Ni-based Superalloy Development for VHTR - Methodology Using Design of Experiments and Thermodynamic Calculation

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1. Introduction

The highly efficient generation of electricity and the production of massive hydrogen are possible using a very high temperature gas-cooled reactor (VHTR) among generation IV nuclear power plants. The structural material for an intermediate heat exchanger (IHX) among numerous components should be endurable at high temperature of up to 950°C during long-term operation [1]. Impurities inevitably introduced in helium as a coolant facilitate the material degradation by corrosion at high temperature [2]. This work is concerning a methodology of Ni-Cr-Co-Mo based superalloy developed for VHTR using the design of experiments (DOE) and thermodynamic calculations.

2. Alloy design and thermodynamic calculation

A total of 32 sets of the Ni-based superalloys with various chemical compositions were formulated based on a fractional factorial design of DOE [3]. The range of the chemical compositions of the designed alloys was selected to be 22–24 wt% of Cr, 11.5–17.0 wt% of Co, 10–12 wt% of Mo, 0–0.5 wt% of W, 0–1 wt% of Ta, and 0.08–0.12 wt% of C. Ta and W were added to improve the mechanical properties of the alloys by a solution hardening process, but Al and Ti, which are known to promote the precipitation of γ' phase (Ni_3Al), were excluded because the γ' phase is not thermodynamically stable above 800 °C.

The thermodynamic stabilities of topologically close-packed (TCP) phases of the alloys were calculated in the temperature range of 600 to 1400 °C using THERMO-CALC software [3]. TCP phases such as σ, μ, and Laves are known to deteriorate the structural integrity of the alloys by reducing their ductility during long-term operation at high temperature [4]. The effects of alloying elements on the stability of TCP phases at 950 °C (the maximum operating temperature of the structural materials for IHX) were analyzed statistically using MINITAB software. Based on the calculations, 16 sets of alloy designs were selected, and mechanical properties such as the yield strength (YS, 0.2% offset) and ultimate tensile strength (UTS) of the alloys at 25 and 950 °C were estimated using JMATPRO software. Considering the thermodynamic stability of the TCP phases and the mechanical strengths, the optimized chemical composition of the alloy as a new material for IHX was proposed using MINITAB software.

3. Results and discussion

Fig. 1 shows the mass fraction of thermodynamically stable phases of one of the alloy designs (Cr 24 wt%, Co 17.0 wt%, Mo 12 wt%, W 0.5 wt%, C 0.08 wt%) as a function of temperature calculated using THERMO-CALC software. The precipitation of the γ' phase was not found as expected, and $M_{23}C_6$ carbide is stable over the maximum operating temperature of 950 °C. The mass fraction of TCP phases tends to decrease with increasing temperature, but the μ phase is still present in a small amount at 0.7 wt% (0.007 as mass fraction).

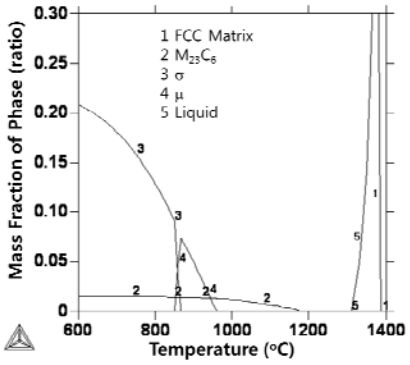

Fig. 1. Mass fraction of thermodynamically stable phases of the superalloy with the chemical composition of 24 wt% Cr, 17 wt% Co, 12 wt% Mo, 0.5 wt% W and 0.08 wt% C calculated as a function of temperature [3].

To find a way to minimize the mass fraction of detrimental TCP phases in the alloy design, the effect of alloying elements was evaluated from the statistical analysis of the mass fraction of TCP phases in 32 sets of alloy designs using a half factorial design of DOE. From the normality test results with a 95% confidence interval, it was revealed that the main effect of Cr, Co, Mo, W and Ta, except C, did not follow the normality, that is, they affect the mass fraction of the TCP phases.

Fig. 2 presents the main effect plots of alloying elements on the mass fraction of the TCP phases at 950 °C. To avoid the precipitation of TCP phases during long-term operation, the composition of Cr, Co, Mo, W and Ta should be reduced within the range designed in this work. However, it is well known that those alloying elements improve the mechanical properties at high temperature by a solution hardening process. To verify their effect, the mechanical properties of the alloys at 950 °C were calculated using JMATPRO software.

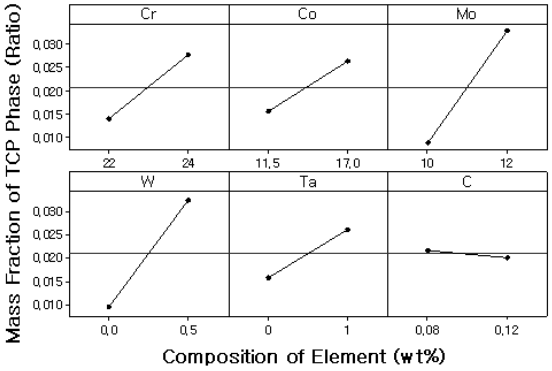

Fig. 2. Main effect plots of alloying elements on mass fraction of TCP phase in the alloys at 950°C [3].

Fig. 3 gives the main effect plots of the alloying elements on the UTS of the alloys at 950 °C. It was obvious that Cr, Co, Mo, and W improve the mechanical properties at high temperature, possibly owing to the solution hardening, while Ta reduces these properties within the range designed in this work.

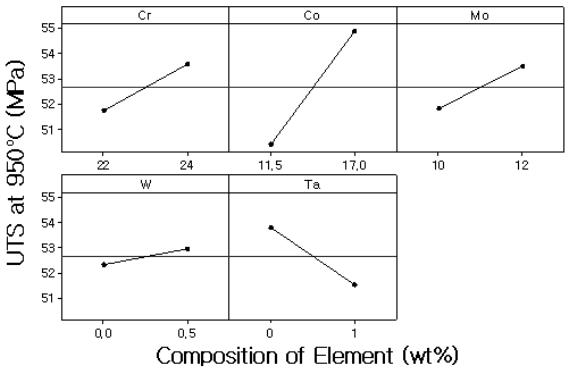

Fig. 3. Main effect plots of the composition of alloying elements on UTS at 950 °C [3].

Considering the thermodynamic stability of the TCP phases and mechanical strengths, the chemical composition of the alloy as a new material for IHX was optimized using MINITAB software. Fig. 4 shows an example of the optimization process, under the specific condition that the mass fraction of the TCP phases at 950 °C was set as 0 in the target value with an allowable range below 0.05, YS at 25 °C was set as 450 MPa with an allowable range above 400 MPa, UTS at 25 °C was set as 850 MPa with an allowable range above 800 MPa, and both YS and UTS at 950 °C were set as 55 MPa with an allowable range above 50 MPa. It was estimated that the alloy with a chemical composition of 22.7 wt% Cr, 17.0 wt% Co, 12.0 wt% Mo, 0.4 wt% Ta and 0.08 wt% C was the optimized one to satisfy the desired performance for the IHX materials of a VHTR .

4. Conclusions

In this work, to develop novel structural materials for the IHX of a VHTR, a more systematic methodology using the design of experiments (DOE) and thermodynamic calculations was proposed. For 32 sets of designs of Ni-Cr-Co-Mo alloys with minor elements of W and Ta, the mass fraction of TCP phases and mechanical properties were calculated, and finally the chemical composition was optimized for further experimental studies by applying the proposed methodology.

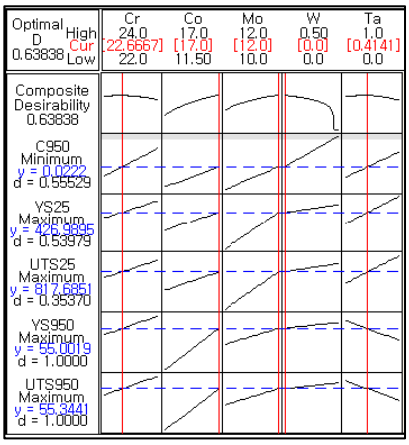

Fig. 4. Optimization plot of chemical composition of a superalloy design having the desired performance for IHX materials of VHTR [3].

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