学 位 論 文 内 容 の 要 約

Summary

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学 位 論 文 題 名

Title of dissertation submitted for the degree

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)

Global warming is one the most serious problem to humanity. To achieve the goals of carbon neutrality by 2050, a major changing of the energy supply system is needed. Nuclear energy is considered to be a zero-CO_2 emission energy source, which could replace the consumption of fossil fuel energy sources economically in a sustainable way. Currently, the commercial applied reactors are mainly Generation II or Generation III light water reactors. With the fast-growing demand of global electricity, developing new advanced reactors with higher efficiency, longer lifetime and enhanced safety aroused much concern. Generation IV reactors such as supercritical water-cooled reactors (SCWR) and gas-cooled fast reactors (GFR) require much higher outlet temperatures (550-850 °C) 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.

The objective of this study is to develop Co-free Cu containing HEAs and evaluate the oxidation resistance and irradiation effect at high temperature and irradiation dose as potential candidate materials for advanced reactors. The formation of protective Al_2O_3 scale is expected on the surface of $Al_xCrCuFeNi_2$ HEAs to improve its oxidation resistance. The damage microstructure and irradiation hardening effect of the alloys will be estimated with comparison of conventional alloy in order to applied on radiation conditions. So far, limited research on the development of Co-free HEAs has been conducted, especially for the evaluation of oxidation and irradiation behavior. Therefore,

the findings of the present work will provide insights into materials design and modification for high temperature nuclear applications.

In chapter 1, the materials challenges and advantages of high entropy alloys for advanced nuclear energy system were introduced. Moreover, the background and objectives of this study were illustrated.

In chapter 2, fundamental theories of high temperature oxidation and irradiation were briefly introduced, and technical methods used in this study were identified.

In chapter 3, the element effect and temperature dependence on oxidation behavior of concentrated solid solution alloys (CSSAs, CuNi, CuNiFe), HEAs ($Cu_{0.3}CrFeNi$, $Al_{0.4}CrCuFeNi_2$) and 316 SS were investigated. The alloys were successfully prepared by arc melting, followed by solution annealing process to obtain simple FCC structure. All the samples were oxidized in the atmospheres containing water vapor at 500, 600, and 700 °C for 25 h to evaluate the oxidation performance. After different durations of exposure (0, 4, 9, 16, 25 h), the mass gains of each sample were measured by using a microbalance (Sartorius, Model MC5) with 1 μg resolution. The steam oxidation experiment indicated a lower mass gain and better oxidation resistance of HEAs than normal 316 SS at 500-700 °C. The oxidation of all alloys indicated parabolic behavior, and the parabolic rate constant increased with increasing temperature. The addition of Fe significantly decreased the oxidation resistance of CuNi alloy even it contains high Ni. The element of Cr and Al is contributing to the protective scale formation in $Cu_{0.3}CrFeNi$, $Al_{0.4}CrCuFeNi_2$ HEAs. Cross-sectional electron probe microanalysis (EPMA) and X-ray diffraction (XRD) results revealed that the $Al_{0.4}CrCuFeNi_2$ showed the best oxidation resistance due to the formation of protective Cr_2O_3 and Al_2O_3 oxide scales.

In chapter 4, to evaluate the effect of Al content on the oxidation resistance, the oxidation behavior of $Al_xCrCuFeNi_2$ (x= 0.2, 0.4, 0.6) HEAs with various Al concentrations (3.9 at%, 7.6 at%, 10.5 at%) was studied at 700 °C in steam. Oxidation experiments were conducted at 700 °C in a steam oxidation equipment by flowing Ar-20 % H_2O gas mixture (Ar purity > 99.9995%) to the samples. The oxide structure and surface/cross-sectional morphology were characterized by X-ray diffraction (XRD, Rigaku SmartLab), scanning electron microscope (SEM, JSM-6510LA) and electron probe microanalysis (EPMA, JEOL JXA-8530F), respectively. Further characterization on the microstructure and chemical composition of the specimens were conducted by transmission electron microscopy (TEM, JEOL JEM-2010) and scanning transmission electron microscopy (STEM, Hitachi HD-2000). The TEM/STEM samples were picked up by focused ion beam system (FIB, Hitachi FB-2100; JEOL JIB-4601F) and milled with a thickness of about 100 nm. The results show that the mass gain of each alloy follows the order of $Al_{0.6}CrCuFeNi_2$ < $Al_{0.4}CrCuFeNi_2$ < $Al_{0.2}CrCuFeNi_2$ after 100 h oxidation. $Al_{0.2}CrCuFeNi_2$ 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 show single parabolic rate constants. The lower solute concentration of 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. Meanwhile, less Cu_2O and NiO oxide and thinner spinel oxide scales were formed on $Al_{0.4}CrCuFeNi_2$ and $Al_{0.6}CrCuFeNi_2$ HEAs. The Al content of $Al_{0.2}CrCuFeNi_2$ alloy were found to be the border line of external Al_2O_3 formation. The analysis of short-term oxidation indicates 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.

In chapter 5, the irradiation effects of $CrCu_{0.3}FeNi$ and $Al_{0.4}CrCuFeNi_2$ HEAs were evaluated by comparison with commercial 316L SS, and the irradiation hardening were correlated with the irradiated microstructure by TEM observation on FIBed samples. The specimens were irradiated with 6.4 MeV Fe^{3+} at 300 °C to a nominal damage peak of about 23 dpa using a dual-beam facility for energy science and technology (DuET) at Kyoto University. After irradiation, the surface morphology of the irradiated and unirradiated region was acquired by an atomic force microscope (AFM, Hitachi AFM400). The lower step height of irradiated and unirradiated region in CrCu0.3FeNi than 316L indicated a higher swelling resistance of HEA. Nano-indentation experiment of single depth indentation at 250 nm showed a higher irradiation hardening of 316L (1.5GPa) than $Al_{0.4}CrCuFeNi_2$ HEA (0.8GPa), while no significant difference of hardening behavior was found by continuous stiffness measurement (CSM) indentation (0-2 μm). The dark field TEM images suggest that the HEAs have similar averaged number density of Frank loop with 316L in the whole damage region. However, in a shallower depth, 316L tends to show a higher loop number density than HEAs. In deeper irradiation area, HEAs present a wider damage distribution and slightly larger amount of defects than 316L, which could be reasonable for the higher irradiation hardening tested by single depth indentation and a similar hardening behavior by CSM indentation.

In chapter 6, the main conclusions and most relevant findings of this study are summarized. This dissertation showed that Co-free $Al_{0.4}CrCuFeNi_2$ HEA 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.