学 位 論 文 内 容 の 要 旨

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学 位 論 文 題 名

Study on Cu-containing High Entropy Alloys for Nuclear Fusion Application
(核融合用の Cu 含有高エントロピー合金に関する研究)

At present, nuclear energy systems have acquired a great deal of expertise through the operation of reactors from generation I to generation III. With a performance target for the next 20 years, the next generation of water-cooled nuclear reactors has been planned to optimize the performance of superseded generations. Aspects such as life, protection, performance, and power production are necessarily related to their design and have been considered. These reactors require radiation doses of up to 100-200 displacements per atom (dpa) and outlet temperatures ranging from 550-850 ℃. The properties that the next generation of nuclear materials would possess include increased resistance to irradiation, swelling, relaxing, growth, and corrosion. No high radiation resistance austenitic stainless steels are currently eligible for extended use at high temperatures for the next generation of nuclear energy systems. High entropy alloys (HEAs) have acquired substantial interest due to their outstanding mechanical properties, good corrosion resistance, and high tolerance to irradiation. Thus, one of the candidate materials for next-generation nuclear reactor components could be FCC type HEAs.

It is noticeable that most of the reported HEAs contained cobalt. Considering a candidate HEA for nuclear application, the radioactive elements should be eliminated from the material design based on radiation shielding requirements. This dissertation contains research work attempting to prepare new face-centered cubic Co-free Cu-containing solid solution concentrated alloys, Cu, CuNi, CuNiFe, $Cu_{0.3}NiFeCr$, $Al_{0.4}CuFeCrNi_2$, and evaluate their properties. Experimental and computational methods have been employed and their microstructure, hardness, tensile strengths, and irradiation effects at 500 ℃ were investigated.

First of all, face-centered cubic Co-free Cu-containing solid solution concentrated alloys, CuNi and CuNiFe alloys of the equal molar ratio were prepared by arc-melting, and $Cu_{0.3}NiFeCr$ and $Al_{0.4}CuFeCrNi_2$ alloys were prepared by induction furnace in a high purity argon atmosphere. The investigation by X-Ray diffractometer (XRD), scanning electron microscope (SEM), and energy dispersive spectroscopy (EDS) were conducted for as-cast and annealed samples. Mechanical properties were also investigated by Vickers microhardness test and tensile test. All the as-cast alloys were identified as single-phase FCC alloys by X-ray diffraction analysis. While, the SEM observation indicated a new Cr-rich phase with Cu-rich phase in the annealed $Cu_{0.3}NiFeCr$ alloy, which is probably due to the low solubility of Cr and Cu in the alloy. After annealing at 1076 ℃ for 120 hours, $Cu_{0.3}NiFeCr$ alloy became a single-phase FCC. Mechanical property examinations indicated the severe lattice distortion in HEA has effects on mechanical properties. The general solid solution effects lead to the highest Vickers hardness and tensile strength in the $Al_{0.4}CuFeCrNi_2$.

Secondly, in order to understand the irradiation effects and the impact of the compositional complexity in Co-free high entropy alloys, high purity Cu-containing solid solution concentrated alloys, CuNi, $Cu_{0.3}NiFeCr$, $Al_{0.4}CuFeCrNi_2$ without apparent pre-existing defect sinks were conducted in-situ ion irradiation experiments with 1 MeV Krypton ion irradiation at 500 ℃ up to 1 dpa. The irradiation effects were assessed through the measurement of the defect type, defect density and defect size. The Orowan equation was applied to estimate the irradiation hardening contributed by stacking fault tetrahedra (SFT), black dot (BD) and Frank loop (FL). In-situ electron irradiation experiment showed that CuNi, $Cu_{0.3}NiFeCr$ alloys but $Al_{0.4}CuFeCrNi_2$ present SFTs. The irradiation introduced a high density of SFTs in CuNi alloy. The high entropy alloy ($Al_{0.4}CuFeCrNi_2$) had the smallest FL size (the highest density), followed by $Cu_{0.3}NiFeCr$ and then CuNi. It reported that the key parameters for the formation of SFTs and FLs are the stacking fault energy (SFE) and the shear modulus. The smaller the ratio of the SFE to the shear modulus, the easier it is to form SFT and large size FLs. The lowest density of SFTs and the smallest FL size in HEA ($Al_{0.4}CuFeCrNi_2$) can be inferred to have a large ratio of the SFE to the shear modulus. In addition, the lowest estimated irradiation hardening in HEA ($Al_{0.4}CuFeCrNi_2$) than in 316H SS indicated the potential for the nuclear application of Co-free high-entropy alloy at 500 ℃.

At last, the first-principles DFT calculations have been conducted to explore the properties and formation energies of point defects (The monovacancy and self-interstitial) in the face-centered cubic Co-free alloys, CuNi, CuNiFe, CuNiFeCr, and $Cu_{0.3}NiFeCr$. The consistency of the results of the XRD measurements and the first estimations confirms the validity of the calculation. Calculated coherent energy and formation enthalpy for CuNi, CuNi, CuNiFer, and $Cu_{0.3}NiFeCr$ alloys indicates that the face-centered Co-free alloys we have developed are stable alloys. And the strongest structural corrugation in equimolar HEA (CuNiFeCr) suggests that higher entropy is a stronger local structural disorder. Also, the computed defect energy (interstitial formation energy: E_i^f) and the vacancy formation energy: E_v^f of the Cu and Ni atoms in these alloys indicate that the different elements can have different energy effects, which may also suggest that the selection of the elements can’t be random when developing a high entropy alloy and that not all the elements can be influenced by the value of the entropy. Furthermore, DFT calculation showed that impurity effects should not be ignored when HEA was used as a nuclear reactor component because those light elements could affect microstructural evolution behaviour in HEAs.

This work has indicated that high purity Co-free Cu-containing high-entropy alloys are potential candidate materials for nuclear fusion reactors at higher operation temperatures.