The Oxidation of Ni-Base Alloys –Thermodynamic Modeling and Calculations

Hans J. Seifert
University of Florida
Department of Materials Science and Engineering
PO Box 116400
Gainesville FL 326111-6400, USA

The oxidation characteristics of numerous Ni-base superalloys, bond coats and overlays have been experimentally investigated over the past decades. The oxidation products of such multi-component alloys depend on the chemical composition and microstructure of the alloys, the physico-chemical environmental conditions and kinetic parameters.

Computational phase studies according to the CALPHAD (CALculation of PHAse Diagrams) approach can contribute to the understanding of the complex oxidation mechanisms of Ni-base alloys. The development of the thermodynamic models has been intensive for the last 25 years when computer software started to be used for complex equilibrium and phase diagram calculations. In view of this progress in calculating phase equilibria, research programs were started to develop thermodynamic databases for the description of alloy oxidation in Ni-Cr-Al based systems.

The thermodynamic modeling requires basic experimental thermodynamic and crystallographic data for the binary and ternary subsystems. These data and experimental phase diagram information are used to adjust model parameters of the analytical descriptions for the Gibbs free energies (thermodynamic optimization). The descriptions for all phases and gas species in a system are combined in thermodynamic databases and can be used for extrapolating multi-component calculations. It facilitates calculations of phase equilibria and thermodynamic functions under conditions not previously subjected to experimental investigations.

Metallic and oxide phases with significant ranges of composition appear in Ni-base systems. To describe the thermodynamic properties of both the metallic and the oxide solution phases, thermodynamic models based on their crystal structures are used [1,2]. The Gibbs free energy of the phases vary with the solid solution composition and the accompanied crystallographic site occupancies of the compound species.

Solution phases in Ni-base systems were treated by the modified quasichemical model or the sublattice model described in the compound energy formalism [3]. The modeling requires descriptions of the solution phases in the binary and ternary sub-systems. The phase diagram calculations in the quaternary Ni-Cr-Al-O system include the ceramic sub-systems Al_2O_3-Cr_2O_3, Al_2O_3-NiO, Cr_2O_3-NiO and Al_2O_3-Cr_2O_3-NiO. Gibbs free energies descriptions of the oxide solution phase $(Al,Cr)_2O_4$ and the partially inverse spinel phase $Ni(Al,Cr)_2O_4$ are developed. This spinel phase can be described with the sublattice description $(Ni^{2+},Al^{3+})(Ni^{2+},Al^{3+})_2(Va)_2(O^{2-})_4$. With such a description the temperature dependent grade of inversion (Al^{3+} fraction on tetrahedral positions) can be calculated. With increasing temperature the cations approximate a statistical distribution.

The thermodynamic datasets allow the calculation of all types of phase diagrams, phase fraction diagrams and phase composition diagrams. These diagrams are used for the discussion of the various aspects of the oxidation processes of Ni-base alloys. Most recently the morphology changes in the oxide layer during the oxidation process of binary and ternary nickel alloys at 1100 °C was described under simplifying assumptions as a sequence of local phase equilibria [4]. The results are in good agreement with experimental data.

References

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