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Effect of Alloying Element and Heat Treatment on Mechanical and Corrosion Property of Ni-Cr-Co-Mo Alloy at 950°C

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1. Introduction

A very high temperature reactor (VHTR) is one of the promising generation IV reactors, and can generate highly efficient electricity and produce a massive amount of hydrogen. In view of the performance of its structural materials, one of key components is an intermediate heat exchanger (IHX), which is exposed to high temperature and a coolant environment of up to 950°C. Under this harsh environment, nickel-based Alloy 617 is being considered as a promising candidate material for IHX material owing to its excellent creep resistances at high temperature, and is thereby being tried for ASME code case approval.

However, the structural integrity of the IHX material should be guaranteed for the long-term operation of nuclear power plants under VHTR operating conditions.

Helium is used as a coolant in a VHTR owing to its high thermal conductivity, inertness, and low neutron absorption. However, helium inevitably includes impurities that create an imbalance in the surface reactivity at the interface of the coolant and the exposed materials.

The carbon monoxide, methane, hydrogen, and water that are formed by the reaction with the graphite in the core induce various surface reactions that lead to material property changes over time [1]. According to previous reports [2,3] it was predicted that the outer oxide layer thickness, internal oxide depth, and carbide-depleted zone depth increase to 116 μm, 600 μm, and 1000 μm, respectively, when Alloy 617 is exposed to a plausible impure helium environment at 950°C for 20 years, based on the reaction rate constant determined from the short time experiment. These values are large enough to pay attention to the material degradation at high temperature, i.e., the life of the IHX. Therefore, finding the range of impurity concentration at which the material is stable, based on the thermodynamics and kinetics determined by a long-term experiment, is very important to the optimum chemistry control for a life extension.

Another countermeasure is to improve the material performance through alloy development. Commercial nickel-based wrought alloy is strengthened by a solid solution and precipitation hardening mechanism in a wide temperature range of 500 to 900°C. The γ' significantly contributes to the strengthening by forming an anti-phase boundary and preventing a dislocation motion at an intermediate temperature range of 700 to 800°C, but is no longer stable above this temperature range [4]. However, the material for an IHX needs to fulfill the mechanical property requirements in a narrow, very high temperature range of 850 to 950°C rather than in a wide temperature range.

Therefore, it is worth making the effort to find an optimum combination of alloying elements and processing parameters showing the best performance. In this work, the mechanical and corrosion properties for nickel-based alloys fabricated in a laboratory were evaluated as a function of the alloying element composition and heat treatment.

2. Experimental

A Ni-based alloy whose main alloy elements are Cr, Co, and Mo was melted by VIM (vacuum induction melting), followed by homogenization at 1200°C for 20 hrs and hot rolling in a temperature range of 1050 to 1150°C. The hot rolling pass and thickness reduction ratio are 3 and 50%, respectively. A subsequent solution annealing, followed by additional heat treatment in the range of 1020 to 1140°C, was conducted at 1175°C. Cooling was conducted using water.

A tensile test for the specimen shown in Fig. 1 was carried out in air at 950°C with a straining rate of 1 mm/min. Prior to the tensile test, a test temperature of 950°C (±2°C accuracy) was attained by an elevation up to 900°C at a rate of 10°C/min, and then 950°C at a rate of 5°C/min, followed by 1 hr stabilization. A corrosion test was performed in air at 950oC up to 250hrs. After the corrosion test, the weight and microstructural changes were observed.

An SEM (scanning electron microscopy, JEOL JSM-6300, Japan) was used to observe the microstructures and analyze the composition of the specimens. An electron back-scatter diffraction (EBSD, Oxford, INCA crystal) analysis was performed on the JEOL JSM-7000F. The specimens were prepared by grinding up to #1500 emery paper and polishing up to 0.3μm alumina powder, followed by etching in 50ml HCl + 2ml H_2O_2 for several seconds.

The precipitate in the matrix was analyzed using a field emission TEM (transmission electron microscopy), equipped with an EDS (JEM-2100F, JEOL).

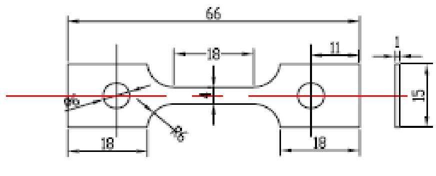
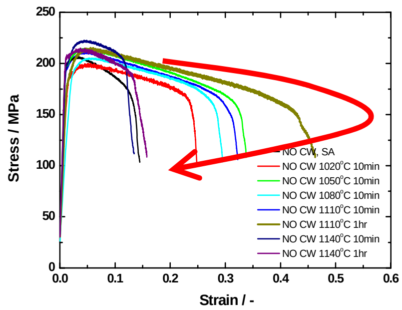


Fig. 1. Schematic drawing of system design.

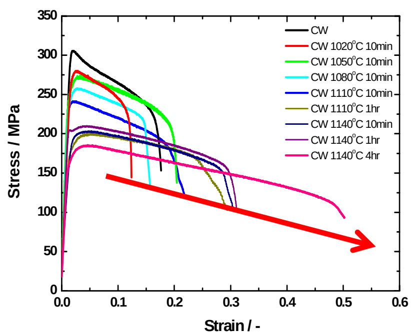
3. Results and discussion

Fig. 2 shows the stress-strain curves at 950°C in air obtained for (a) subsequent heat-treated specimens and (b) cold worked specimens, followed by subsequent heat treatment after solution annealing as a function of subsequent heat-treatment temperature. The tensile stress was decreased with strain. At a very high temperature, the dislocation recovery is dominant, compared to strain hardening causing a stress decrease with elongation.

In the case of additionally heat treated specimens, the yield and tensile strengths are similar, irrespective of the heat treatment condition. The ductility increased with the heat treatment temperature and then drastically decreased at 1140°C almost to elongation to a rupture of the solution annealed specimen. From the experimental results, it is reasonable that the grain boundary is effectively strengthened up to 1110°C. It seems that the abrupt decrease at 1140°C is related to a loss of carbide stability at the grain boundary. Carbide can harden the material based on the precipitation hardening mechanism. However, the carbon content and carbide forming elements such as Cr and Mo are decreased in the matrix owing to carbide formation, leading to a decrease of the solid solution hardening effect. By a balancing of the precipitation hardening and solid solution hardening mechanisms, the yield and tensile strengths are almost the same, irrespective of the heat treatment condition.



(a)



(b)

Fig. 2. Stress-strain curves at 950°C in air obtained for (a) heat treated specimens and (b) cold working + heat treated specimens after solution annealing as a function of subsequent heat treatment temperature.

Unlike additional heat-treated specimens, the cold worked specimens followed by subsequent heat treatment show a different behavior. The yield and tensile strengths are decreased with the heat treatment temperature. The ductility increased with the heat treatment temperature continuously up to 1140°C. A decrease of strength is caused by a combination of the dislocation removal, carbide precipitation hardening, and lowering of the solid solution hardening. It is notable that the ductility increased without a drastic decrease, as shown in Fig. 5(a). At 1110°C for 1hr, the ductility for the specimen without cold working was at maximum and larger than that for the specimen with cold working, while the ductility for the specimen without cold working was smaller than the ductility for the specimen with cold working at 1140°C. It is conceivable that carbide stability is improved by cold working.

Mo was beneficial to high-temperature ductility while Cr was detrimental to high-temperature ductility. This was differentiated from the carbide composition. Co seems to modify carbide leading to mechanical property change at 950°C. A high-temperature ductility of 76% was achieved by combination of alloying element and heat treatment without a significant loss of yield strength or tensile strength, which is comparable to commercial Ni-based superalloy. However, it was found that there is a drawback on the corrosion rate. Surface oxide was detached during the corrosion test, not protecting corrosion. Aluminium seems to act as an anti-corrosive role in Ni-based alloy.

4. Summary

Elongation to rupture was increased by additional heat treatment and cold working, followed by additional heat treatment in a temperature range of 1020 to 1110°C where carbide is stable, indicating that the intergranular carbide contributes to the grain boundary strengthening.

The temperature where the carbide decorates the grain boundary effectively increased for the CW specimen, indicating that carbide stability was increased by the cold working. This was discussed with the difference in carbide formation kinetics between no CW and CW specimens.

The mechanical property and corrosion property were evaluated as a function of the main element composition. The ductility was increased and decreased by increasing Mo and Cr, respectively.

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