Effect of heat treatment process on microstructure and hardness of Ni_{48}Co_{30}Cr_{16}Al_{3}Ti_{3} high entropy alloy

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Abstract—Ni_{48}Co_{30}Cr_{16}Al_{3}Ti_{3} HEA was made by suspension melting, and treated by different heat treatment methods. The microstructure, phase composition and microhardness of the prepared alloy samples were analyzed by means of XRD, SEM, X-ray energy spectrum analyzer and microhardness tester. And the results show that the Ni_{48}Co_{30}Cr_{16}Al_{3}Ti_{3} HEA after different heat treatments has face centered cubic structure, and the alloy structure presents dendrite morphology. Under different heat treatment conditions, the diffraction peaks of the alloy samples treated by secondary aging at (800°C×12h+1000°C×4h) are the highest and strongest, and the precipitates of the alloy samples treated by aging at (800°C×12h) are the most dense and subtle. The distribution of elements in the samples are relatively uniform, but after heat treatments, part of the alloy grain structure and grain boundaries dissolve, the degree of dissolution increases with the increase of heat treatment time, so that some elements are not distributed in the alloy structure and grain boundaries. The microhardness value of alloy samples first increases and then decreases with the prolongation of heat treatment time, and the microhardness values of the samples were the highest after aging treatment at (800°C×12h), which was 357HV₁.

1. Introduction
The design idea of traditional alloys is to obtain excellent properties by adding a small amount of other elements on the basis of one or two main elements, such as aluminum alloy and titanium alloy [1]. With the continuous development of the alloy design theory, in 2004, Yeh et al. [2] from Taiwan successfully broke through the traditional design concept of alloy materials and proposed a new design concept of alloy, namely high entropy alloy (HEA). Compared with traditional alloy materials, high entropy alloy has cocktail effect, high entropy effect, lattice distortion effect and hysteretic diffusion effect, which make it have excellent mechanical properties and physical and chemical properties [3,4]. Therefore, the
application prospect of high entropy alloy is very broad and has high research value, which has attracted extensive attention in academic field and industrial manufacturing field [5-6].

AlCoCrNiTi alloy is a common system [7]. At present, most of the researches on it focuses on the properties, composition and microstructure of as-cast alloy [8]. Although the ductility of as-cast HEA is better, its strength is low, its grain size is relatively coarse, and it is easy to form holes and other defects in the process of suction casting. This greatly limits its application [9]. As the properties of alloys are related to their structure, studies have shown [10] that appropriate heat treatment can improve their microstructure and thus increase their strength. Munitz et al. [11] conducted heat treatment of AlCoCrNiTi high entropy alloy at different temperatures, and found that heat treatment at 650-975 °C transformed the phase with BCC structure between the dendrites of the alloy into a hard and brittle σ phase, which increased the hardness of the alloy. Zhao [12] studied the hardness of annealed AlCrNiTi HEA. And the results showed that the hardness increased first and then decreased with the increase of annealing temperature because the internal structure of the alloy was strengthened and coarsened by annealing, and reached the maximum value at 800 °C. Although scholars have gradually carried out research on heat treatment of high entropy alloy, there is no literature to verify the effect of different aging treatment on the properties and structure of AlCoCrNiTi alloy. Therefore, this study took Ni48Co30Cr16Al3Ti3 high entropy alloy as the research object, prepared the alloy by suspension smelting and arc smelting, and studied the changes of microstructure and hardness of the alloy after different aging treatment, so as to provide technical guidance and data support for the further development and utilization of the HEA and expand the application range of the alloy.

2. Materials and Methods
High purity Ni, Co, Cr, Al and Ti (purity > 99.9%) were used as materials. The HEA was prepared by suspension smelting and arc smelting under the protection of argon. The alloy is repeated 5 times to make its composition uniform. The HEA ingots obtained from melting are cut and prepared as samples, and treated according to the heat treatment process shown in Tab. 1.

| Heat treatment process | Solid solution treatment | Aging treatment |
|------------------------|-------------------------|----------------|
| 1                      | 1200 °C×10 h            |                |
| 2                      | 1200 °C×10 h            | 800 °C×6 h     |
| 3                      | 1200 °C×10 h            | 800 °C×12 h    |
| 4                      | 1200 °C×10 h            | 800 °C×24 h    |
| 5                      | 1200 °C×10 h            | 800 °C×72 h    |
| 6                      | 1200 °C×10 h            | 800 °C×12 h+1000 °C×4 h |
| 7                      | 1200 °C×10 h            | 800 °C×24 h+1000 °C×4 h |

The phase and crystal structure of the samples was analyzed by Bruke-axs-d8 X-ray diffractometer (XRD) manufactured in Germany. The microstructure of the alloy samples was analyzed by Jeol/JSM-5610LV scanning electron microscope (SEM) manufactured in Japan. The composition of alloy samples was analyzed by X-ray energy dispersive spectrometer (EDS) attached to SEM. Hv-1000 micro-Vickers hardness tester was used to test the hardness of the alloy sample with a load of 1kg and a retention time of 15s. For every same alloy sample, 8 different equidistance positions were selected to test, and the average value of each hardness value was taken as the final hardness value to ensure the accuracy of the test results.

3. Test Results and Discussions

3.1. XRD analysis of Ni48Co30Cr16Al3Ti3 high entropy alloy
Fig.1 shows the XRD patterns of Ni48Co30Cr16Al3Ti3 high entropy alloy under different heat treatment processes and its local enlargement. From Fig.1, we can clearly see that under different treatment processes, and crystal structures of Ni48Co30Cr16Al3Ti3 are all FCC structures. Although the intensities
of the diffraction peaks are different, the angles of appearance are basically the same. The diffraction peak of the sample after secondary aging treatment at (1000°C×4h) is the highest, followed by the alloy after aging treatment at (800°C×12h) and (800°C×24h). It can be seen from the local enlarged image that the alloy after aging treatment at (800°C×12h+1000°C×4h) produces a small peak at 43.8°, which is inferred to be impurity phase in combination with Jade software analysis. Compared with the solid solution sample, the diffraction peak of the alloy after aging treatment (800°C×12h) shifted to the left. The atomic radius is larger than that of Co, Cr, etc. After the precipitation of the second phase, due to the interaction between atoms, lattice distortion occurs, so that the lattice constant of the FCC phase increases, resulting in the shift of the XRD diffraction peak.

![XRD patterns](image)

**Fig. 1** XRD patterns of Ni₀₅Co₀₅₃₀₈Cr₁₆Al₃Ti₃ HEA under different heat treatment processes  
(a): XRD diffraction pattern  
(b): Partial enlargement of XRD diffraction pattern

3.2. **SEM analysis of Ni₄₈Co₃₀Cr₁₆Al₃Ti₃ HEA**

Fig. 2 is the SEM image of Ni₄₈Co₃₀Cr₁₆Al₃Ti₃ high-entropy alloy only after solution treatment at (1200°C×10h), which is used as a comparison sample to help study the structure of HEA. Figures (a), (b) are the morphologies of the alloys when the magnification is 100 times and 500 times, respectively. We can clearly observe the surface texture and triangular boundary grains.

![SEM images](image)

**Fig. 2** Ni₄₈Co₃₀Cr₁₆Al₃Ti₃ high entropy alloy at (1200°C×10h) SEM after solution treatment  
(a): 100 times (b): 500 times

Fig. 3 is the SEM figure of Ni₄₈Co₃₀Cr₁₆Al₃Ti₃ high entropy alloy after solution treatment at (1200°C×10h) and different aging treatment. As can be seen from Fig. 3, after different aging treatments, the micro-structure of Ni₄₈Co₃₀Cr₁₆Al₃Ti₃ alloy is braids, the polycrystalline structure, grain boundary and a large number of fine precipitates composed of many neatly arranged polygonal grains can be clearly observed. With the extension of aging time, sample grain boundary gradually begins to dissolve, and the precipitated phase becomes more dense and fine. Meanwhile, the dendrite arrangement becomes orderly and more uniform, and the columnar crystals change into equiaxed dendrites. The dendrite spacing gradually occupies the main body and the area occupied gradually
increases. After secondary aging treatment, the microstructure, precipitates and grain boundaries of the alloy were seriously damaged by high temperature dissolution, which led to serious degradation of the properties.

![Fig. 3 SEM of Ni_{48}Co_{30}Cr_{16}Al_{3}Ti_{3} high entropy alloy after different aging treatments](image)

(a)、(a1): (800°C×6h) (b)、(b1): (800°C×12h) (c)、(c1): (800°C×24h) (d)、(d1): (800°C×72h) (e)、(e1): (800°C×12 h+1000 °C×4 h) (f)、(f1): (800°C×24 h+1000 °C×4 h)

3.3. EDS analysis of Ni_{48}Co_{30}Cr_{16}Al_{3}Ti_{3} HEA

The surface morphology of Ni_{48}Co_{30}Cr_{16}Al_{3}Ti_{3} HEA under different heat treatment conditions was obtained by SEM analysis, and the EDS diagram of the alloy was analyzed to obtain the distribution of specific elements.

Fig. 4 shows the EDS layered images of alloys subjected to different heat treatments and the distribution of all elements in the alloy cross-section. From Fig. 4, we can clearly see the distribution of different elements in the Ni_{48}Co_{30}Cr_{16}Al_{3}Ti_{3} HEA. Some positions in the surface scan of the alloy only treated by solution treatment at (1200°C+10h) have no distribution of elements due to the formation of loose shrinkage cavities or impurities. With the increase of aging time, Al element is gradually precipitated. After (800°C+24h), the distribution of each element in the alloy is the most uniform. When the aging time is further extended, the alloy structure and grain boundaries are dissolved, and the dissolution of the three grain boundaries is the most. Seriously, resulting in the absence of elements at the grain boundary junction.
Fig. 4 Section morphology and element distribution of Ni$_{48}$Co$_{30}$Cr$_{16}$Al$_3$Ti$_3$ high entropy alloy after different heat treatment

(a): (1200°C×10h)  (b): (800°C×6h)  (c): (800°C×12h)  (d): (800°C×24h)  
(e): (800°C×72h)  (f): (800°C×12 h+1000°C×4 h)  (g): (800°C×24 h+1000°C×4 h)
3.4. Hardness Test of Ni_{48}Co_{30}Cr_{16}Al_{3}Ti_{3} High Entropy Alloy

Fig. 5 shows the microhardness of Ni_{48}Co_{30}Cr_{16}Al_{3}Ti_{3} high entropy alloy under different heat treatment processes. From Fig. 5, the hardness of the HEA after solution treatment only at (1200°C×10 h) is 165.5HV1. After solution treatment at (1200°C×10h), the hardness of the alloy is 165.5HV1. After (800°C×6h), (800°C×12h), (800°C×24h), (800°C×72h), (800°C×12h +1000°C×4h) and (800°C×24h+1000°C×4h) the microhardness values of the aged alloy are 336.23HV1, 357HV1, 342.7HV1, 338.5HV1, 328.43HV1 and 288.66HV1, respectively. The hardness of Ni_{48}Co_{30}Cr_{16}Al_{3}Ti_{3} high entropy alloy after solution treatment at (1200°C×10h) is the lowest, and then increases with the increase of heat treatment time. The microhardness of Ni_{48}Co_{30}Cr_{16}Al_{3}Ti_{3} high entropy alloy after aging treatment at (800°C×12h) reaches the peak value, and then decreases with the increase of heat treatment time. Therefore, after appropriate heat treatment can obviously increase the Ni_{48}Co_{30}Cr_{16}Al_{3}Ti_{3} microhardness values of high entropy alloys, combining with the former in the face of alloy microstructure analysis, alloy in after a certain time of aging treatment, its organization is more small, element diffusion, phase and precipitate the nanostructures, lead to precipitation strengthening, to improve the hardness of alloy. However, with the increase of the time, the structure and grain boundary of some samples were seriously dissolved, which reduced the microhardness of the alloys.

![Fig. 5 Microhardness of Ni_{48}Co_{30}Cr_{16}Al_{3}Ti_{3} high entropy alloy under different heat treatment processes](image)

4. Conclusion

Based on the results and discussions presented above, the conclusions are obtained as below:

1. The crystal structure of Ni_{48}Co_{30}Cr_{16}Al_{3}Ti_{3} alloy is FCC structure, which does not change with the change of heat treatment process. New NiAl intermetallic compounds were precipitated, with the increase of aging time.

2. Under different heat treatment conditions, the microstructure of Ni_{48}Co_{30}Cr_{16}Al_{3}Ti_{3} HEA is braided, and a large number of nanoparticles are dispersed. With the increase of aging time, part of the grain structure and grain boundary of the alloy will dissolve. This affects the properties of the alloy.

3. After proper heat treatment, the microhardness of Ni_{48}Co_{30}Cr_{16}Al_{3}Ti_{3} alloy with high entropy can be significantly increased. The microhardness of Ni_{48}Co_{30}Cr_{16}Al_{3}Ti_{3} alloy with high entropy after solution treatment at (1200°C×10h) is the lowest. The microhardness value of the alloy after aging
treatment at (800°C×12 h) is the highest among the seven heat treatment processes, which is about 357 HV1.

(4) After comprehensive comparison, it can be seen that the solution treatment at (1200°C×10h) followed by the aging treatment at (800°C×12h) is a relatively better heat treatment process for Ni48Co30Cr16Al3Ti3 high entropy alloy.

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