Study on corrosion resistance of high-entropy alloy in medium acid liquid and chemical properties

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Abstract. High-entropy alloy is a new alloy which is different from traditional alloys. The high entropy alloys were started in Tsing Hua University of Taiwan since 1995 by Yeh et al. Consisting of a variety of elements, each element occupying a similar compared with other alloy elements to form a high entropy. We could define high entropy alloys as having approximately equal concentrations, made up of a group of 5 to 11 major elements. In general, the content of each element is not more than 35% by weight of the alloy. During the investigation it turned out that this alloy has a high hardness and is also corrosion proof and also strength and good thermal stability. In the experimental area, scientists used different tools, including traditional casting, mechanical alloying, sputtering, splat-quenching to obtain the high entropy alloys with different alloying elements and then to investigate the corresponding microstructures and mechanical, chemical, thermal, and electronic performances. The present study is aimed to investigate the corrosion resistance in a different medium acid and try to put in evidence the mechanical properties. Forasmuch of the wide composition range and the enormous number of alloy systems in high entropy alloys, the mechanical properties of high entropy alloys can vary significantly. In terms of hardness, the most critical factors are: hardness/strength of each composing phase in the alloy, distribution of the composing phases. The corrosion resistance of an high entropy alloy was made in acid liquid such as 10%HNO₃-3%HF, 10%H₂SO₄, 5%HCl and then was investigated, respectively with weight loss experiment. Weight loss test was carried out by put the samples into the acid solution for corrosion. The solution was maintained at a constant room temperature. The liquid formulations used for tests were 3% hydrofluoric acid with 10% nitric acid, 10% sulphuric acid, 5% hydrochloric acid. Weight loss of the samples was measured by electronic scale.

1. Introduction

High entropy alloys have received a special attention in past few years. The first researches conducted on such an alloy were made in 1981 by B. Cantor. In 1995 J.W Yeh began to deepen research on high entropy alloys. Were produced around 40 alloys having the alloying elements Ti, V, Cr, Fe, Co, Ni etc. However the term of high entropy alloy was accepted by science in 2003. High entropy alloys have been defined as consisting of five or more elements, each one having a concentration between 5 and 35 at.% [1].
Acid solutions are generally used for the removal of undesirable scale and rust in several industrial processes. Hydrochloric and sulphuric acids are widely used in the pickling processes of metals. Use of inhibitors is one of the most practical methods for protection in the face of corrosion especially in acid solutions to prevent metal dissolution and acid intake. The use of organic compounds containing oxygen, sulphur and nitrogen to reduce corrosion attack on steel has been studied in some details. Sulphur and nitrogen containing compounds are more effective as corrosion inhibitor in sulphuric acid and hydrochloric acid [2].

High entropy alloys subject to corrosion in such environments H$_2$SO$_4$ and HCl acid showed a high resistance to corrosion. For example CuCrFeNiMn high entropy alloy immersed in H$_2$SO$_4$ at ambient temperature (~25°C) showed that the alloys display a good general corrosion resistance that is mainly influenced by the Cu content and elemental segregation degree. The corrosion resistance degrades when increasing Cu content and elemental segregation degree. The corrosion resistance of NiCoCrFeMnCuC in 10 % HNO$_3$ - 3 % HF, 10 % H$_2$SO$_4$, 5 % HCl and 10 % HF has simple crystal structures with face-centered cubic crystal structure FCC and Quartet and has excellent corrosion resistance in some medium acid liquids [3, 4, 5].

2. Experimental procedures

2.1. Test materials

The type of high entropy alloys manufactured was a five-component alloy of AlCrNiCuMn. Cylindrical alloy ingot (20 cm in diameter and 4 mm thick) were prepared from a compound of pure elements. High purity elemental Al, Cr, Cu, Mn, and Ni were used as gross materials and prepared by induction melting in a medium frequency induction furnace for 8000 Hz. The chemical composition of the alloy given in table 1, is determined using EDAX.

| Elements | Al     | Cr      | Ni     | Cu    | Mn    |
|----------|--------|---------|--------|-------|-------|
| High entropy alloy | 5,08   | 6,72    | 19,09  | 47.80 | 21,29 |

2.2. Microstructural characterization

The metallographic samples of the high entropy alloy AlCrNiCuMn were first mechanically wet ground using a SiC grit paper, then polished with Al$_2$O$_3$ powder of 1 μm diameter, succeed by a chemical etch with NITAL. The mechanically process purpose to put into evidence structural constituents. The development follows the structure via surface attack with chemical reagents, solutions in general. Microstructural characterization was performed by electron microscopy on LMHII VegaTescan equipment using a secondary electron detector at a voltage of 30 kV electron gun.

3. Results and discussions

3.1. Microstructural characterization for high entropy alloy AlCrNiCuMn before immersion

In figure 1 we can observe that the high entropy alloy AlCrNiCuMn has a typical dendritic structure and the dendritic areas are rich in Cr. Cr-rich areas were observed in EDAX analyzes. Figure 2 presents the distribution of elements in the high entropy alloy AlCrNiCuMn. After the analysis of the distribution it is seen that in our high entropy alloy can be formed some different phase like: Al-Cu, Cu-Ni, Al-Ni.
3.2. Microstructural characterization for high entropy alloy AlCrNiCuMn immersed in different acid medium

Another The high entropy alloy AlCrNiCuMn was immersed for 120h in three acid medium namely 3% HF+10% HNO₃, 10% H₂SO₄ and 5%HCl. The samples that were immersed were cute by wire cutting into 8x8x8mm in size. The solution was maintained at a constant room temperature (~25°C). In the figures below are presented the high entropy alloy AlCrNiCuMn immersed in different acid medium. Figure 3 is presented SEM micrography for AlCrNiCuMn immersed in 3% HF+10% HNO₃, Al and Mn have a negative effect but Cr and Ni increase corrosion resistance.
After the chemical analysis it could be observed that the alloying elements of high entropy alloy having been subjected to immersion in three different acid medium had a quantitative change. For the sample immersed in 3% HF+10%HNO₃, Al, Cr and Ni alloy undergoes an increase but Mn and Cu suffer an decrease, in the other two cases the samples that was immersed in 10%H₂SO₄ and 5%HCl only Al and Cr increases while the other three alloying elements Mn, Cu and Ni decreases. All these are given in table 2.

| Table 2 | Chemical composition (wt.%) of the test material AlCrNiCuMn immersed in three different acid medium. |
|---------|--------------------------------------------------------------------------------------------------|
| Al      | Cr       | Ni       | Cu       | Mn       |
| 3% HF+10 %HNO₃ | 6,22 | 10,05 | 20,21 | 42,04 | 21,45 |
| 10% H₂SO₄    | 7,38 | 8,72 | 17,37 | 45,41 | 21,09 |
| 5%HCl        | 5,47 | 9,59 | 16,18 | 48,36 | 20,37 |
3.3. Chemical analysis in points

Figure 6 shows the chemical analysis in points for the high entropy alloy AlCrNiCuMn immersed in 3% HF+10 %HNO₃ for 120h. In point A the chemical analysis shows a high quantity of Cu, point B on the figure represents an area rich in Cu and Ni but in point C the predominant alloying element is Cr.

Figure 6. The chemical analysis in points for high entropy alloy AlCrNiCuMn immersed in 3% HF+10 %HNO₃.

Figure 7 shows the chemical analysis in points for the high entropy alloy AlCrNiCuMn immersed in 10% H₂SO₄ for 120h. In point A the chemical analysis shows a high quantity of Cu,Ni and Mn, point B on the figure represents an area rich in Cu and Ni but in point C the predominant alloying element is Cu and Mn. For the high entropy alloy AlCrNiCuMn immersed in 5%HCl the chemical analysis is identical to the first chemical analysis for the sample immersed in 3% HF+10 %HNO₃ (figure 8).

Figure 7. The chemical analysis in points for high entropy alloy AlCrNiCuMn immersed in 10% H₂SO₄.

Figure 8. The chemical analysis in points for high entropy alloy AlCrNiCuMn immersed in 5%HCl.

Figures 9, 10, 11 presented some graphs for the weight loss of test material AlCrNiCuMn immersed for 120h in 3% hydrofluoric acid with 10% nitric acid, 10% sulfuric acid and 5% hydrochloric acid. In graphs 9, 10 it can be seen that in the first 48 hours the high entropy alloy AlCrNiCuMn has a bigger weight loss, but for the high entropy alloy AlCrNiCuMn immersed in 5%HCl the weight loss becomes visible in the first 24 hours.
Figure 9. Weight loss for high entropy alloy AlCrNiCuMn immersed in 10%HNO$_3$-3%HF for 120h.

Figure 10. Weight loss for high entropy alloy AlCrNiCuMn immersed in 10%H$_2$SO$_4$ for 120h.

Figure 11. Weight loss for high entropy alloy AlCrNiCuMn immersed in 5% HCl for 120h.

4. Conclusions

Corrosion tests were carried out in three different acid medium for 120h.

Alloying elements from high entropy alloy had suffered various modifications.

AlCrNiCuMn gets good performance of corrosion resistance. Weight loss is only about 4% in 10%HNO$_3$-3%HF liquid, about 0.4% in 10%H$_2$SO$_4$ liquid, about 0.7% in 5%HCl liquid and only after about 120 hours.

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References

[1] Ranganathan S 2003 Curr. Sci. 85 pp1404-1406
[2] Tang Z, Huang L, He W and Liaw P K 2014 Entropy 16 pp 895-911
[3] Mary J, Nagalakshmi R, Rajendran S and Epshipha R 2014 Eur. Chem. Bull 3 pp 1031-1035
[4] Chou Y L, Wang Y C, Yeh J W and Shih H C 2010 Corr. Sci. 52 pp 3481–3491
[5] Liu Z, Zeng J and Zhan H 2012 Appl. Mech. Mater. 117-119 pp 1816-1819