ALLOYING BEHAVIOR OF THE RARE EARTH METALS WITH MANGANESE

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General features of the phase equilibria for binary and ternary systems formed by rare earth metals (REM or R) with Mn and other d-metals and p-elements (Me) are described and reviewed. On passing from the R-Mn alloys of the light REM to those of the heavy ones, a progressive change in the shape of the phase diagrams and an increasing stability of the intermediate phases (RMn12, RsMn23, and RMn12) is noticed. In particular, no compounds and a miscibility gap in the liquid state can be observed for La and Ce (which in this case behave like the alkaline earths). In the Pr-Mn and Nd-Mn systems no intermediate phases are stable down to room temperature. The peculiar trend of the R-Mn alloys is, moreover, compared with that exhibited by systems of transition metals close to manganese in the Periodic Table. In the ternary systems R-Mn-Me (the R-Mn-Al, R-Mn-Si and R-Mn-Ge ones were considered) and R-R'-Mn the dependence of the main phase equilibrium characteristics on the atomic radii of REM was observed, too. For the R-R'-Mn alloys a comparison is made between the experimental data (literature data and the authors' results) and those which can be predicted on the basis of the general alloying behavior of REM.

INTRODUCTION

The properties of alloys containing rare earth metals (REM or R) and manganese, especially R- Me-Mn (Me = metal), may be of interest in view of possible technical applications, such as magnetic materials, etc.

The properties and characteristics of these alloys, moreover, are especially interesting in a presentation of the general alloying behavior of the REM. If we consider, in fact, a scheme of types of alloys formed by the different elements with the REM, we have patterns such as those summarized in Fig. 1 which gives, as an example, the compound formation capability of two typical trivalent REM, one "light" and one "heavier." Considering different elements of the rare earth family we generally have very similar behavior for the so-called "trivalent" REM. For the alloys with a given partner, on passing from one REM to the subsequent ones, we have indeed a small gradual variation but within a similar (general) pattern. On the other hand, in Fig. 1 we observe two different kinds of behavior in relation to the compound formation capability according to the position of the other components in the Periodic Table. We can consider two types of element partners: those which do not form any compound (for instance, Ti, Nb, etc. which give simple phase diagrams) and elements which form a more or less large number of compounds. These elements include the last transition metals and the elements of the p-block of the Periodic Table. The regions of the Periodic Table corresponding to the highest stability of the compounds are around the noble metals and towards the right. These compounds are characterized by high or very high melting points and high negative values of $\Delta H_{\text{form}}$. The boundary between the two types of elements (those forming and those not forming compounds with the trivalent REM) is represented by the elements close to manganese in the Periodic Table.
Fig. 1. Compound formation capability of two typical trivalent REM — La (a) and Gd (b). The number of intermediate phases formed with the different elements (here presented in the order of the Periodic Table) is given. "0" means that the phase diagram has been studied and no compounds have been found; "-" means that the phase diagram has not been studied and no compounds have been identified.

Fig. 2. Stoichiometries and crystal structures of R—Mn phases.

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The stoichiometries of the phases and their crystal structures for different R—Mn systems are shown in Fig. 2. The effect of pressure on R—Mn phases has also been reported in the literature, in particular the investigation of the high-pressure synthesis of RMn₂ compounds with the MgZn₂ (Laves) structure [72Eat] and the study of the Yb-Mn system [83Tvy]).

On passing from the first to the subsequent REM we may notice the following trend. The La—Mn system [42Rol] is characterized by very weak interactions: no compounds are formed and complete immiscibility in the solid state and a quite large miscibility gap also in the liquid state is found (Fig. 3a). A similar phase diagram is given by the Ce—Mn system [52Ian, 64Tha]. With the heavy REM we have the formation of a certain number of intermediate compounds: a typical example may be that reported in Fig. 3b where we see the compounds HoMn₁₂, Ho₆Mn₂₃, and HoMn₂ (with the latter being a Laves phase) being stable in a temperature range from quite high to room temperature. The trends of the liquidus curves (their crossing when extrapolated, etc.), however, are not completely clear and should be verified further [940ka]. The stoichiometries (and the corresponding crystal structures) and the sequence of peritectic reactions have been described for nearly all the R—Mn systems [67Kir, 70Kir]. On passing from the light to the heavy REM we have a certain number of