

Designing Ni-base superalloys for an electrolytic reduction process of a spent nuclear fuel

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1. Introduction

The electrolytic reduction of a spent oxide fuel and a UREX+1a product or a spent advanced burner reactor oxide fuel involves the liberation of oxygen in a molten LiCl electrolyte, which results in a chemically aggressive environment that is too corrosive for most typical structural materials. In addition, the Uranium and TRU components in the reduced spent oxide fuel and UREX+1a products may form eutectics and liquid phases during a reduction process that increases the potential for a corrosion of the cell cathode. Even so, the electrochemical process vessel, structural cell components, and the electrical supply materials must each be resilient in the presence of oxygen, TRU and molten salt components, and various impurities at ~650°C to enable high processing rates and an extended service life.

Hence, the objective of this study is to develop advanced structural materials that will contribute toward the implementation of a new advanced technology for the electrolytic reduction of a spent oxide nuclear fuel and a UREX+1a product or a spent advanced burner reactor oxide fuel in a molten salt electrolyte. This study includes the modification of commercial alloys for a better corrosion resistance to an oxidative environment of a molten salt containing fuel elements.

2. Experimental and Results

Pseudo binary phase diagrams were constructed by using a commercial thermodynamic database, FACTSage, in order to understand the phase stability of the Ni-Cr-Al-Si-Nb alloy system as shown in Fig. 1.

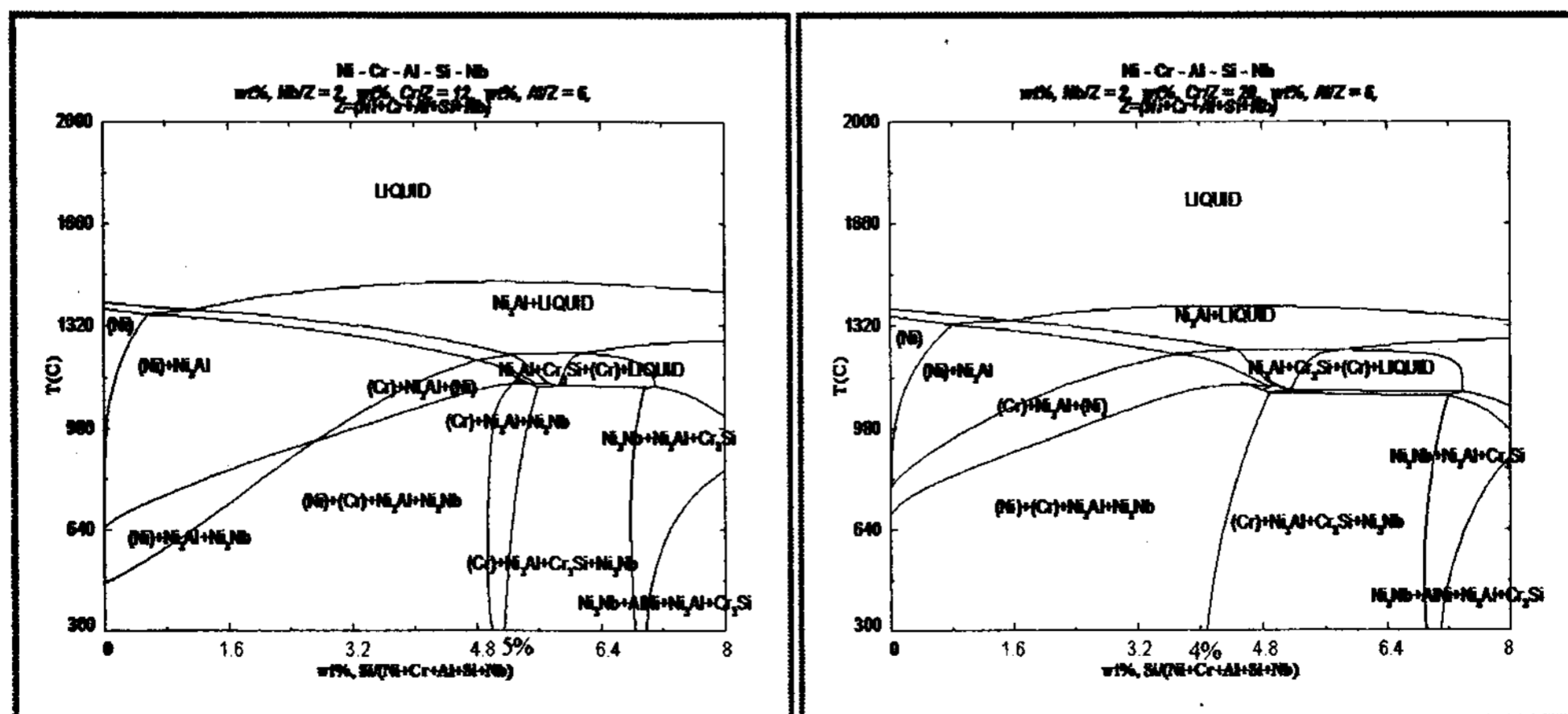


Fig. 1. Effect of the chromium content on the phase equilibria of the (Ni-Cr-Al-Nb)-Si pseudo binary phase diagrams

From the thermodynamic analysis results, commercial 713LC was modified with silicon and chromium. And a trace amount of zirconium and yttrium was added to observe the corrosion behavior change.

For the corrosion test, LiCl-Li₂O molten salt was introduced into the MgO test crucible at room temperature and then heated at 300 °C for 3 hrs in an Ar atmosphere to prevent any moisture pick-up. After reaching the set corrosion condition, the samples and alumina tube (6Φ) were immersed into the molten salt, and mixed gas was supplied thorough an alumina tube. The test condition is shown in Table 1. When the test was completed, the corrosion products were removed from the molten salt and cleaned by an ultrasonic washing. After a drying for more than 24 hrs, the weight variation was measured. The corrosion products and fine structures of the corroded samples were analyzed by XRD (X-ray Diffractometer, Rigaku, DMAX/1200), SEM (Scanning Electron Microscope, Jeol, JSM-6300), and EDS (Energy Dispersive X-ray Spectroscopy, Jeol, JSM-6,300).

Table. 1. The corrosion test conditions

| | | | |
|-------------|----------------------|----------------|--------------------------------|
| Temperature | 650 °C | Salt | LiCl-3wt.% Li ₂ O |
| Test Time | 1, 3, 7, 9 day | Test vessel | MgO |
| Gas Sparge | Ar-10%O ₂ | Gas Inlet Tube | Al ₂ O ₃ |

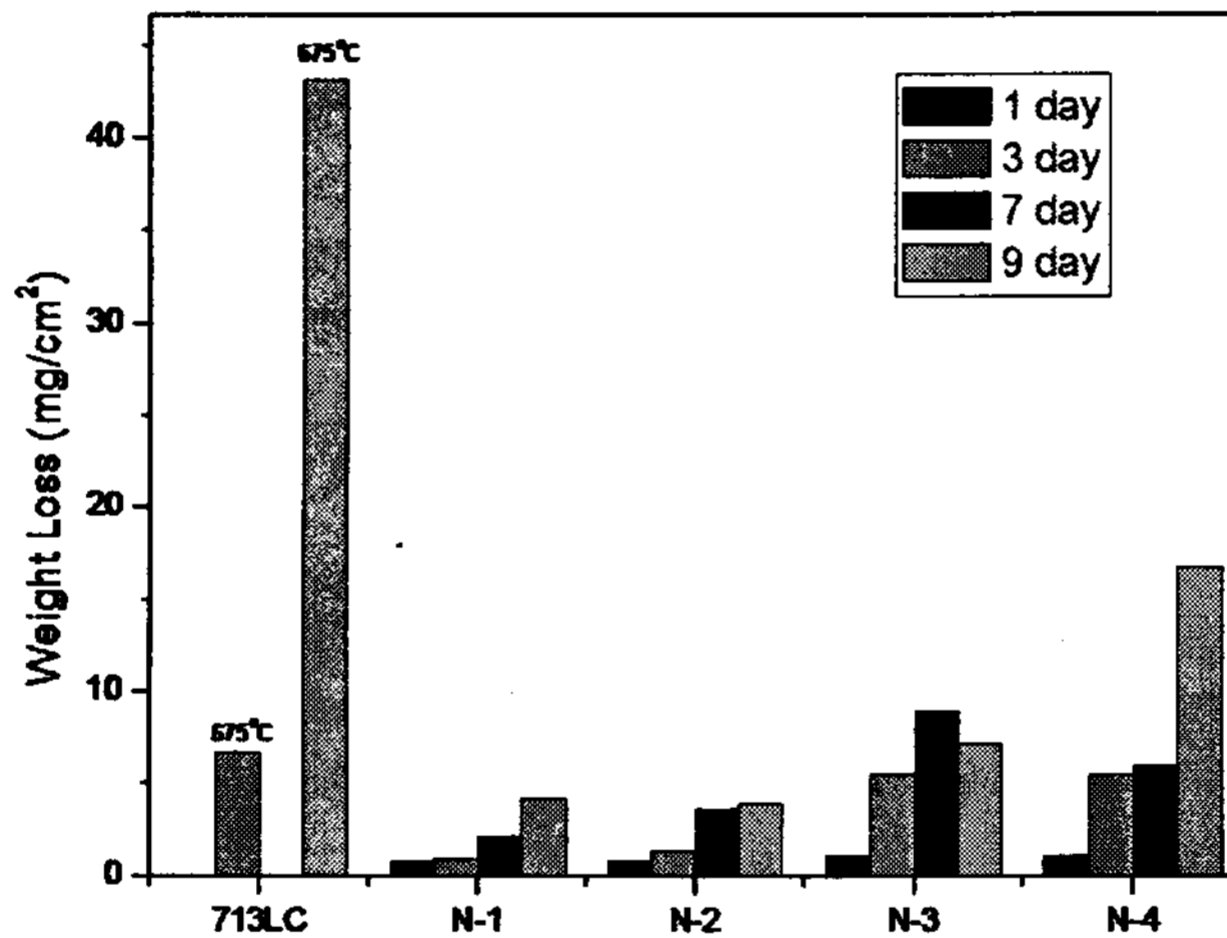


Fig. 2. Weight loss of the alloys corroded at 650 °C as a function of the time

Figure 2 shows the weight loss of the alloys corroded at 650 °C as a function of the time. The weight loss is drastically decreased when compared to the commercial 713LC. Especially the weight loss of sample numbers 1 and 2 are below 5 mg/cm² for the 9 days experiment. The corrosion resistance of a structural material is mainly dependent on the condition of the protective oxide layer. So, the corrosion products which were obtained during the cleaning step of the adhered salt were analyzed by XRD. The corrosion products of sample number 2 are mainly composed of NiO, metallic nickel, nickel chromium oxide spinel and chromium oxide as shown in Fig. 17. Aluminum and silicon oxides which are one of the alloying elements were not found among the corrosion products. This may imply that the oxide phases containing aluminum and silicon were retained in the oxide layer.

3. Conclusion

The research results show that the corrosion rates of the newly designed alloys were drastically decreased when compared to that of the commercial Inconel 713LC and a four times lower corrosion rate, 0.3 mm/yr was achieved. It was found that Si, Cr and Al diffused to the surface and formed a protective oxide layer, thus inhibited an internal intrusion of the oxygen ion.