学 位 論 文 内 容 の 要 旨

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学 位 論 文 題 名

Oxidation behavior and irradiation effects of Co-free FCC high entropy alloys for nuclear application
(原子力用 Co フリー FCC ハイエントロピー合金の酸化挙動と照射効果)

The research and development of advanced nuclear power systems are critically important for achieving the goals of carbon neutrality by 2060. Generation IV reactors such as supercritical water-cooled reactors (SCWR) and gas-cooled fast reactors (GFR) require much higher outlet temperatures (550-850 ℃) and radiation doses (up to 100-200 dpa), which are out of the tolerance limits of the current austenitic stainless steels and ferritic/martensitic steels. New structure materials with high corrosion and irradiation resistance are urgently required for extended use at high temperatures and high doses. Co-free high entropy alloys (HEA) attract many concerns due to the reduced radioactivity and high-temperature stability, which could be one of the candidate materials for next-generation nuclear reactor components. This dissertation contains research work attempting to develop Co-free Cu-containing HEAs and evaluate their oxidation and irradiation resistance by comparison with traditional alloys. Experimental methods have been conducted to investigate the steam oxidation behavior and irradiation induced degradation of the alloys.

First of all, a group of Co-free concentrated solid solution alloys (CSSA): CuNi, CuNiFe, $Cu_{0.3}CrFeNi$ and $Al_{0.4}CrCuFeNi_2$ HEAs were successfully prepared by arc melting, followed by solution annealing process to obtain simple FCC structure. The alloys were oxidized in the atmospheres containing water vapor at 500, 600, and 700 ℃ for 25 h to evaluate the oxidation performance. The oxidation of all alloys indicated parabolic behavior, and those appeared to have better corrosion resistance than 316 SS. The parabolic rate constant increased with increasing temperature. Cross-sectional electron probe microanalysis (EPMA) and X-ray diffraction (XRD) results revealed that the addition of Cr and Al significantly improved the oxidation resistance of the alloys. $Al_{0.4}CrCuFeNi_2$ showed the best oxidation resistance in this study due to the formation of protective Cr_2O_3 and Al_2O_3 scale.

Secondly, in order to understand the effect of Al content on the oxidation resistance of HEAs, three FCC-typed $Al_xCrCuFeNi_2$ HEAs (x = 0.2, 0.4, 0.6) with increasing Al concentration were selected to investigate the steam oxidation behavior at 700 ℃ for 100 h. The mass gain of the alloy decreased with Al content increased. $Al_{0.2}CrCuFeNi_2$ HEA showed two-stage oxidation kinetics with an initial fast-growing stage before 25 h and a slow-growing stage within 100 h, while $Al_{0.4}CrCuFeNi_2$ and $Al_{0.6}CrCuFeNi_2$ HEAs showed single parabolic rate constants. Detailed analysis by XRD, EPMA and scanning transmission electron microscope (STEM) indicated that the lower Al in $Al_{0.2}CrCuFeNi_2$ alloy led to a discontinuous Al_2O_3 distribution and much thicker Fe-Ni rich spinel oxides formation. By increasing Al content, the oxide scale thickness decreased significantly by the establishment of continuous external Cr_2O_3 and Al_2O_3 oxide scales. The analysis of short-term oxidation indicated that the early formation of continuous Al_2O_3 scale in the initial stage of oxidation contributes to the enhanced oxidation resistance of high Al content alloys.

At last, the irradiation induced defects and hardening of $Cu_{0.3}CrFeNi$ and $Al_{0.4}CrCuFeNi_2$ HEAs with comparison of 316L SS was evaluated by ion irradiation at 300 ℃. The surface morphology acquired by atomic force microscope shows a decrease in step height from 7.2 nm in 316L to 4.6 nm in $Cu_{0.3}CrFeNi$ after irradiation, indicating a lower surface swelling of HEA. Nano-indentation experiments at 250 nm depth showed that $Al_{0.4}CrCuFeNi_2$ HEA exhibit lower irradiation hardening (0.8GPa) than 316L (1.5GPa), while the continuous stiffness measurement indicated a comparable hardening of HEAs with 316 SS. Transmission electron microscope (TEM) observations of the Frank loops suggested the HEAs have similar averaged Frank loop number density (ND) with 316L in the whole damage region. However, 316L tends to show a higher ND than HEAs in a shallower depth, which contribute to the higher irradiation hardening tested by 250 nm depth indentation. The measured hardening and corresponding defect microstructure indicated a comparable irradiation resistance of $Cu_{0.3}CrFeNi$ and $Al_{0.4}CrCuFeNi_2$ HEAs with 316L in current irradiation condition.

This study indicated that Co-free $Al_xCrCuFeNi_2$ HEAs possess outstanding oxidation resistance at high temperatures and comparable irradiation resistance with conventional stainless steels, which could be potential candidate materials for advanced nuclear reactors.