

MUTUAL SOLUBILITIES OF MOLTEN TRANSITION METALS AND OXIDES

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Introduction Strong evidence exists that the earth's outer core is less dense than pure iron at appropriate P,T conditions owing to the presence of a substantial amount of low atomic weight element(s). Sulphur has been widely considered to be the principal light element in the core. However, it is difficult to understand how sulphur, a highly volatile element in the solar nebula, could have been condensed much more efficiently in the earth than several elements possessing higher condensation temperatures, e.g. Na, K, F, Cl, Zn (1). Ringwood (1) accordingly investigated an alternative hypothesis that the principal light element in the core is oxygen, an element which already accounts for about 50 percent of the mass of the mantle. This interpretation requires that molten metallic iron and iron oxide possess a wide field of miscibility at the P,T conditions pertaining in the outer core.

Existing metallurgical data on the solubility of FeO in molten Fe at ambient pressure can be used to calculate an extrapolated phase diagram for Fe-FeO at high temperatures (1). This diagram implies solubilities of 30 wt% FeO in Fe at 3000°C and 55% FeO at 3500°C, temperatures which are appropriate for the outer core. Shock wave measurements of the density of FeO at core pressures show that its present density could be readily explained by the presence of about 40% of FeO (2). Studies of the effect of pressure on the Fe-FeO phase diagram (1, 3) show that this factor is likely to increase the solubility of FeO in molten Fe.

The above evidence supports the hypothesis that the core contains a large proportion of dissolved FeO. This hypothesis is further strengthened by more general studies of solubility relationships between transition metals and their oxides at high temperature, which demonstrate that the proposed behaviour of the Fe-FeO system is by no means exceptional. Rather, it is a manifestation of entirely "normal" behaviour. Thus, existing data (4, 5) show that the following transition metals and their oxides are entirely miscible in the molten state: Sc-Sc₂O₃, Ti-TiO, V-VO. Moreover, complete miscibility is also observed in the related Cu-Cu₂O system at high temperatures (6). We discuss, below, new experimental data bearing on the mutual solubilities of Ni-NiO, and Co-CoO which contribute to understanding of these relationships.

Experimental The systems were studied by heating small slugs of nickel and cobalt contained in crucibles fabricated from the corresponding oxide (NiO,CoO) to a given temperature, usually at 3 GPa pressure, quenching, and examining the resultant textures by reflected light microscopy. This technique required that the metallic oxide should possess a substantially higher melting point than the corresponding metal, so that it is capable of providing an impervious container. During heating, the metal slug (small in volume compared to the oxide container) dissolves oxide from the walls of the container. On rapid quenching, the oxide is precipitated from the metal phase in characteristic quench textures. Because the oxide is precipitated in the solid state, dendritic habits are often developed, clearly showing that the metal and its oxide were originally in solution. Melting temperatures (°C) of metals and their corresponding oxides are as follows: Ni 1453, NiO 1984; Co 1495, CoO 1795. Experiments were carried out under pressure, usually 3 GPa, which had the effect of increasing the melting point of the oxide relative to the metal-oxide eutectic by a further 100 - 150°C. Experiments were carried out in an

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internally heated, solid pressure medium piston cylinder high P,T apparatus with a diameter of 1.24 cm. Heaters used consisted of graphite, molybdenum and iridium. The choice between heaters was determined by the need to prevent contamination (which generally restricted use of graphite to $\leq 1700^{\circ}\text{C}$) and to prevent reduction of oxide phase to metal. Length of runs was typically about three minutes. Temperature was monitored by means of Pt - Pt 10% Rh and W- Re thermocouples.

Nickel-Nickel Oxide Small slugs of nickel, typically 2mm in dimension, were totally enclosed in nickel oxide and inserted in alundum capsules. Samples were subjected to 3 GPa, then temperature was increased to the desired value for three minutes, after which the charge was quenched by terminating the power. The sample was then examined by microscopy and electronprobe. Runs were carried out at 50°C intervals extending between 1550°C and 1950°C .

At 1550°C , the metal phase was essentially pure, with very few NiO inclusions. At 1600°C the metal contained a wide distribution of finely dendritic nickel oxide which had evidently been precipitated from the melt. As temperature increased up to 1800°C , the proportion of quench NiO increased until the volume of quench NiO was comparable with the volume of metal. At 1900°C and 1950°C , the volumes of quench oxide dendrites exceeded those of the metal. The textural relationships are interpreted as implying more than 50 percent solubility of nickel oxide in molten nickel above 1800°C .

Cobalt-Cobalt Oxide The experimental configuration was similar to that employed for the Ni-NiO investigation except that magnesium oxide containers were used above 1700°C , instead of alundum. Cobalt oxide cylinders were hot-pressed around small slugs of cobalt metal and then inserted into the MgO containers. Graphite heaters were used to 1700°C and iridium above this temperature. The solubility of cobalt oxide in cobalt was very small at 1600°C but the amount of quench CoO increased substantially as the temperature was raised in runs at 1700, 1800 and 1900°C . The oxide typically precipitated as long delicately fibrous dendrites. However in some runs, particularly where cooling was slower, segregation into dispersed equidimensional grains occurred. Preliminary studies indicate that the solubility of CoO in molten Co at 1950°C is about 10 wt percent. Additional detailed studies will be required to confirm this estimate, and are in progress. It is evident that the solubility of CoO increases quite dramatically from 1600°C to 1950°C and that much higher solubilities can be expected above 2000°C .

Solubility relationships in the system Co-CoO are quite similar to those in Fe-FeO at 1550 - 1700°C (4). At higher temperatures, in the vicinity of 1950°C the solubility of CoO in Co appears to be about twice as high as that of FeO in Fe. The system Co-CoO thus provides a good model for Fe-FeO. Because of experimental difficulties, it is difficult to obtain measurements of the solubility of FeO in Fe above 2000°C . However, there is a probability that these measurements may be possible in the system Co-CoO and further experiments will be designed to explore this.

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