The thermodynamic database of ZrO_2-Gd_2O_3-Y_2O_3-Al_2O_3 system for TBC applications

The database was developed in Max-Planck-Institute Institute for Metal Research

Contact persons: O. Fabrichnaya, Ch. Wang, M. Zinkevich

Content

I. Application of TBC database

The system ZrO_2-Gd_2O_3-Y_2O_3-Al_2O_3 presents interests for different fields of technology. The yttria stabilised zirconia (YSZ) has various industrial applications [04Che, 04Fab]. For example, phase with fluorite structure is used as a solid electrolyte [93Min]. Tetragonal phase with 6-8 wt. % Y_2O_3 is used as thermal barrier coating (TBC) on metal substrate [04Lev]. Co-doping of traditional YSZ by Gd enhances an insulating efficiency of thermal barrier system (TBC). Rebollo et al. [03Reb] found that metastable tetragonal phase t' stabilized by Gd alone is less resistant to partitioning at high temperature than its Y counterpart with the same amount of stabilizer. However, modest substitution of Gd for Y does not degrade the stability and may improve it in some cases. Materials, based on co-doping of zirconia with Y and Gd, are of interest as possible new TBC [02Nic, 04Por]. The pyrochlore structure formed in the ZrO_2-Gd_2O_3 system is also of interest as alternative material for TBC [02Wu, 04Lev]. However, the $Gd_2Zr_2O_7$ pyrochlore is prone to interact with TGO forming perovskite structure which results in TBC failure [04Lev]. New TBC based on double-layer systems with first layer of YSZ and a top layer made of pyrochlore materials shows better performance at high temperature than one-layer YSZ [04Lev, 04Vas]. The multilayer coating $Y_3Al_5O_{12}$ (YAG)/YSZ is suggested to enhance bond coat oxidation resistance. A thin layer of α-Al_2O_3 (thermally grown oxide, TGO) forms between metallic bond coat (BC) and TBC in the process of thermal cycling. Therefore, phase relations in the ZrO_2-Gd_2O_3-Y_2O_3-Al_2O_3 system are important to understand the interactions

between TBC and TGO, stability issues of TBC materials and interactions within multilayer TBC.

The thermodynamic database for the ZrO_2-Gd_2O_3-Y_2O_3-Al_2O_3 system is developed to calculate equilibria at temperatures 298-3000 K. To assess thermodynamic parameters, experimental data on phase equilibria at temperatures 1100-3000 °C have been used along with different kind of calorimetric measurements and vapour pressure data. Since high temperature data were used to develop this database the results of calculations are reliable at 1100-3000 °C, while extrapolation to lower temperature could result in uncertainty. The T^0-lines for diffusionless transformations e.g., Fluorite=Tetragonal can also be calculated using this database. Also driving forces for partitioning of non-equilibrium phase to equilibrium assemblage can be calculated. User should be cautious when calculating phase relations in the Gd_2O_3-Y_2O_3-Al_2O_3 system, because the experimental data are not available for this ternary system. The database should not be used to calculate equilibria in metallic, metal-oxygen systems and those involving gas phase.

II. Phase modelling

Most of the phases stable in the system are solid solutions and they are described by compound energy formalism. Liquid phase is described by two-sublattice partially ionic liquid model. Two phases, δ-$Zr_3Y_4O_{12}$ and corundum Al_2O_3, are assumed to be stoichiometric compounds. The models of phases are presented in Table 1.

Table 1. Phases stable in the ZrO_2-$GdO_{1.5}$-$YO_{1.5}$-$AlO_{1.5}$ system

Phase	Database name	Model
Fluorite-ZrO_2 Tetragonal-ZrO_2 Monoclinic-ZrO_2	FLUORITE TETR MONO	$(Gd^{+3},Y^{+3},Al^{+3},Zr^{+4})_1(O^{-2},Va)_2$
Cubic-C Monoclinic-B Hexagonal-H	M2O3C M2O3B M2O3H	$(Gd^{+3},Y^{+3},Zr^{+4})_2(O^{-2},Va)_1(O^{-2})_3$
Hexagonal-A Cubic-X	M2O3A M2O3X	$(Gd^{+3},Y^{+3})_2(Va)_1(O^{-2})_3$
δ-$Zr_3Y_4O_{12}$ α-Al_2O_3	ZR3Y4O12 CORUNDUM	$(Zr^{+4})_3(Y^{+3})_4(O^{-2})_{12}$
Pyrochlore-$Gd_2Zr_2O_7$	OPYRO	$(Gd^{+3},Zr^{+4})_2(Zr^{+4},Gd^{+3})_2(O^{-2},Va)_6(O^{-2})_1(Va,O^{-2})_1$
Monoclinic-LnAM Perovskite-LnAP Garnet-LnAG	MAM MAP MAG	$(Gd^{+3},Y^{+3})_4(Al^{+3})_2(O^{-2})_9$ $(Gd^{+3},Y^{+3})_1(Al^{+3})_1(O^{-2})_3$ $(Gd^{+3},Y^{+3})_3(Al^{+3})_5(O^{-2})_{12}$
Liquid	IONIC_LIQ	$(Gd^{+3},Y^{+3},Zr^{+4})_P(O^{-2},AlO_{3/2})_Q$

III. State of validation

III.1. Oxides (Al_2O_3, ZrO_2, Y_2O_3, Gd_2O_3)

The thermodynamic data for pure oxides are accepted for Al_2O_3 from [93Hal], ZrO_2 and Y_2O_3 from [04Fab] and Gd_2O_3 from [05Lak1]. A small deviation from stoichiometry in oxide phases in the system of Zr-O [04Wan] and Y-O [98Swa] is not taken into account.

III.2. Binary systems (ZrO_2-Y_2O_3, ZrO_2-Gd_2O_3, ZrO_2-Al_2O_3, Gd_2O_3-Al_2O_3, Y_2O_3-Al_2O_3, Gd_2O_3-Y_2O_3)

The assessment of thermodynamic parameters in the ZrO_2-Y_2O_3 system based on phase equilibrium data, calorimetric measurements and vapour pressure data is described in [05Fab1]. The ZrO_2-Gd_2O_3 and Gd_2O_3-Al_2O_3 thermodynamic descriptions were derived in [05Lak1] based on phase equilibrium data and calorimetric measurements. The descriptions of ZrO_2-Al_2O_3 and Gd_2O_3-Y_2O_3 systems ([05Lak1] and [05Fab1] respectively) are based on phase equilibrium data only and therefore they are less reliable. The thermodynamic parameters of system were re-assessed in [04Fab] using phase equilibrium data and calorimetric measurements. It should be also mentioned that the descriptions of the ZrO_2-Y_2O_3 and ZrO_2-Gd_2O_3 systems were checked for consistency with tie-lines in ternary systems ZrO_2-Y_2O_3-Al_2O_3 and ZrO_2-Gd_2O_3-Al_2O_3.

III.3. Ternary systems (ZrO_2-Y_2O_3-Al_2O_3, ZrO_2-Gd_2O_3-Al_2O_3, ZrO_2-Gd_2O_3-Y_2O_3, Gd_2O_3-Y_2O_3-Al_2O_3)

The thermodynamic database for the ZrO_2-Gd_2O_3-Al_2O_3 system was derived by combining binary descriptions. The ternary parameter for liquid phase was assessed to fit experimental liquidus surface [05Lak1]. The calculated isothermal sections are in reasonable agreement with experimental data [05Lak1, 05Lec]. The thermodynamic database for the ZrO_2-Y_2O_3-Al_2O_3 system was derived by combining binary descriptions [05Lak2]. The ternary parameter for liquid phase was assessed to fit experimental liquidus surface [97Lak]. The calculated isothermal sections are in reasonable agreement with experimental data [05Lak2]. The calculated isoplethal sections are in reasonable agreement with experimental data of [97Lak] except for high temperature liquidus data. The thermodynamic database for the ZrO_2-Gd_2O_3-Y_2O_3 system was derived by combining binary descriptions in [05Fab1]. The calculated isothermal sections in the range 1473-1873 K were checked experimentally [05Fab1]. According to calculations liquidus surface of this system contains only one invariant point at 2589 K. Experimental data for liquidus surface are not available and ternary interactions in liquid are assumed to be zero. The thermodynamic database for the Gd_2O_3-Y_2O_3-Al_2O_3 system was derived by combining binary

descriptions in [05Fab2]. It is assumed that YAM and GAM and YAP and GAP form complete series of solid solutions LnAM and LnAP respectively, while YAG has limited solubility of $Gd_3Al_5O_{12}$ forming LnAG solid solution. The experimental data for the Gd_2O_3-Y_2O_3-Al_2O_3 system is not available so far. The calculated liquidus surface is in agreement with prediction of Lakiza [05Fab2].

III.4. Quaternary system

The thermodynamic database for the ZrO_2-Gd_2O_3-Y_2O_3-Al_2O_3 system was derived by combining ternary descriptions in [05Lak1, 05Lak2, 05Fab1, 05Fab2]. Experimental data are not available for this system. However, if binary extrapolations give good agreement with experimental data in ternary system [05Lak1, 05Lak2, 05Fab1] it is assumed that extrapolations to quaternary system will give realistic results too.

IV. References

[93Min] N.Q. Minh, Ceramic fuel cells. J. Am. Ceram. Soc. 76 (1993) 563-588.

[93Hal] Hallstedt, B., Thermodynamic calculation of some subsystems in the Al-Ca-Mg-Si-O system. J. Phase Equilibria, 1993, **14**, 662-675.

[97Lak] Lakiza S.M., Lopato L.M., Stable and metastable phase relations in the system Alumina -Zirconia-Yttria. J. Amer. Ceram. Soc., 1997, **80**, 893-902.

[98Swa] Swamy V., Seifert H.J., Aldinger F., Thermodynamic properties of Y_2O_3 phases and the yttrium-oxygen phase diagram. J. Alloys Comp. 1998, 269, 201-207.

[02Nic] Nicholls J.R., Lawson K.J., Johnstone A., and Rickerby D.S., Methods to reduce the thermal conductivity of EB-PVD TBCs. Surface and Coatings Technology, 2002, 151-152, 383-391.

[02Wu] Wu, J., Wei, X., Padture, N.P., Klemens, P.G., Gell, M., Garcia, E., Miranzo, P., and Osendi M.I., Low-Thermal-Conductivity Rare-Earth Zirconates for Potential Thermal-Barrier-Coating Application. J. Am. Ceram.Soc., 2002, **85**, 3031-3035.

[03Reb] Rebollo, N.R., Fabrichnaya, O., and Levi, C.G., Phase stability of Y+Gd co-doped zirconia. Z. Metallkd., 2003, **95**, 163-170.

[04Che] M. Chen, B. Hallstedt, and L.J. Gauckler, Thermodynamic modelling of the ZrO_2-$YO_{1.5}$ system. Solid State Ionics 170 (2004) 255-274.

[04Fab] Fabrichnaya, O., Aldinger F., Assessment of thermodynamic parameters in the system ZrO_2-Y_2O_3-Al_2O_3. Z. Metallkd., 2004, **95**, 27-39.

[04Por] Portinha A., Teixeira V., Carneiro J., Costa M.F., Barradas N.P., and Sequeira A.D.

Stabilization of ZrO_2 coatings with Gd_2O_3. Surf. Coat. Techn. 2004, 188-189, 107-115.

[04Lev] Levi, C.G, Emerging materials and processes for thermal barrier system. Current Opinion in Solid State and Materials Science, 2004, 8, 77-91.

[04Vas] Weissen R., Traeger F., Stoever D., New thermal barrier coatings based on pyrochlore/YSZ double-layer systems. Int. J. Appl. Ceram. Technol. 2004, 1, 351-361.

[04Wan] Wang Ch., Zinkevich M., Aldinger F. On the thermodynamic modeling of the Zr-O system. Calphad 2004, 28, 281-292.

[05Lak1] Lakiza S., Fabrichnaya O., Wang Ch, Zinkevich M., and Aldinger F., Phase diagram of the ZrO_2-Gd_2O_3-Al_2O_3 system. J. Eur. Ceram. Soc. (2005) in press.

[05Fab1] Fabrichnaya O., Wang Ch., Zinkevich M., Levi C.G., Aldinger F., Phase equilibria and thermodynamic propreties of the ZrO_2-$GdO_{1.5}$-$YO_{1.5}$ system. J. Phase Equilibria and Diffusion (2005) (submitted).

[05Lec] R.M. Leckie, S. Kraemer, M. Ruhle, and C.G. Levi, Thermochemical compatibility between Alumina and ZrO_2-$GdO_{3/2}$ thermal barrier coatings, Acta Materialia, 2005 (in press).

[05Lak2] Lakiza S., Fabrichnaya O., Zinkevich M., and Aldinger F., Phase relations in the ZrO_2-$YO_{1.5}$-$AlO_{1.5}$ system. Calphad (submitted).

[05Fab2] Fabrichnaya O., Lakiza S., Wang Ch., Zinkevich M., Levi C.G., Aldinger F., The thermodynamic database for the ZrO_2-$GdO_{1.5}$-$YO_{1.5}$-$AlO_{1.5}$ system: application for thermal barrier coating. J. Eur. Ceram. Soc. (submitted).