crx LWHEAs have been prepared by powder metallurgy technology, and the influence of different Cr content on the microstructures and properties of the alloys have been studied. The results show that AlTiVZr0.2Cr alloys are mainly composed of body-centered cubic solid solution (BCC), face-centered cubic solid solution (FCC), and Al2Zr, AlTi2 and Cr2Ti intermetallic compounds. The addition of Cr element promotes the transformation of alloys from FCC structure to BCC structure and generate new phase Cr2Ti.

The addition of Cr content increases the density and hardness of the alloys. The higher the content of Cr is, the higher the density and hardness is, and AlTiVZr0.2Cr alloy has the highest hardness (685.3 HV). The compressive strength and elastic modulus increase with the increase of Cr content. The maximum compressive strength and elastic modulus of AlTiVZr0.2Cr alloy are 1180.36 MPa and 30221.36 MPa respectively. The addition of Cr content will also improves the friction coefficient and wear resistance of the alloys. With the increase of Cr content, the friction coefficient and wear resistance show the trend of increasing first and then decreasing. AlTiVZr0.2Cr0.4 alloy has the highest friction coefficient and the best wear resistance, the average friction coefficient and wear loss are 0.931 and 0.264 mm³ respectively.

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