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Neutron diffraction study of the reduction of $NiAl_2O_4$

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The reduction of a solid $NiAl_2O_4$ cylinder to a metal-ceramic composite consisting of Ni particles in an Al_2O_3 matrix was monitored *in situ* at 1220 °C with neutron powder diffraction. The reaction kinetics was determined with a time resolution of 30 min. The reduction is associated with a volume shrinkage. A comparison of finite element calculations and the changes in the measured lattice parameters suggests that creep has relaxed the residual strains that would otherwise result from the volume shrinkage. The data also indicate that structural evolution in unreduced $NiAl_2O_4$ via a change in the cationic sublattice towards inverse spinel occurred and that led to a variation in lattice parameters. © *2000 American Institute of Physics.* [S0003-6951(00)02806-0]

The reduction of the spinel oxide $NiAl_2O_4$ to a metal-ceramic composite of Ni and Al_2O_3 has been the subject of several recent studies.[1–4] Producing a composite in this fashion is attractive because it offers the ability to control microstructure by manipulating processing variables such as reduction temperature, time, initial oxide density, dopants, and oxygen activity in the atmosphere (the driving force). A critical issue that affects the microstructure evolution during the reaction is the associated volume change, which for this system is predicted to be about -18% (based on crystallographic densities), but is somewhat lower in reality.[4] In a solid sample, one possible consequence of this shrinkage is the generation of residual stress between the reduced and unreduced regions. If not relaxed, these stresses can be large enough to cause cracking.[1,2]

By monitoring the reduction *in situ* using neutron powder diffraction, our aim was to elucidate the phase and strain evolution. By identifying the strain generation and relaxation mechanisms, we hope to be able to manipulate the residual stresses. Neutron diffraction is uniquely suited for this study since neutrons penetrate deep and allow *in situ* studies.

The neutron powder diffractometer (NPD) at the Lujan Center, Los Alamos National Laboratory was utilized. The reduction was performed in a controlled-atmosphere furnace with a retort tube made of amorphous silica. The specimen was a hot isostatically pressed cylinder of 9 mm in diameter and 51 mm long with an initial porosity of 12%. The specimen was heated first in N_2 to 1220 °C. Diffraction spectra were recorded at several temperatures during heating and at the reduction temperature, prior to the application of the reducing atmosphere. The reaction was initiated by introducing a 10% $CO+N_2$ mixture into the furnace which yielded an estimated oxygen partial pressure of about 10^{-16} atm and well below the spinel stability limit.[1,5] Data were collected at 30 min intervals to monitor the progress of the reduction which was complete in 20 h (also confirmed by metallography). Analysis of the diffraction data was carried out using a Rietveld package.[6] Examination of the sample after reduction revealed only 5.1% volume shrinkage. This lower-than-expected value is due to the generation of porosity in the α-Al_2O_3 matrix (estimated to be about 23% using the method described in a previous study[4]).

The reaction products were Ni and α-Al_2O_3 as predicted by the phase diagram.[5] The neutron diffraction data yield unambiguous information about the phase (weight) fractions and lattice parameters. Potentially, both can provide insights into the physical mechanisms occurring during the reaction, however, there are complicating factors.

Consider first the phase fractions shown versus time in Fig. 1. In principle, one could calculate the reaction layer thickness as a function of time from which an inference about the rate-controlling mechanism could be made. However, this calculation would have to be predicated on the assumption that the reaction front progresses uniformly into

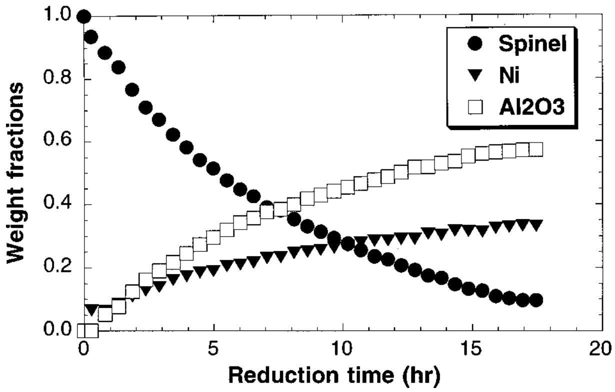

FIG. 1. Phase evolution during reduction. The average Al_2O_3/Ni weight fraction ratio obtained by Rietveld analysis was 1.62 which compares favorably with the value predicted by the phase diagram (1.74) (see Ref. 5). Although the specimen was completely reduced, the last part of the data was omitted due to poor Rietveld fits resulting from the low amount of spinel left.

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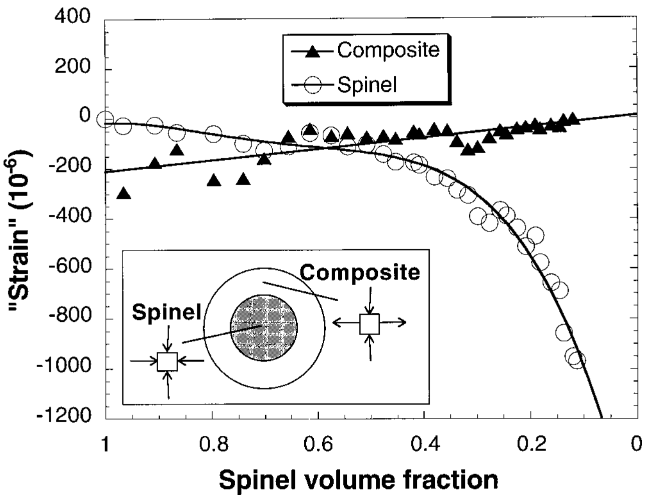

FIG. 2. Change in the lattice constants (''strain'') during reduction. The ''strain'' in the reduced composite was calculated from the measured ''strain'' in Ni and α-Al_2O_3 using the rule of mixtures (20 vol. % Ni in an α-Al_2O_3 matrix was assumed). The insert shows a schematic of the specimen cross section and the stress state predicted to result from the volume shrinkage in the reduced layer.

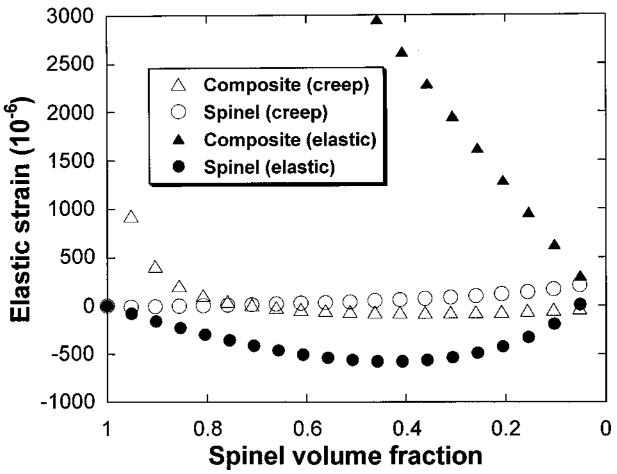

FIG. 3. Finite element model predictions of average composite and unreduced spinel elastic strains as a function of unreduced spinel volume fraction. Two cases are compared: pure elastic deformation and creep in all regions.

the sample. Moreover, one would need the instantaneous density at each time (to convert from weight fraction to volume fraction). Although the assumption of a uniform reaction front is validated,[2–4] the prediction of instantaneous density is difficult, especially in view of the low observed shrinkage and generation of porosity in α-Al_2O_3. A further complication in kinetics analysis is the cylindrical geometry of the specimen. This invalidates the use of the ''traditional'' kinetics models that assume planar reaction fronts.[7] All of these issues are discussed in a future publication.[8]

Turning instead to the lattice parameters, we observed significant changes in the spinel lattice parameter, *a*, during the reduction. These changes were converted to ''strains'' with respect to the value of *a* (~8.14 Å) at the reduction temperature, but prior to reduction (Fig. 2). Since there is no Ni and α-Al_2O_3 at the beginning of the reaction, the lattice constants of these phases obtained at the end of the reduction (before cooling) were taken as ''strain-free'' references. This was justified by the fact that the reaction proceeded to completion in this sample. This way, lattice parameter changes due to, for instance, dissolution of other elements in either Ni or α-Al_2O_3 were also accounted for.

There are at least two possible explanations for the changes in the lattice constants during reduction: (i) elastic strain due to the volume shrinkage, and (ii) structural changes in the unreduced spinel. Shrinkage of the exterior is expected to introduce a compressive in-plane strain in the unreduced spinel (Fig. 2, insert). In the absence of relaxation, the strain in unreduced spinel would increase in compression as the reaction proceeds. In the reduced region, a balancing strain of radial compression and tangential (or hoop) tension would be expected perpendicular to sample axis (Fig. 2, insert). Note that, since the whole specimen is sampled by the neutron beam, the measurement integrates the component of strain along the scattering vector and yields an average of radial and tangential strain components (the details are explained elsewhere[9]).

For insight into the elastic strain evolution, an axisymmetric finite element model was created and calculations performed using the ABAQUS™ code. In the model, both the unreduced and reduced regions were treated as single phase, isotropic materials with experimentally determined elastic constants [spinel, Young's modulus, $E=240\,\mathrm{GPa}$, Poisson's ratio, $\nu=0.3$; reduced region, $E=150\,\mathrm{GPa}$, $\nu=0.2$ (Ref. 4)]. The strain evolution for 5.1% volume shrinkage is shown in Fig. 3 for two cases: one assumes elastic behavior (no stress relaxation), and the other assumes power-law creep with typical α-Al_2O_3 behavior. The constitutive law[10] used in all regions of the sample was steady-state creep rate, $\dot{\epsilon}=A\sigma^n$, where $A=3.33\times10^{-10}\,\mathrm{s}^{-1}\,(\mathrm{MPa})^{-n}$, σ is equivalent (von Mises) stress in MPa and $n=1.69$.[11] The material parameters were determined by Robertson *et al.*[11] using an α-Al_2O_3 with average grain size of 1–2 μm under uniaxial tension and compression at 1250 °C. The justification for our use of these parameters is that grain size, temperature, and stress level in Ref. 11 were similar to those in this study. Moreover, there are no experimental data on the creep behavior of either spinel or the reduced composite. The creep calculation should therefore be viewed as representative and qualitative.

In comparing Figs. 2 and 3, the most obvious observation is that the strain response of the sample does not completely agree with either the elastic or the creep calculations. At this stage, it is not possible to rule out stress relaxation via creep because the lack of elastic strain in the composite can be attributed to this mechanism. Since the elastic and creep calculations should, in principle, bracket the measured response, we explored alternative mechanisms that might explain the changes in lattice parameters in Fig. 2.

One possible mechanism that can modify the spinel lattice constant is the cationic disorder. $NiAl_2O_4$ can transform from a normal spinel, $(Ni^{2+})[Al_2^{3+}]O_4$, to an inverse spinel, (Al)[NiAl]O_4 and *vice versa* with a small energy change.[12] In this process, the larger Ni^{2+} ions which occupy the tetrahedral (8*a*) sites in normal spinel move to the octahedral (16*d*) sites in inverse spinel, while half of the smaller Al^{3+} ions move in the opposite direction.[12] The extent of this move is measured by the disorder or inversion parameter, *I* (the fraction of tetrahedral sites occupied by the Al ions, *I*

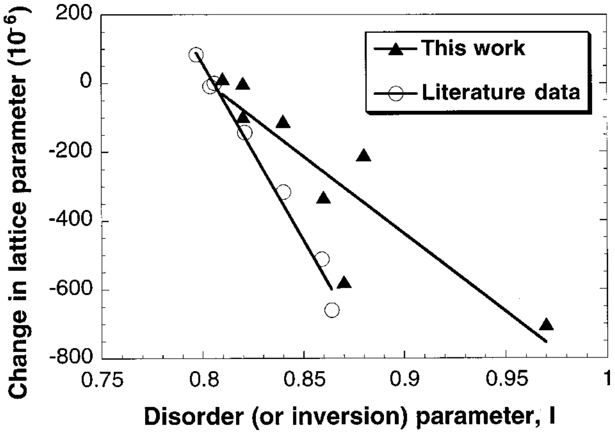

FIG. 4. Evolution of the relative change in spinel lattice parameter as a function of cationic disorder. The literature data are from Ref. 13.

$=0$ for normal spinel and $I=1$ for inverse spinel). Previous studies suggest that the lattice constant of spinel decreases as the disorder parameter increases to better accommodate the Ni ions.[12,13] If it occurs during reduction, it would lead to an apparent compressive ''strain'' in the spinel which would obviously not result in any balancing ''strain'' in the composite. Structural analysis via Rietveld refinement on our data suggested that the unreduced spinel becomes more inverse during the reduction (Fig. 4).[14] This behavior contradicts previous observations[12,13] that, during high temperature heat treatments of spinel (without reducing it), its disorder parameter would approach the random value of 2/3 (instead of 1 found in our case). We speculate that the spinel shrinks to relieve the stress generated by the reduction process. This would result in no significant measurable ''strain'' in the reduced region. It is worth noting that the magnitude of the lattice constant change in the spinel in Fig. 2 is comparable to the one in Fig. 4.

Based on these preliminary results, it is clear that significant changes in lattice constants occur during the reduction of $NiAl_2O_4$. However, the interpretation of these changes, especially in unreduced $NiAl_2O_4$, requires care since at least two alternative and maybe concurrent mechanisms are possible: creep in all phases and structural changes in spinel. Nevertheless, neutron diffraction proved to be a powerful method to investigate, *in situ*, the partial reduction of $NiAl_2O_4$.

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