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Peculiarities of Components' Interaction in Rare Earth–Transition Metal–Silicon Systems in $R(M_xSi_{1-x})_{2-y}$ Composition Region

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The explanation of ternary compounds, forming with AlB_2 structure type in the rare earth metal–transition metal–silicon systems, implements on base of analysis of the dependence of the valence-electron concentration *versus* the kind of the transition metals in their solid solutions in the binary compounds with AlB_2, α-$ThSi_2$, and α-$GdSi_2$ structure types appropriate to the rare earth–silicon systems. There is shown that the silicon content (as the electron donor) during formation of the ternary compounds with AlB_2 structure type is dependent on the kind of transition metal and this content is decreased in the series of the compounds with Fe, Co, Ni, and Cu consecutively. The experimental data on concentrational intervals of the stability ranges of these ternary compounds are proposed to the qualitative evaluation of the effective valency of the transition metal atoms.

Key words: phase equilibria, intermetallic compounds, ternary systems, silicides, solid solutions

In the R–M–Si systems (where R = Sc, Y, La, rare-earth elements, and U; M = Zr, Hf, Nb, Ta, Cr, Mo, W, Mn, Re, Fe, Co, Ni, Cu and Rh) it was established that the solubility of M components in the binary compounds of the R–Si systems did not exceed 10 atomic per cent [1–5]. The special interest is developed to the solid solutions based on $RSi_{2-1.56}$ silicides. In some cases they are characterized by a large extent of solubility (for example, in binary $CeSi_{2-1.65}$ up to 17 at.% of Mn are solved, in binary $YSi_{1.56}$ — up to 27 at.% of Ni). Quite often the direction of the solubility deviates from the permanent concentration line of the R component. The direction of the homogeneity regions of the solid solutions based on $YSi_{1.56}$ compound, that were found in isothermal sections of Y - {Cr, Mn, Fe, Co, or Ni} - Si systems (Fig. 1), may be explained by various mechanisms of its formation. The homogeneity region of the solid solution must coincide with the straight line between the vertex of the phase triangle (M) and $YSi_{1.56}$ composition (the line *a* in Fig.1), if the solid solution is generated by the M atoms intercalation into the vacancies of the initial structure. The deviation of the homogeneity range direction of the solid solutions from the straight line *a* is connected

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with the substitution of the vacancies by the statistical composition of (M, Si) atoms. The ratio M/Si depends on M component.

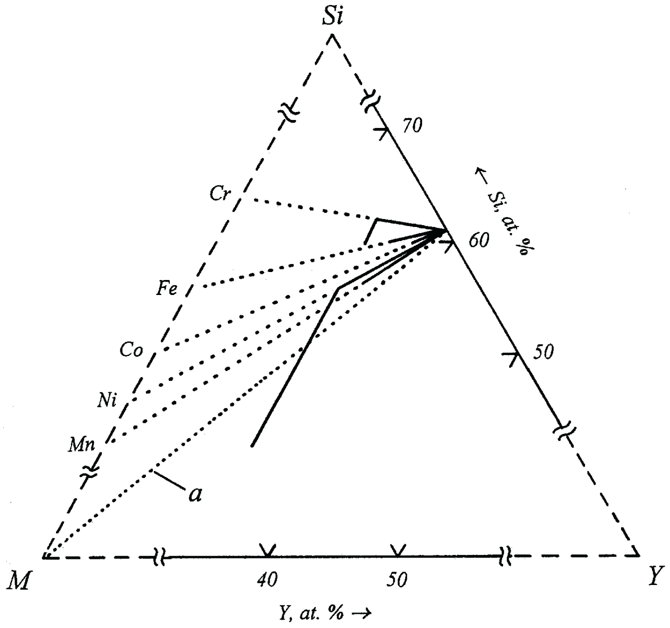

Figure 1. Arrangement of solid solutions based on $Y(M_x,Si_{1-x})_{2-y}$ compounds in Y–M–Si systems (M = Cr, Mn, Fe, Co, or Ni).

It was mentioned in [6] that the valence-electron concentration (*VEC*) (*i.e.* the mean number of the valent electrons per atom [7]) greatly affects on phases' generation, namely with AlB_2, α-$ThSi_2$, and α-$GdSi_2$ structure types. There was considered for these compounds that Si atoms were directly bonded between themselves and formed the networks and cores in the lattice space. The transition metal atoms reduce *VEC* in comparison with initial binary rare earth silicides and change the band structure of the compounds, when the formation of the solid solutions, based on such binary compounds, takes place. The largest deficiency of the electrons in the valence band is created by Cr. Less deficiency of *VEC* is introduced by Fe and still less deficiency by Mn and Co, respectively. Ni gives a low influence on *VEC*. To compensate of *VEC* reduction in $Y(Si_{1-x}M_x)_{1.56}$ there are needed additional electron donors, namely silicon atoms, to fill the silicon sublattice vacancies together with M component. The quantity of these Si atoms must be to such an extent increased as the more deficiency of *VEC* introduced is by one or either transition metal.

Already known solid solutions of Fe or Si based on binary Gd_2Si_3 and $Y(Si_{1-x}Mo_x)_{1.56}$ compounds also confirm this explanation. In view of these points, as a rule, we evaluate the stabilization of ternary compounds with AlB_2 structure type in La–{Fe,Co, or Ni}–Si systems. Small stability regions are characteristic of these solutions based on the binary $LaSi_{2-x}$ compound (α-$ThSi_2$ structure type). Homogeneity regions of the ternary compounds with AlB_2 structure type naturally displace to the lower silicon content direction and to the larger transition metal content direction, when we pass from the Fe containing systems to the systems with cobalt or nickel (Fig. 2*b*).

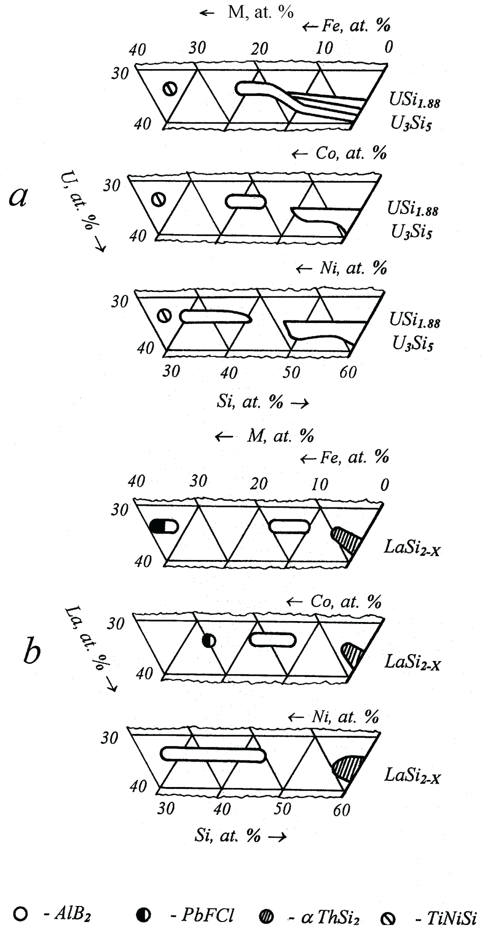

Figure 2. Solid solutions and ternary compounds of U–M–Si systems (M = Fe, Co, or Ni) in the regions closed to $USi_{1.88}$ and U_3Si_5 compositions (a); solid solutions and ternary compounds of La–M–Si systems (M = Fe, Co, or Ni) in the regions closed to $LaSi_{2-x}$ composition (b).

Such tendency is observed in Ce–{Fe,Co,Ni, or Cu}–Si systems (Fig. 3). Furthermore, two ternary compounds with AlB_2 structure type are formed in the Ce–Cu–Si system. Thus, the metals with the most filled up *d*-shell form the ternary compounds with AlB_2 structure type for the greatest content of M component. And *vice versa*, the reduction of the *d*-electrons number in appropriate transition metal leads to this phase formation for decreased M content.

There are solid solutions $U_3(Fe_xSi_{1-x})_5$ and $U(Fe_xSi_{1-x})_{1.88}$ up to 22 at.% Fe in the U–Fe–Si system (Fig. 2a). In the similar systems with Co or Ni the expansion of these solid solution regions is reduced and ternary compounds with the AlB_2 structure type are observed. As in the Ce–{Co or Ni}–Si systems (Fig. 3) the compounds have considerably expanded homogeneity regions. The maximum silicon contents in these regions are equal to 51 and 48 at.% of Si, respectively. This also confirms the conclusion about the increase of silicon content for stabilization of the phase with AlB_2 structure type in the iron ternary system in comparison with appropriate cobalt system, a still lower Si content is needed to stabilize this phase in the nickel ternary system.

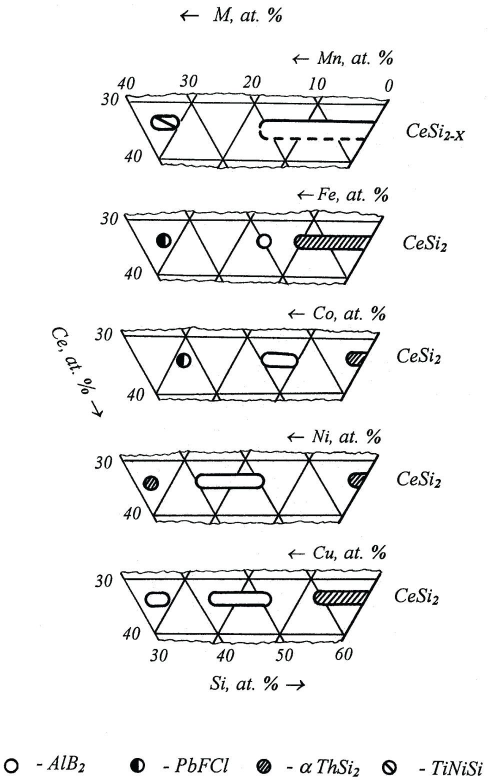

Figure 3. Solid solutions and ternary compounds in Ce–M–Si systems (M = Mn, Fe, Ni, or Cu) in the regions closed to $CeSi_2$ composition.

In Eu–{Fe, Co, Ni, or Cu}–Si ternary systems the substitutional solid solutions with large extension, based on the $EuSi_2$ compound with α-$ThSi_2$ structure type, are absent [5] (see Fig. 4). Ternary compounds with the AlB_2 structure are absent in such ternary system with Fe. In the Eu–Co–Si system this compound is formed at 33 at.% Co. In Ni ternary system this compound is formed at 50 at.% Ni, and in Cu ternary system – at 45 ÷60 at.% Cu. In [5] it was shown that the effective valency V_{eff} of Eu atoms in the $EuCo_{0.33}Si_{1.67}$ and $EuCu_{0.84}Si_{1.2}$ compounds is equal to +2. It may be proposed that the reduction in V_{eff} of rare earth atoms in this case leads to the *VEC* decrease. As a result, the binary compound with α-$ThSi_2$ structure is stable at stoichiometric composition.

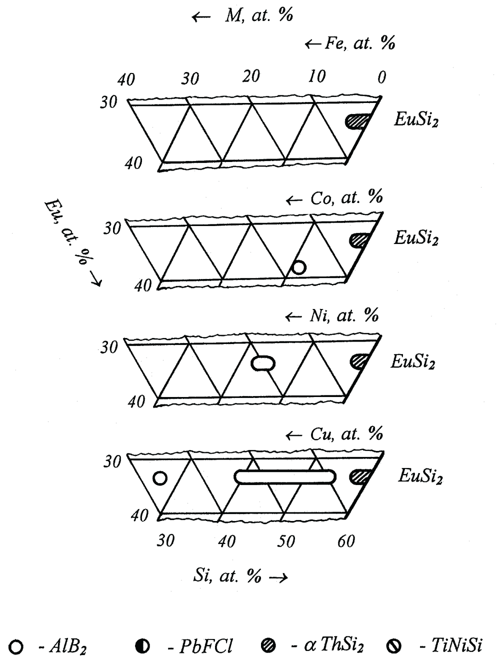

Figure 4. Solid solutions and ternary compounds in Eu–M–Si systems (M = Fe, Co, Ni, or Cu) in the regions closed to $EuSi_2$ composition.

Taking into account the experimental data on concentration regions of the solutions with M and Si and postulating the *VEC* value (for example in $YSi_{1.56}$ $VEC = 9.24$) we qualitatively evaluate the V_{eff} change of the transition metal atoms in these solutions. We may conclude that in these solid solutions and ternary compounds with AlB_2 structure type the *d*-shell of a transition metal is essentially different from *d*-shell of an appropriate pure transition metal. It is quite possible that the V_{eff} values are in a relation with the real energy band structure of the $R(M_xSi_{1-x})_{2-y}$ compounds. The values of the relative valencies of transition metals in binary and ternary silicides derived by this hypothesis is quite undiscrepant with the idea suggested in the work [6, p. 264]. These valencies may be accepted as initial for further calculations of the element valencies in ternary silicide compounds and for the estimation of the relative changes in valency of the transition and rare earth metals as well.

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