

Beating the Miscibility Barrier between Iron Group Elements and Magnesium by High-Pressure Alloying

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Iron and magnesium are almost immiscible at ambient pressure. The low solubility of Mg in Fe is due to a very large size mismatch between the alloy components. However, the compressibility of Mg is much higher than that of Fe, and therefore the difference in atomic sizes between elements decreases dramatically with pressure. Based on the predictions of *ab initio* calculations, we demonstrate in a series of experiments in a multianvil apparatus and in electrically and laser-heated diamond anvil cells that high pressure promotes solubility of magnesium in iron. At the megabar pressure range, more than 10 at. % of Mg can dissolve in Fe and then the alloy can be quenched to ambient conditions. A generality of the concept of high-pressure alloying between immiscible elements is demonstrated by its application to two other Fe group elements, Co and Ni.

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Alloying is one of the most efficient ways of improving materials' performance. The iron-based alloys (steels) are at the heart of the modern industry. Magnesium-based alloys (first of all with aluminum, zinc, and lead) are rapidly making their way into different technological applications. At the same time, iron-magnesium alloys have not been synthesized yet, because Fe and Mg are almost immiscible at ambient pressure. It is now generally recognized that all metals and compounds show some solubility in the solid or liquid state, but the extent of solid solubility is different for different cases [1]. The maximum solid solubility of Fe in Mg is 0.00041 at. % Fe, and the Mg concentration at the eutectic point is estimated to be less than 0.008 at. % [2]. Below 1273 K the solubility of Mg in Fe is below the detection limit, while the maximum solid solubility of Mg in δ -Fe is approximately 0.25 at. % Mg at the monotectic temperature [3]. There is clear evidence that magnesium and iron do not mix in the liquid state at ambient pressure. Different paths are exploited nowadays to synthesize alloys between immiscible elements, e.g., mechanical alloying, by means of ball milling or thin film alloying using deposition techniques [4–6]. Here we suggest an alternative path for overcoming the miscibility barrier between iron and magnesium, via high-pressure alloying.

In Fig. 1 we show results of our *ab initio* electronic structure and total energy study for pure Fe, Mg, and Fe-Mg alloys. The calculations were carried out in the frame-

work of density functional theory, employing the generalized gradient approximation of Perdew *et al.* [7] for the exchange-correlation energy and the one-electron potential. The Kohn-Sham equations were solved using the exact muffin-tin orbitals all-electron method in combination with the coherent potential approximation (CPA) [8]. The details of the calculations are similar to those reported in Ref. [9]. The charge correlations were treated within the screened impurity model, which ensures excellent agreement between the CPA and supercell techniques for the treatment of substitutional disorder [10–12]. The $3p$, $3d$, and $4s$ electrons of Fe and the $3s$ electrons of Mg were treated as valence electrons, and the core states were recalculated at each iteration within the soft-core approximation. A sufficiently dense mesh was used for calculating the reciprocal space and energy integrals, so that the total energy was converged to within 0.1 meV. The dependence of the total energy on volume for each system was described by a Birch-Murnaghan equation, and the theoretical values of the pressure were derived from the fit. Possible effects due to magnetism at low pressure are not included, because at pressures of interest all systems are nonmagnetic [9,13]. Moreover, on the scale of Fig. 1 magnetism contributes very little to the pressure-volume relations [Fig. 1(a)] and the mixing enthalpies [Fig. 1(b)]. The mixing enthalpy is calculated at temperature $T = 0$ K. The nonmagnetic hexagonal-close-packed (hcp) phase of Fe and the body-centered-cubic (bcc) phase of Mg were

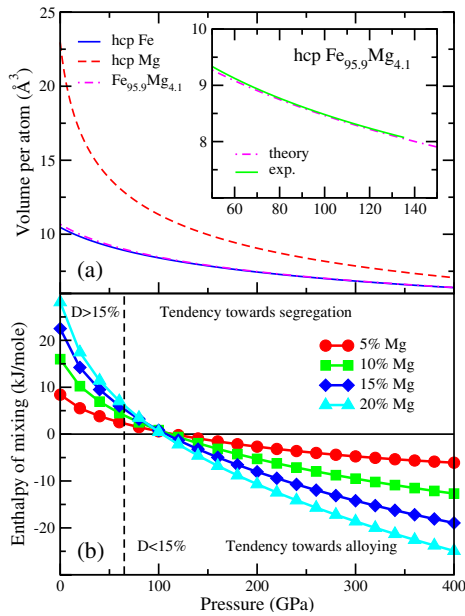


FIG. 1 (color online). (a) Theoretically determined pressure-volume dependencies for nonmagnetic hcp Fe (solid line), hcp Mg (dashed line), and hcp Fe-4.1 at. % Mg alloy (dot-dashed line). The pressure-volume dependence for the high-pressure bcc phase of Mg is virtually indistinguishable from that for the hcp Mg on the scale of this figure, and therefore it is not shown. The inset in (a) compares experimental and theoretical pressure-volume dependence for hcp-structured Fe-4.1 at. % Mg alloy. The experimental data were obtained at ambient temperature (see Table I, supplementary materials [15]). The solid line shows the fit of experimental data with the 3rd order Birch-Murnaghan equation of state with the bulk modulus $K_{300} = 162(3)$ GPa, $K' = 5.72(5)$, and $\rho_0 = 8.082(1)$ g/cm³. The dot-dashed line shows the theoretical equation of state from the main frame of the figure. The excellent agreement between theory and experiment, seen in the figure, illuminates that theory correctly describes the Fe-Mg solid solution. (b) Theoretically determined mixing enthalpies (in kJ/mole) of random hcp Fe_{0.95}Mg_{0.05} (line with circles), Fe_{0.9}Mg_{0.1} (line with squares), Fe_{0.85}Mg_{0.15} (line with diamonds), and Fe_{0.8}Mg_{0.2} (line with triangles) alloys as a function of pressure. The nonmagnetic hcp phase of Fe and the bcc phase of Mg were chosen as standard states at all pressures. Vertical dashed line in (b) gives an estimated pressure where the difference (D) in atomic sizes between Fe and Mg is 15%.

chosen as standard states at all pressures. Note that the negative mixing enthalpy indicates a tendency of the system towards alloying, and vice versa, the positive sign indicates a tendency towards phase segregation. The reliability of our theoretical treatment is illustrated in the inset in Fig. 1(a), where we compare the theoretical and experimental pressure-volume relations for hcp Fe-Mg alloys with 4.1 at. % Mg (see below).

As is evident from Fig. 1(b), at low pressure the mixing enthalpy for Fe-Mg alloys is large and positive, in agreement with very low solubility of Mg in Fe. Apparently, this is also in complete agreement with one of the well-known Hume-Rothery rules for metallic alloys, which states that

the formation of disordered metallic alloys is very unlikely if atomic sizes of alloy constituents differ by more than 15% [1]. However, compressibility of Mg is much higher than that of Fe, and therefore the difference in atomic sizes between these two elements decreases dramatically with pressure, as is clearly seen in Fig. 1(a). This raises the possibility that alloying of iron and magnesium (as well as, by analogy, alloying of Ni and Mg, and Co and Mg) may be more favorable under high-pressure conditions.

Indeed, theoretical calculations predict [Fig. 1(b)] that the mixing enthalpy of disordered Fe-rich hcp Fe-Mg alloys changes sign at about 100 GPa. This means that already at zero temperature there is a transition from the tendency towards phase separation between Fe and Mg at low pressure to the tendency towards alloying at higher pressure. With increasing temperature the tendency towards alloying increases further due to the entropy contribution. Indeed, experiments in large-volume apparatus [14] (Table I, supplementary material [15]) indicate that at pressure of about 20 GPa and temperature of 2470 K more than 4 at. % of magnesium can dissolve in molten iron. Stability of this alloy at higher pressure, however, has not been studied so far.

The Fe-4.1 at. % Mg alloy synthesized in a multianvil apparatus at 20 GPa was used as starting material in diamond anvil cells experiments (see supplementary materials for experimental details [15]). At ambient conditions Fe-4.1 at. % Mg alloy has a bcc structure, and under compression in a NaCl or MgO pressure medium at 10 to 13 GPa it transforms to a new phase with hcp structure (Fig. 2). No further transformation was observed on compression to 135(5) GPa at ambient temperature. Laser heating of the Fe-4.1 at. % Mg alloy in NaCl pressure medium at 125(5) GPa and 3200(200) K does not affect the diffraction pattern of a hcp-structured alloy (Fig. 2), and no sign of decomposition or chemical reaction was detected in the material quenched to ambient conditions. Using the diamond anvil cell technique, we determined the equation of state (EOS) of hcp-phase Fe-4.1 at. % Mg [inset in Fig. 1(a) and Table II, supplementary materials [15]] synthesized in a multianvil apparatus (Table I, supplementary materials [15]). As a pressure medium and a pressure standard, sodium chloride was used and stresses were relaxed by annealing samples with laser radiation. Using the 3rd order Birch-Murnaghan EOS, the bulk modulus $K_{300} = 162(3)$ GPa, $K' = 5.72(5)$, and $\rho_0 = 8.082(1)$ g/cm³ were found. Corresponding values for pure ϵ -Fe (hcp structured) [13] are as follows: $K_{300} = 156$ GPa, $K' = 5.81$, and $\rho_0 = 8.281$ g/cm³. At 130 GPa the molar volume of Fe-4.1 at. % Mg alloy is just about 0.4% larger than the molar volume of ϵ -Fe, in agreement with our theory, which predicts this difference to be 0.5%. This suggests that the difference in densities of pure iron and low Mg-concentration iron-magnesium alloy comes mainly from the difference in atomic masses of iron

studies. At 25(2) GPa and 2300(100) °C we found that 4.2(5) at. % Mg dissolves in iron, in agreement with results of multianvil experiments. Figure 3 shows a backscattering electron image of a metallic droplet of about 3.5 μm in diameter found in the quenched sample after the experiment at 89(3) GPa and 3400(200) °C. On the average, the droplet contains 7.8(5) at. % Mg. Note that the droplet contains small exsolved blobs in the quenched liquid metal, and the marginal region of the metal is free of these blobs. This observation suggests that on quenching, the first crystallized portion of the metal was enriched with iron, and magnesium preferably partitioned into a liquid phase. At 126(3) GPa and 3650(250) K, the highest pressures and temperatures achieved in our experiments, more than 10 at. % Mg could be dissolve in liquid iron (Table I, supplementary materials [15]).

An important and actually nontrivial result of our combined study is that the first Hume-Rothery rule is applicable for alloying of elements at high pressure with a correction for their compressibility. In order to show a generality of our concept of high-pressure alloying between immiscible elements, we investigate a possibility to alloy Mg with two close chemical analogues of iron, namely, nickel and cobalt. Although the latter form intermetallic compounds with magnesium, the solubility of Mg in these metals is also negligibly low [3]. Based on the equations of state of Mg, Co, Ni, and Fe [13,18] and the first Hume-Rothery rule, we estimated, without any complex quantum mechanical calculations, that at pressure above 40–50 GPa magnesium could dissolve in cobalt, nickel, or iron (see supplementary materials [15]). Following the same methodology, we conducted experiments on alloying Ni and Mg at 86(5) GPa and 3300(200) K, and Co and Mg at 105(5) GPa and 3450(250) K. We found that at conditions of our experiments about 9 at. % Mg could dissolve in Ni and more than 12 at. % Mg in Co (Table I, supplementary materials [15]).

Our observations also suggest that magnesium can be an important light element in Earth's outer core. An important point here is that magnesium is not simply one more element in a long list of light elements proposed to be present in the Earth core. It is one of the most abundant of the Earth elements, which was *never* before seriously considered to be present in the core because at *ambient conditions* magnesium simply does not alloy with the iron. All current estimates of the composition of Earth's mantle are based on assumption that *there is no Mg* in the core.

In conclusion, we demonstrated both theoretically and experimentally that pressure could significantly affect the ability of elements to form alloys. Iron and magnesium, nickel and magnesium, and cobalt and magnesium practically immiscible at ambient pressure could form an alloy with about 10 at. % Mg in the megabar pressure range.

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