Effect of Ce addition on microstructure and hardness of (Ni$_2$CoFe)$_{86}$Ti$_8$Al$_6$ high entropy alloy

Chong Liu$^1$, Chenglei Wang$^1$$^b$, Zhenjun Zhang$^2$$^c$, Hong Tan$^1$d, Yingguang Xie$^1$, Haiqing Qin$^2$, Xin Li$^1$, Mulin Liang$^1$, Weijie Liu$^1$, Jijie Yang$^1$

1 School of Materials Science and Engineering, and Guangxi Key Laboratory of Information Materials, and Engineering Research Center of Electronic Information Materials and Devices, Ministry of Education, Guilin University of Electronic Technology, Guilin 541004, P.R. China.

2 Guangxi Key Laboratory of Superhard Material, National Engineering Research Center for Special Mineral Material, China Nonferrous Metal (Guilin) Geology and Mining Co., Ltd., Guilin 541004, P.R. China.

$^a$lc494984798@163.com, $^b$clw0919@163.com, $^c$277062516@qq.com, $^d$200250625@glmc.edu.cn

Abstract—The effects of different Ce contents on the microstructure and hardness of (Ni$_2$CoFe)$_{86-x}$Ti$_8$Al$_6$Ce$_x$ (x = 0, 0.1, 0.3, 0.5, 0.7, 1.0 molar ratio) high entropy alloys were systematically studied. The results show that the addition of Ce promotes the precipitation of new FCC and BCC phases. The precipitates were promoted by Ce, and the grains and structures were refined by Ce. With the gradual increase of Ce content, the hardness gradually increases. The microhardness (HV) of (Ni$_2$CoFe)$_{86}$Ti$_8$Al$_6$Ce HEA is 458.6. The increase of precipitate volume fraction and fine grain strengthening are the main reasons for the increase of hardness.

1. Introduction
High entropy alloys break through the traditional design concept of one or two main elements, develop the alloy design system to the field of multiple elements, and propose a new perspective of alloy design$^{[1-3]}$. Due to the special combination of various metal elements, high entropy alloys exhibit the freedom of composition, the diversity of organization and the uniqueness of performance, showing amazing advantages in the field of engineering applications$^{[4]}$. On the one hand, it provides the possibility to design more high-entropy alloys with excellent properties, on the other hand, it also brings great challenges to the composition design of high entropy alloys$^{[5]}$.

Alloying is a common method to improve the hardness of traditional alloys$^{[6-7]}$. Similar methods are also widely used on high-entropy alloys. Ye et al.$^{[8]}$ studied the effect of Ti content on the microstructure and mechanical properties of (CuCoFeNi)Ti$_x$ HEA, and found that the structure of the alloy changed from the initial single-phase fcc structure to the mixed structure of fcc+Laves, both the Laves phase content and the hardness of the alloys increase with increasing Ti content. Antonov et al.$^{[9]}$ studied the effects of different Nb, Co and Fe contents on the microstructure and mechanical properties of Fe-Co-Ni-Cr-Al-Nb high-entropy alloys, and found that the addition of Nb was beneficial to the formation of γ' in the alloy, and with the increase of Nb content, the volume fraction of γ' phase also increases gradually, which improves the hardness of the alloy, but the excessive
concentration of Nb promoted the formation of Laves phase and NiAl phase. Some other alloying effects, such as V, Nb, Mo, Si, Ti have also been paid attention to by many researchers\cite{10-12}. Therefore, the influence laws of alloying elements on the microstructure and mechanical properties of high-entropy alloys and their influence mechanisms have positive significance for the development of high entropy alloys. A large number of research results show that Ce addition has a significant effect on improving the hardness of the alloy. Ahmad et al.\cite{13} studied the mechanical properties of alloys with and without Ce addition, and found that the quality index and tensile strength of Mg-Ai-Si-Cu alloys were improved after adding 0.1 wt% Ce, the hardness of the matrix alloy also increases with the increase of Ce concentration. Park et al.\cite{14} used nanoindentation technology to study the microstructure and mechanical properties of Mg-xCe-0.5Zn alloy, and found that elastic modulus and the average indentation hardness of Mg-xCe-0.5Zn alloy increased with the increase of Ce addition.

Therefore, the microstructure and hardness of (Ni\textsubscript{2}CoFe)\textsubscript{86-x}Ti\textsubscript{8}Al\textsubscript{6}Ce\textsubscript{x} (x=0, 0.1, 0.3, 0.5, 0.7, 1.0) high entropy alloy have been systematically studied, and the law between microstructure and hardness have been analyzed.

2. Experiment method
The smelting raw materials are Al, Fe, Co, Ni, Ti and Ce with mass fraction of 99.9%. The vacuum arc melting furnace is used to smelt and prepare in a pure argon atmosphere. The inside of the furnace body is evacuated to a vacuum, and the furnace is first washed with high-purity argon gas for three times, and then high-purity argon gas is introduced to the internal pressure of 1×10\textsuperscript{-4} Pa. The samples were polished with 400-mesh SiC sandpaper to a smooth surface, and the cleaned samples were polished with 400, 600, 800, 1000, 1200, 1500, and 2000-mesh sandpapers, then polished and corroded. D8-ADVANCE X-ray diffraction analyzer was used to analyze the phase structure of the samples. The diffraction angle was 10\degree ~90\degree, the voltage was 50KV, the current was 40mA, and the scanning speed was 12\degree/min. HV-1000 hardness micrometer was used to measure the hardness of the alloy. The ground samples were used to ensure that the upper and lower sides were parallel, and the surface to be measured was well polished. Each sample is marked with 5 points, averaged, and a load is applied. The load is 5N, and the dwell time is 30s. The microstructure of the prepared alloy was analyzed by a Quantas FEG 450 field emission scanning electron microscope, and the composition distribution of the alloy was detected by the attached energy spectrometer.

3. Test Results and Discussions
3.1. Phase composition of (Ni\textsubscript{2}CoFe)\textsubscript{86-x}Ti\textsubscript{8}Al\textsubscript{6}Ce\textsubscript{x} high-entropy alloy
Fig. 1 shows the XRD pattern of the (Ni\textsubscript{2}CoFe)\textsubscript{86-x}Ti\textsubscript{8}Al\textsubscript{6}Ce\textsubscript{x} (x=0, 0.1, 0.3, 0.5, 0.7, 1.0) high-entropy alloy. It can be seen that when there is no Ce, there are only FCC phase diffraction peaks. When the molar fraction of Ce is 0.1\%~0.7\%, the diffraction peak of Ni\textsubscript{3}AlTi phase of FCC structure appears, and the AlFe\textsubscript{3} diffraction peak of weak BCC structure appears, so it can be determined that the microstructure of the alloy is FCC phase and Ni\textsubscript{3}AlTi phase, and a small amount of AlFe\textsubscript{3} phase is precipitated, which indicates that Ce will promote the precipitation of the precipitated phase. With the gradual increase of Ce content, more and more precipitates are precipitated When the molar fraction of Ce is 1.0\%, the diffraction peak intensity of the precipitated phase is the highest, while the intensity of the FCC diffraction peak is lower, which shows that the FCC phase gradually transforms into the L\textsubscript{12} phase.
3.2. Microstructure of (Ni\textsubscript{2}CoFe\textsubscript{86-x}Ti\textsubscript{8}Al\textsubscript{6}Ce\textsubscript{x} (x=0, 0.1, 0.3, 0.5, 0.7, 1.0) HEA

Fig. 2. shows the SEM microstructure morphology of (Ni\textsubscript{2}CoFe\textsubscript{86-x}Ti\textsubscript{8}Al\textsubscript{6}Ce\textsubscript{x} alloy with high entropy. It can be seen that the crystals of (Ni\textsubscript{2}CoFe\textsubscript{86-x}Ti\textsubscript{8}Al\textsubscript{6}Ce\textsubscript{x} HEA are dendritic and evenly distributed, and the alloy structure exhibits typical dendritic growth characteristics, mainly composed of dendrite (DR) and interdendritic (ID) structures. With the increase of Ce volume fraction, the microstructure of the alloy becomes very fine, and the grains become finer and denser. This is because the addition of Ce makes the dislocation slip blocked by the grain boundary, resulting in dislocation packing in the grain, which makes it difficult to slip and leads to fine grain strengthening. The original (Ni\textsubscript{2}CoFe\textsubscript{86}Ti\textsubscript{8}Al\textsubscript{6} HEA has a single FCC phase, which is consistent with the XRD diffraction peak results. When x=0.1, a new phase begins to form in the alloy. The phase analysis by XRD and the EDS results of each point in Fig. 2 show that this phase is the Ni\textsubscript{3}AlTi phase with FCC structure. With the increase of x, the number of new phases increases obviously, and the peak value of Ni\textsubscript{3}AlTi phase in the XRD diffraction peak increases significantly. When x=1.0, the content of Ni\textsubscript{3}AlTi phase is higher.

From the EDS results of each point in Table. 1, it can be seen that Ni, Al, Ti and Fe elements are enriched in the dendrites, while there is basically no Ce element on the dendrites, indicating that Ce promotes the precipitation of Ni\textsubscript{3}AlTi and AlFe\textsubscript{3} in the dendrites. With the gradual increase of Ce content, the volume fraction of precipitated phase and the content of precipitated elements also gradually increased, which is consistent with the analysis results of XRD.
3.3. Microhardness of (Ni₂CoFe)₈₆ₓTi₈Al₆Ceₓ high entropy alloy

Fig. 3 shows the average hardness curve of (Ni₂CoFe)₈₆₋ₓTi₈Al₆Ceₓ high entropy alloy. The average hardness was measured five times, and the average hardness (HV) of (Ni₂CoFe)₈₆ₓTi₈Al₆Ceₓ high-entropy alloy (x=0, 0.1, 0.3, 0.5, 0.7, 1.0) was calculated to be 408.2, 435.8, 438.3, 446.6, 456.4, 458.6. The average hardness of the alloy increases with the increase of Ce content. When x=1.0, the hardness is the largest, which is 458.6HV. The increase of the volume fraction of the precipitated phase and the strengthening of the grain refinement are the main reasons for the increase in the hardness.
4. Conclusion
From the above results and analysis, the following conclusions can be drawn:

1. With the increase of Ce content, the Ni$_2$AlTi phase with FCC structure is formed in the (Ni$_2$CoFe)$_{86}$Ti$_8$Al$_6$ matrix high-entropy alloy of single-phase FCC, and the BCC phase with Al and Fe elements is simultaneously formed. Ce promotes the precipitation of the precipitation phase.

2. With the increase of Ce content, the volume fraction of the (Ni$_2$CoFe)$_{86-x}$Ti$_8$Al$_6$Ce$_x$ HEA precipitation phase increases gradually, the grain size becomes smaller, and the structure becomes denser.

3. With the increase of Ce content from 0 to 1.0, the microhardness of (Ni$_2$CoFe)$_{86-x}$Ti$_8$Al$_6$Ce$_x$ HEA increased from 408.2 to 458.6 in the matrix. The increase in volume fraction of precipitates and the strengthening of grain refinement are the main reasons for the increase in hardness.

Acknowledgments
The authors wish to thank the National Natural Science Foundation of China (52161011), the Major Research Plan of the National Natural Science Foundation of China (92166112), China Postdoctoral Science Foundation Funded Project (2020M681092), Natural Science Foundation of Guangxi Province (2018GXNSFAA281244, and 2020GXNSFAA297060), Guangdong Basic and Applied Basic Research Foundation (2020B151542004), Guangxi Key Laboratory of Information Materials (211024-Z, 211003-K, and 201016-Z), Scientific Research and Technology Development Program of Guilin (2020010903 and 20210217-6), and Supported by the Open Project Program of Wuhan National Laboratory for Optoelectronics (2021WNLOKF010), the Projects of MOE Key Lab of Disaster Forecast and Control in Engineering in Jinan University (20200904006), Engineering Research Center of Electronic Information Materials and Devices, Ministry of Education (EIMD-AB202009), and Innovation Project of GUET Graduate Education (2020YCXSS118, and 2022YCXSS200) for the financial support given to this work.

References
[1] Yeh, J.W., Chen, S.K., Lin, S.J., et al. (2004) Nanostructured High-Entropy Alloys with Multiple Principal Elements: Novel Alloy Design Concepts and Outcomes[J]. Advanced Engineering
[2] Yang, T., Zhao, Y.L., Tong, Y., et al. (2018) Multicomponent intermetallic nanoparticles and superb mechanical behaviors of complex alloys[J]. Science, 362: 933-937.
[3] V Kuteneva, S., V Gladkovsky, S., Vichuzhanin, D.I., et al. (2022) Microstructure and properties of layered metal/rubber composites subjected to cyclic and impact loading[J]. Composite Structures, 285: 115078.
[4] Ye, Y.F., Wang, Q., Lu, J., et al. (2016) High-entropy alloy: challenges and Prospects[J]. Materials Today, 19(6): 349-362.
[5] Guo, N.N., Wang, L., Su, Y.Q., et al. (2015) Microstructure and properties of novel qnin principal element alloys with refractory elements[J]. China Foundry, 5: 319-325.
[6] Mandal, A., Mihira, A. (2015) Effect of strontium and Misch Metal on Al–14Si–3Mg Alloy[J]. Trans Indian Inst Met, 68(6): 1181-1185.
[7] Wang, H.T., Huang, B.X., Wang, L.J. (2011) Effects of Vanadium Microalloying on Hardness of Alloy ZG270-500[J]. Advanced Materials Research, 216: 397-401.
[8] Ye, X.C., Wang, T., Xu, Z.Y., et al. (2020) Effect of Ti content on microstructure and mechanical properties of CuCoFeNi high-entropy alloys[J]. International Journal of Minerals, Metallurgy and Materials, 27(10): 6.
[9] S. Antonov, M. Detrios, S. Tin. Design of Novel Precipitate-Strengthened Al-Co-Cr-Fe-Nb-Ni High-Entropy Superalloys[J]. Metallurgical and Materials Transactions A, 2018,017: 4399-9.
[10] Feng, H., Wang, Z., Peng, C., et al. (2016) Designing eutectic high entropy alloys of CoCrFeNiNbx[J]. Journal of Alloys and Compounds, 656: 284-289.
[11] Qza, B., Yza, B., Gya, B., et al. (2015) The effect of vanadium on microstructure and mechanical properties of Fe-based high-strength alloys[J]. Results in Physics, 57: 67-72.
[12] Kochi, M., Koizumi, H., Murakami, M., et al. (2011) Hardness and microstructure of Ti-15Mo-5Zr-3Al alloy for dental casting[J]. Acta Odontologica Scandinavica, 69(6): 328-333.
[13] Ahmad, R., Smael, M., Shahizan, N.R., et al. (2017) Reduction in secondary dendrite arm spacing in cast eutectic Al-Si piston alloys by cerium addition[J]. International Journal of Minerals Metallurgy and Materials, 24(01): 93-103.
[14] Park, K.C., Kim, B.H., Park, Y.H., et al. (2010) Evaluation of microstructure and mechanical properties of Mg-xCe-0.5Zn alloys by nano-indentation[J]. Transactions of Nonferrous Metals Society of China, 20(7): 4.