

highly sensitive to strain-induced distortions of the crystal lattice. Practical applications of ir and Raman spectroscopy to zirconia technology are discussed.

*Basic Science Division will participate with Electronics Division in Joint Session III, "Powder Preparation and Characterization" — page 494.*

*Basic Science Division will participate with White Wares Division in Joint Session IV, "Mechanical Properties and Surface Treatments" — page 496.*

*Basic Science Division will participate with Electronics Division in Joint Session V, "Conductivity and Electrolytes" — page 498.*

tion showed less than ideal parabolic behavior. Major reaction products were  $\text{NiO}$ ,  $\text{Cr}_2\text{O}_3$ ,  $\text{Al}_2\text{O}_5$ ,  $\text{NiAl}_2\text{O}_4$  and a yttrium-aluminum oxide phase. Relative amounts of these were a function of temperature, oxygen pressure and elapsed time of reaction. Addition of yttrium increased the general oxidation resistance; however, yttrium content  $\geq 0.3$  wt% led to grain boundary oxidation below the surface, which is undesirable from a mechanical property standpoint. Some mechanisms by which yttrium is believed to exert its beneficial influence on the overall attack are discussed.

3:00-3:15 p.m.

**45-B-70. TGA of the Oxidation of a  $\text{ZrB}_2$  Body Containing SiC**  
W. C. TRIPP,\* Systems Research Labs., Dayton, Ohio, and  
H. C. GRAHAM, Aerospace Research Labs., Wright-Patterson  
AFB, Ohio.

Oxidation kinetics of  $\text{ZrB}_2 + 20$  vol% SiC were studied from  $800^\circ$ - $1500^\circ\text{C}$  at an oxygen pressure of 250 torr. Since volatile oxides are formed during oxidation, weighing techniques were developed to collect and weigh any oxidation products formed that are condensable within the temperature limits of the system. The balance system measures oxygen consumption, net sample weight change and vaporization rate. By comparing results of these measuring techniques, the relative importance of vaporization on the kinetics can be evaluated. Vaporization of  $\text{B}_2\text{O}_3$  is significantly retarded above  $1100^\circ\text{C}$  by the formation of  $\text{SiO}_2$ . Apparent anomalies shown by measurements of net weight change are resolved by the additional data provided by oxygen consumption and vaporization rate measurements. Effect on the oxidation kinetics of the addition of SiC is shown by comparing these results with results of a previous study on  $\text{ZrB}_2$ .

3:20-3:35 p.m.

**46-B-70. TGA Oxidation-Reduction Kinetics in  $\text{MnO}$**

I. BRANSKY, Ohio State University Research Fdn., Wright-Patterson AFB; N. M. TALLAN\* and J. M. WIMMER, Aerospace Research Labs., Wright-Patterson AFB, Ohio; and M. GIVISHI, Technion, Haifa, Israel.

Gravimetric measurements of the kinetics of oxidation and reduction of single crystal  $\text{MnO}_{1-x}$  between fixed consumption intervals  $\Delta x$  were made to study chemical diffusion in this oxide. Measurements were made from  $1100^\circ$  to  $1450^\circ\text{C}$ ; the oxygen partial pressure range was established by  $\text{CO}_2/\text{CO}$  ratios from 1 to 100. Studies of the kinetics as a function of argon dilution of the  $\text{CO}_2/\text{CO}$  mixtures, as a function of the total pressure of the  $\text{CO}_2/\text{CO}$  mixtures, and as a function of specimen thickness all showed a significant influence of the surface reaction rate. Kinetics of oxidation and reduction, at constant temperature and total pressure, were found to decrease rapidly with increasing  $\text{CO}_2/\text{CO}$  ratio. The relation between these apparent changes in oxidation-reduction rates and the influence of surface reaction is discussed.

3:40-3:55 p.m.

**47-B-70. Oxidation-Reduction Kinetics in  $\text{CoO}$**

J. M. WIMMER,\* Aerospace Research Labs., Wright-Patterson AFB, and I. Bransky, Ohio State University Research Fdn., Wright-Patterson AFB, Ohio.

Oxidation-reduction kinetics of  $\text{CoO}$  were studied as a function of temperature,  $1000^\circ$ - $1300^\circ\text{C}$ , and deviation from stoichiometry, up to 1%, by TGA and electrical conductivity measurements. It appears that the kinetics are controlled mainly by bulk diffusion so that a chemical diffusion coefficient,  $D$ , can be calculated from the data. Dependence of  $D$  on temperature and stoichiometry will be discussed.

4:00-4:15 p.m.

**48-B-70. Oxidation/Vaporization Rates of  $\text{Cr}_2\text{O}_3$**

H. C. GRAHAM\* and H. H. DAVIS, Aerospace Research Labs., Wright-Patterson AFB, Ohio.

Weight loss of  $\text{Cr}_2\text{O}_3$  in oxidizing environments at  $1200^\circ\text{C}$  was measured using TGA. Dependence of the weight loss on oxygen partial pressure, gas flow rate, and total pressure was determined independently using oxygen/argon gas mixtures. Mechanism of weight loss is the oxidation of  $\text{Cr}_2\text{O}_3$  to  $\text{CrO}_3$  and its subsequent vaporization. A mass transport coefficient for vaporization of  $\text{CrO}_3$  under these conditions is calculated.

4:20-4:35 p.m.

**49-B-70. Oxidation of Ni-Cr-1%  $\text{ThO}_2$  Alloys at  $1200^\circ\text{C}$**

H. H. DAVIS\* and H. C. GRAHAM, Aerospace Research Labs., Wright-Patterson AFB, and I. KVERNES, Ohio State University Research Fdn., Wright-Patterson AFB, Ohio.

High temperature oxidation of three Ni-Cr alloys containing

Room 230 (Civic Center)

### "Oxidation — Reduction Kinetics"

Session Chairman: PAUL J. JORGENSEN  
Stanford Research Institute, Menlo Park, Calif.

2:00-2:15 p.m.

**42-B-70. Low Temperature Parahydrogen Conversion on  $\text{Gd}_2\text{O}_3$  and  $\text{Y}_2\text{O}_3$**

V. F. CAPOZZI and D. R. ROSSINGTON,\* Alfred University, Alfred, N. Y.

Low temperature ( $77^\circ$  and  $90^\circ\text{K}$ ) paraortho hydrogen conversion was studied on two rare-earth oxides,  $\text{Gd}_2\text{O}_3$  and  $\text{Y}_2\text{O}_3$ . Activation energies, orders of reaction, absolute reaction rates and reaction mechanisms are given, together with the equilibrium surface coverage by adsorbed hydrogen. At these temperatures, conversion reaction proceeds via a physical mechanism on paramagnetic surface sites, and the experimental results are compared with calculated results for three possible physical mechanisms: collisional, vibrational, and translational. It is concluded that the parahydrogen conversion on  $\text{Gd}_2\text{O}_3$  is paramagnetic, proceeding by the vibrational mechanism. On  $\text{Y}_2\text{O}_3$  the vibrational mechanism is also predominant, with a possible small contribution by the collisional mechanism. There is some evidence that for  $\text{Y}_2\text{O}_3$  there may be a contribution by surface free valencies from surface distortion following removal of adsorbed water.

2:20-2:35 p.m.

**43-B-70. A Thermodynamic Study of the Ruthenium-Oxygen System**

R. W. VEST\* and P. DASGUPTA, Purdue University, Lafayette, Ind.

TGA was used to determine the boundary between the Ru and  $\text{RuO}_2$  phase fields from  $820^\circ$  to  $1130^\circ\text{C}$  and the oxygen partial pressure range of  $1.6 \times 10^{-4}$  to  $10^{-2}$  atm. The Gibbs free energy of formation and standard enthalpy and entropy changes for  $\text{RuO}_2(s)$  were obtained from the experimentally determined transition temperatures between the two phase fields at various oxygen partial pressures. Results are compared to extrapolated values of earlier studies, and the influence of the higher oxides ( $\text{RuO}_3$  and  $\text{RuO}_4$ ) is discussed.

2:40-2:55 p.m.

**44-B-70. Influence of Yttrium Additions on the Oxidation Behavior of Ni-Cr-Al Base Alloys at High Temperatures**

I. A. KVERNES, Ohio State University Research Fdn., Wright-Patterson AFB, Ohio.

Influence of yttrium additions on the oxidation behavior of Ni-9%, Cr-6% Al alloys in pure oxygen was studied from  $800^\circ$ - $1200^\circ\text{C}$ . Experimental methods included TGA, X-ray diffraction, metallographic techniques, electron microprobe analysis and electron microscope studies. In general, oxida-