

The Pressure Medium as a Solid-State Oxygen Buffer

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Abstract. We present a simple method to buffer oxygen fugacity at high pressures and high temperatures where the traditional 'double capsule' method is inappropriate. The pressure medium is doped with a metal which partially reacts with the free oxygen in the pore spaces of the cell. The resultant finely intergrown metal-metal oxide assemblage buffers the oxygen fugacity in the sample as long as the capsule and furnace materials are oxygen permeable.

Introduction

The control of oxygen fugacity is fundamental to good phase relation studies in systems containing multivalent transition metal ions. Additionally, changes in oxygen fugacity affect the transport properties of minerals through their defect concentrations. The development of solid-state oxygen buffers (Eugster, 1957; Huebner, 1971) facilitated experiments with carefully controlled oxygen environment in solid-media high pressure vessels. The traditional double capsule method consists of a hydrogen permeable capsule containing the experimental charge, surrounded by the solid state buffer inside an outer capsule. The oxygen fugacity is communicated to the sample by hydrogen diffusion through the inner capsule. However, certain experiments, such as electrical conductivity and acoustic velocity measurements, and most synchrotron multi-anvil experiments require that the sample is not encapsulated in metal foil capsules. These, in addition to the very high pressure multi-anvil experiments, where the sample volume is too small for double capsules, have necessarily been performed un-buffered. Here we describe an alternative method for buffering oxygen fugacity in multi-anvil press experiments in cases where the double-capsule method is inappropriate. The pressure medium is mixed with the reduced component of a solid state buffer assemblage. Some of this reduced component reacts with excess oxygen in pore spaces in the pressure medium to produce the oxidised component, allowing buffering of the sample.

Experimental method

Experiments were performed in the Walker-type multi-anvil cell installed at University College London. The pressure medium consisted of Aremco Ceramcast 584 ceramic with 10 percent of the buffer metal by weight. This mixture was cast into 14 mm edge length octahedra with an integral cast gasket. The cast octahedra were cured at room temperature for 1 week, 110 °C for 48 hours and 350 °C for 24 hours prior to use. This was compressed using 8 mm truncation anvils of Sandvic 6uf Tungsten Carbide. Pressure generation in the doped octahedra was identical to the 'pure' ceramcast; room temperature calibrations (Bi I-II, III-V; Sn) and high temperature calibrations (α - γ Fe₂SiO₄ at 1100 °C; coesite-stishovite at

1100 and 1500 °C) have been described elsewhere (Taniguchi et al, 1995).

Sliding oxygen sensors were used to measure the oxygen fugacity imposed by the cell (Pownceby & O'Neill, 1994; 1995). These consisted of a three to one (by weight) mixture of either (Ni,Mn)O and Ni metal, or NiO and (Ni,Pd) alloy. Manganese oxide starting material was prepared by reducing MnO₂ under CO:CO₂ mixtures at 1300 °C for 24 hours. Mixtures of NiO, MnO and Ni were ground together under acetone in an agate mill until the grain size was approximately 5 µm and this starting material was pressed into slugs of 1.6 mm diameter and 2 mm length for the high pressure experiments. Nickel-Palladium alloys were synthesised by reacting 50 µm Pd wire with NiO under CO:CO₂ mixtures at 1300 °C for 24 to 72 hours. These were cut into 200 µm lengths and pressed with 5 µm NiO powder into slugs for the experiments. Sensor compositions (table 1) were selected such that equilibrium was approached from more oxidising and more reducing compositions. These reversal reactions allowed the oxygen fugacity of the buffering reaction to be tightly bracketed. Only one sensor was used per experiment to ensure that sensor was reacting to the imposed oxygen fugacity and not self-buffering.

The sample was encapsulated in 300 µm wall thickness corundum and placed in a cylindrical graphite furnace with a chromel-alumel thermocouple located axially. There was no thermal insulation between the furnace and the pressure medium. All experiments were performed at 1263 K and 5 GPa, the thermocouple emf was not corrected for pressure. The anvil reference temperature was measured using a second K-type thermocouple located with the weld at the truncation of one anvil which was not being used as the furnace terminal. After thermal quenching, the pressure was slowly released and the sample was recovered.

Results and Discussion

Samples were equilibrated with Ni-, Fe- and Re-doped octahedra and samples and cells sectioned for electron microprobe analysis. Figure 1 shows a backscattered electron image of a Ni-(Ni,Mn)O sample which had been reacted under reducing conditions for 6 hours. There has been considerable recrystallisation as evidenced by the large grain size and the good triple junctions of the oxide. In addition, the small (~0.5

Table 1. Starting compositions of sliding redox sensors

$X_{Ox}^{Ni \dagger}$	1	1	0.90	0.10	0.05	0
$X_{Me}^{Ni \dagger}$	0	0.86	1	1	1	1
$LogfO_2^{\ddagger}$	-	-9.72	-9.91	-11.21	-11.72	-

\dagger Mole fraction nickel in oxide/metal solid solution

\ddagger Oxygen fugacity calculated for 5 GPa, 1263 K from Pownceby & O'Neill, 1994, 1995.

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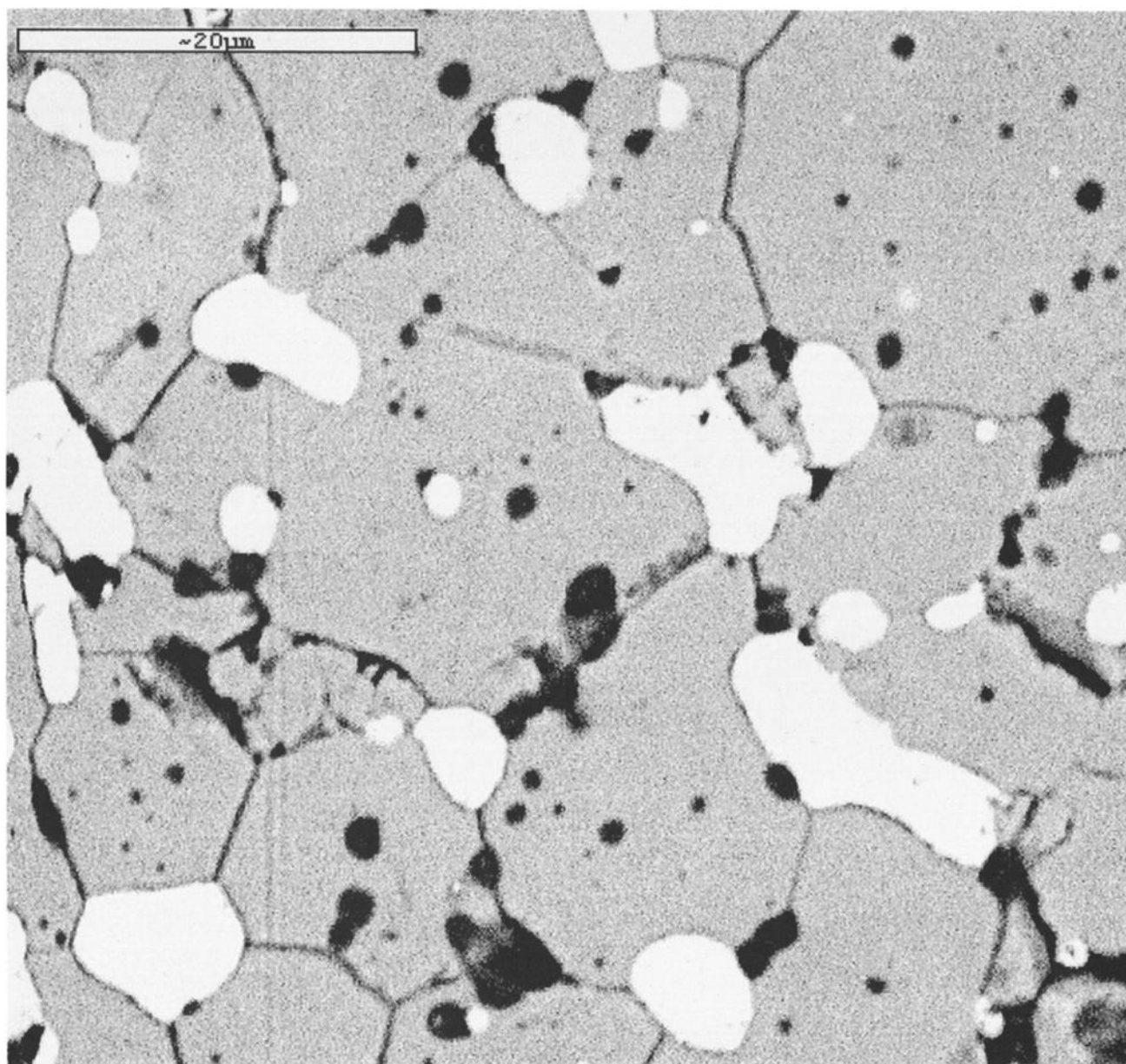


Figure 1. Sliding sensor sample after 6 hours in Fe-doped cell at 1263K. The (Ni,Mn)O is strongly recrystallised, with large grain size and equilibrium grain boundary texture. The large bright rounded grains are the original metal in the starting material, but the small bright regions within the oxide grains are nickel metal which has exsolved from the oxide during the experiment. The black regions are holes produced by loss of nickel grains during polishing.

Table 2. Final compositions of sliding redox sensors

Buffer [†]	C	Re	Re	Ni	Ni	Ni	Ni	Fe	Fe	Fe
Type [‡]	R	O	R	O	O	R	R	O	O	O
Duration	3h	2h	4h	0.5h	2h	2h	0.5h	2h	6h	2.5h
$X_{\text{Ox}}^{\text{Ni}}$	1	1	1	1	1	0.95(1)	0.92(2)	0.057(4)	0.047(6)	0.035(1)
$X_{\text{Me}}^{\text{Ni}}$	0.13(2)	0.21(1)	0.27(2)	0.93(1)	0.97(1)	1	1	1	1	1
$\text{Log}f_{\text{O}_2}$	-6.84	-7.59	-8.02	-9.77	-9.80	-9.87	-9.90	-11.62	-11.77	-12.00

Oxygen fugacity calculated for 5 GPa, 1263 K from Pownceby & O'Neill, 1994, 1995.

[†] Metal dopant in octahedra; C denotes buffering by the graphite furnace

[‡] O = equilibrium approached from more oxidised composition; R = equilibrium approached from reduced composition

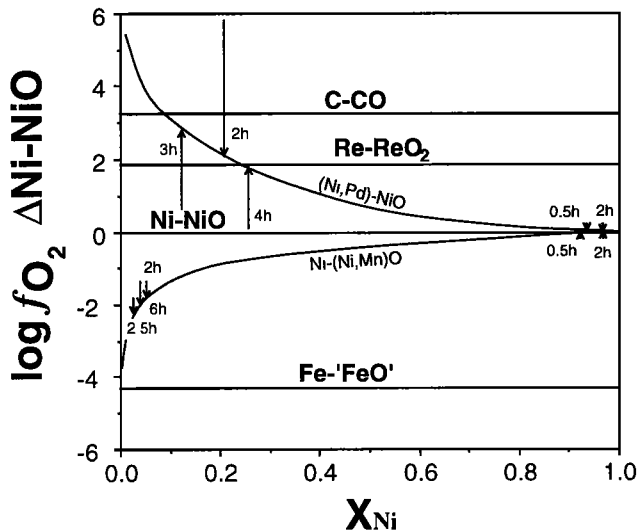


Figure 2. Results of reversal sensor experiments. Mole fraction Ni in the (Ni,Mn)O and (Ni,Pd) solid solutions versus oxygen fugacity calculated relative to Ni-NiO at 5 GPa, 1263 K. The curves show the composition-oxygen fugacity relations for the Ni-(Ni,Mn)O and (Ni,Pd)-NiO sensors. Arrows indicate the composition of the recovered sensor, with the tail at the oxygen fugacity of the starting composition. The Re-ReO and Ni-NiO buffers are bracketed to better than 0.3 log units implying that the cells are truly buffering the sample. The

μm) dark spots in the oxide are holes where nickel grains have plucked out during polishing. This fine grained nickel was exsolved from the oxide during the experiment. Analyses of recovered sensor compositions are given in table 2 and plotted

in figure 2, relative to the Ni-NiO buffer. Arrows indicate the direction of approach, with the positions of the tails at the oxygen fugacity of the sensor's starting composition. All experiments show convergence on the relative oxygen buffer, with the equilibrium oxygen fugacity generally bracketed to better than 0.5 log units. The exception to this is for the Fe-'FeO' buffer, where the sensors were still 2 log units more oxidised than the buffer, even after 6 hours. However, at the extreme oxide composition in equilibrium with the Fe-'FeO' buffer, 2 log units in f_{O_2} corresponds to a variation of only 3% in the oxide. The fact that the sensor was still moving towards the composition for Fe-'FeO' buffering after durations of 6 hours, indicates that the problem is one of kinetics in the sensor material rather than a lack of buffering.

Examination of the pressure medium after recovery confirms that the sample is being buffered by the metal-oxide assemblage. Figure 3 shows a section through an Fe-doped cell, recovered after a 2 hour duration experiment, showing the graphite furnace (dark), reacted (pale) and unreacted zones of the pressure medium. Inset is a backscattered electron image of the central region, next to the furnace. The large dark grains are MgO, with a bright rim of (Fe,Mg)O. The white grains are finely intergrown Fe and FeO. The presence of MgO apparently enhances the oxidation of Fe, by reducing the FeO activity, but within the groundmass of the ceramcast (cryptocrystalline or amorphous mixture of magnesia, alumina and silica) wüstite is stable and commonly occurs in intimate contact with metallic iron. The equilibrium oxygen fugacity of the buffer mixture will vary with temperature through the cell, but the sample is buffered by the mixture next to the furnace: the peripheral, cooler, regions of the cell have a lower equilibrium oxygen fugacity than adjacent to the furnace. This may cause oxygen to diffuse away from the furnace, reducing wüstite in the hot zone. The presence of iron and wüstite next to the furnace in cells recovered after 6 hour experiments

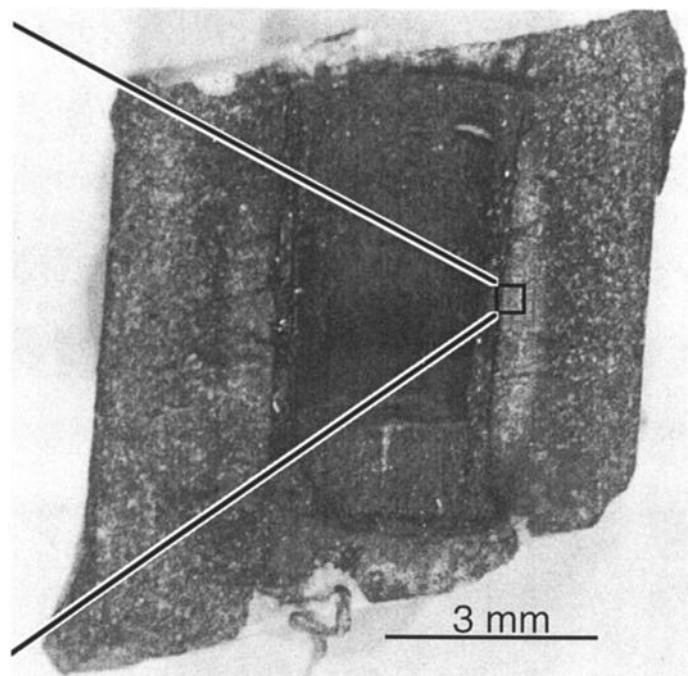


Figure 3. Broken Fe-doped cell after 2 hour experiment. The reacted zone next to the furnace is clear, as well as a darker zone around that where no reaction is apparent in the Fe, but the pressure medium is better sintered than further out. The inset shows a backscattered electron image of the region immediately next to the furnace. The bright regions consist of Fe and 'FeO' in intimate contact, the dark grains are MgO with (Fe,Mg)O solid-solution rims and the intermediate grey groundmass consists of magnesia, alumina and silica with no apparent structure at the resolution of the microprobe.

indicates that, the oxygen fugacity is still being buffered at Fe-'FeO' in the high temperature region. Indeed, our experiments buffering magnesiowüstite using this technique for electrical conductivity measurements suggest that at 2000 K, the buffer is effective for durations in excess of 1 hour. Similar relations are seen in the Ni- and Re-doped cells, but they are less clear because less oxidation of the buffer metal had occurred. If thermal insulation had been used between the furnace and the pressure medium the oxygen fugacity imposed on the sample would, by extension of the above argument, be more reducing than that of the relevant buffer at the sample temperature. It is possible that the oxygen fugacity of the buffer assemblage is communicated to the sample via hydrogen diffusion as in the traditional double-capsule technique, since the ceramcast pressure medium is not fully dehydrated during curing. If this is the case, samples in traditional precious metal capsules could be buffered by this technique, although the authors have not tried this.

Conclusions

Oxygen fugacity can be very simply buffered in solid-media high-pressure, high-temperature apparatus, where it is impossible to use traditional metal capsules by doping the pressure medium with metals. These partially react with the free oxygen in the pore spaces of the pressure medium to produce metal-metal oxide buffers. We have successfully used this technique to control the redox state of samples during electrical conductivity measurements (Dobson et al, 1997). We see no reason why metals should not be mixed with the readily available castable zirconias and used as thermal insulation in the traditional semisintered MgO multi-anvil cells. In

addition, this technique could easily be adapted for use in synchrotron cells by insertion of an amorphous X-ray path to minimise unwanted diffraction from the pressure medium.

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