# CRYSTAL STRUCTURE OF COMPOUNDS AND PHASE EQUILIBRIA IN TERNARY SYSTEMS OF TWO TRANSITION METALS AND SILICON

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As the result of a complete or partial study of the phase equilibria in a number of ternary systems containing two transition metals (elements with unfilled electron levels 4d, 5d and 6d) and silicon, 39 ternary metallic compounds have been discovered. Compounds have been found in the systems Sc(Ti, V, Cr, Mn, Zr, Nb, Mo, Hf, Ta, W, Re) – Fe (Co, Ni) – Si. In the systems Cr(Mn) – Fe – Si, Cr – Mn – Si, Fe – Co(Ni) – Si, Co – Ni – Si, V – Mo – Si and Re – Fe(Ni) – Si, no ternary metallic compounds have been discovered.*

The alloys were manufactured from metals of high purity principally by high-purity melting in corundum crucibles in an atmosphere of inert gas. Some of the alloys were made by electric arc melting (V – Mo – Si alloys) or by melting in a Tamman furnace (alloys containing W, Ta and Re). The phase equilibria were investigated by x-ray and microstructure methods.

Table 1 gives the characteristics of the ternary metallic compounds found.

The structural types T, $\lambda_1$, $\lambda_2$, $\chi$, $\pi$, $\sigma$, R, $\mu$ and $\eta$, of which we have found representatives in the ternary systems of two transition metals and silicon, are related to each other. The structures corresponding to them are closest packings of atoms of different sizes [5]. In the atoms of smaller size (atoms of Fe, Co, Ni and also Si), they are characterized by a coordination number 12 and a coordination polygon in the form of a icosahedron. Atoms of larger size (atoms of Sc, Ti, V, Cr, Mn, Zr, Nb, Mo, Hf, Ta, W and Re) have a coordination number of 13, 14, 15, 16 or 17.

The structure type $Cu_2MnAl$ (H-phases) has a coordination number 14. H-phases are formed at compositions close to the T-phases, having in common with them a coordination number 14 and a similar configuration of atoms.

In all the compounds found, silicon acts as a metal component. In the majority, its atoms are in the same positions as are also the atoms of Fe, Co and Ni; consequently, the effective sizes of the atoms Fe, Co, Ni and Si are similar. In isolated cases (in compounds of Cr and V), silicon may replace some of the atoms of larger size, for example chromium in the compound $(Cr, Si)_3Ni_2Si$, or even replace all positions having coordination numbers greater than 12 [compounds $V_3Co_5Si_2$ and $V_3Ni_5Si_2$, for which the probable distribution of the atoms corresponds to the formulas $Si_5(V, Co)_{24}$ and $Si_5(V, Ni)_{24}$].

In the investigated systems Cr(Mn) – Fe(Co, Ni) – Si, Cr – Mn – Si, Fe – Co(Ni) – Si, Co–Ni–Si and also V–Mo–Si, we found a continuous series of solid solutions (css) or limited solubility as between binary silicides. Table 2 gives the results obtained in the investigation of these systems. The mutual solubility of the silicides in the systems $Me_1 – Me_2 – Si$ (where Me = Cr, Mn, Fe, Co) has also been studied in [6], and the mutual solubility of the silicides in the ternary system Mn – Fe – Si in [7].

The results we have obtained and other published investigations [8-17] indicate some regularities in the structure of ternary metallic systems containing two transition metals and silicon. Of all the 276 possible ternary systems, so far phase equilibria in 60 systems have been studied fully or partly. Their characteristics are shown in Table 3. The table does not include systems not yet investigated having as one component the metals: Y, Tc, Ru, Rh, Pd, La, Os, Ir and Pt.

The data in Table 3 show that all the ternary systems investigated may be divided into two groups. The first group comprises systems in which are formed ternary metallic compounds possessing crystal structures with closest packing of atoms of different sizes. This is characteristic only for systems containing as one component a transition

* The system Cr(Mn, Mo, W) – Fe(Co, Ni) – Si has been studied previously [1-4]; the system V – Mo – Si has been studied jointly with E. M. Savitskii, V. V. Baron and Yu. V. Efimov.

TABLE 1. Ternary Metallic Compounds of Two Transition Metals and Silicon

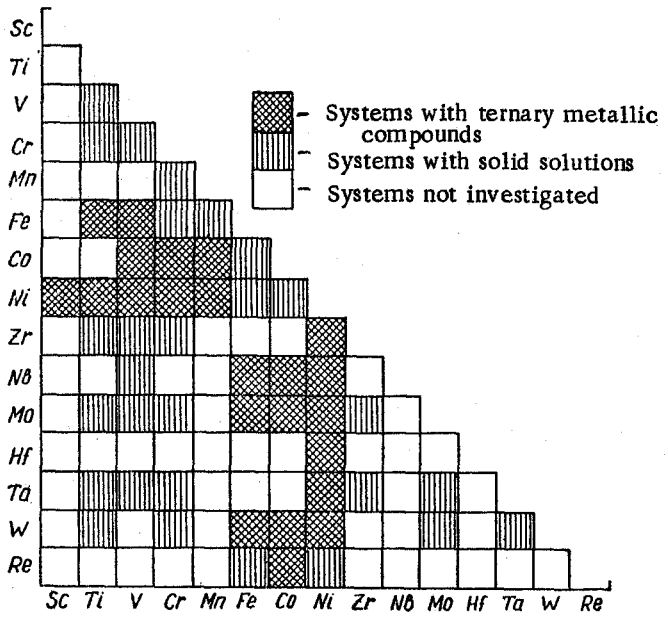
| Compound | Phase designation, structure type | Coordination number | Lattice constants, A | |
|---|---|---|---|---|
| | | | *a* | *c* |
| $MnNi_{1,55}Si_{0,45}$ | $\lambda_2$; $MgCu_2$ | 12,16 | 6,686 | — |
| $VCo_{1,1}Si_{0,9}$ | $\lambda_1$; $MgZn_2$ | 12,16 | 4,710 | 7,424 |
| $VNi_{1,2}Si_{0,8}$ | $\lambda_1$; $MgZn_2$ | 12,16 | 4,711 | 7,461 |
| $MnCo_{1,1}Si_{0,9}$ | $\lambda_1$; $MgZn_2$ | 12,16 | 4,747 | 7,467 |
| $MnNi_{1,1}Si_{0,9}$ | $\lambda_1$; $MgZn_2$ | 12,16 | 4,762 | 7,507 |
| MoFeSi | $\lambda_1$; $MgZn_2$ | 12,16 | 4,751 | 7,662 |
| MoCoSi | $\lambda_1$; $MgZn_2$ | 12,16 | 4,744 | 7,570 |
| MoNiSi | $\lambda_1$; $MgZn_2$ | 12,16 | 4,744 | 7,578 |
| WFeSi | $\lambda_1$; $MgZn_2$ | 12,16 | 4,738 | 7,666 |
| WCoSi | $\lambda_1$; $MgZn_2$ | 12,16 | 4,733 | 7,721 |
| WNiSi | $\lambda_1$; $MgZn_2$ | 12,16 | 4,734 | 7,578 |
| $Re_2Co_3Si$ | $\mu$; $W_6Fe_7$ | 12,14<br>15,16 | 4,633 | 25,514 |
| $Sc_6Ni_{16}Si_7$ | $T$; $Mg_6Cu_{16}Si_7$ | 12,13<br>14,17 | 11,45 | — |
| $Ti_6Ni_{16}Si_7$ | $T$; $Mg_6Cu_{16}Si_7$ | 14,17 | 11,22 | — |
| $V_6Ni_{16}Si_7$ | $T$; $Mg_6Cu_{16}Si_7$ | 14,17 | 11,13 | — |
| $Cr_{9,5}Ni_{12,5}Si_7$ | $T$; $Mg_6Cu_{16}Si_7$ | 14,17 | 11,10 | — |
| $Mn_6Ni_{16}Si_7$ | $T$; $Mg_6Cu_{16}Si_7$ | 14,17 | 11,15 | — |
| $Zr_6Ni_{16}Si_7$ | $T$; $Mg_6Cu_{16}Si_7$ | 14,17 | 11,47 | — |
| $Nb_6Ni_{16}Si_7$ | $T$; $Mg_6Cu_{16}Si_7$ | 14,17 | 11,24 | — |
| $Hf_6Ni_{16}Si_7$ | $T$; $Mg_6Cu_{16}Si_7$ | 14,17 | 11,39 | — |
| $Ta_6Ni_{16}Si_7$ | $T$; $Mg_6Cu_{16}Si_7$ | 14,17 | 11,22 | — |
| $MnCo_2Si$ | $H$; $Cu_2MnAl$ | 8+6 | 5,670 | — |
| $VCo_2Si$ | $H$; $Cu_2MnAl$ | 8+6 | 5,659 | — |
| $Cr_3Ni_5Si_2$ | $\pi$; $\beta$-Mn, $Au_4Al$ | 12,14 | 6,108 | — |
| $Cr_3Co_5Si_2$ | $\chi$; $\alpha$-Mn, $Ti_5Re_{24}$ | 12,14,16 | 8,687 | — |
| $V_3Fe_5Si_2$ | $\chi$; $\alpha$-Mn, $Ti_5Re_{24}$ | 12,14,16 | 8,843 | — |
| $V_3Co_5Si_2$ | $\chi$; $\alpha$-Mn, $Ti_5Re_{24}$ | 12,14,16 | 8,747 | — |
| $V_3Ni_2Si$ | $\eta$; $Ti_2Ni$, $W_3Fe_3C$ | 12,14 | 10,78 | — |
| $(Cr, Si)_3Ni_2Si$ | $\eta$; $Ti_2Ni$, $W_3Fe_3C$ | 12,14 | 10,62 | — |
| $Mn_3Ni_2Si$ | $\eta$; $Ti_2Ni$, $W_3Fe_3C$ | 12,14 | 10,75 | — |
| $Nb_3Ni_2Si$ | $\eta$; $Ti_2Ni$, $W_3Fe_3C$ | 12,14 | 11,19 | — |
| $Ta_3Ni_2Si$ | $\eta$; $Ti_2Ni$, $W_3Fe_3C$ | 12,14 | 11,15 | — |
| $Cr_{6,5}Ni_{2,5}Si_{1,0}$ | $\sigma$; CrFe | 12,14,15 | 8,787 | 4,570 |
| $V_2Fe_2Si$ | $R$; (Mo—Cr—Co) | 12,14<br>15,16 | 10,799 | 19,243 |
| $V_5Co_3Si_2$ | $R$; (Mo—Cr—Co) | 15,16 | 10,787 | 19,199 |
| $V_6Ni_3Si$ | $R$; (Mo—Cr—Co) | 15,16 | 10,81 | 19,28 |
| $Cr_3Co_3Si_2$ | $R$; (Mo—Cr—Co) | 15,16 | 10,587 | 18,930 |
| $Mn_5Co_2Si_3$ | $R$; (Mo—Cr—Co) | 15,16 | 10,755 | 19,126 |
| $(Mn, Ni)_7Si_3$ | $R$; (Mo—Cr—Co) | 15,16 | 10,81 | 19,28 |

TABLE 2. Mutual Solubility of Some Silicides of Transition Metals

| Silicides investigated, I – II | Solubility in the compound, mole % | | Silicides investigated, I – II | Solubility in the compound, mole % | |
|---|---|---|---|---|---|
| | I | II | | I | II |
| CrSi–MnSi | css | | $Mn_3Si$–$Fe_3Si$* | css | |
| $CrSi_2$–$FeSi_2$ | < 5 | < 5 | MnSi–CoSi | ~ 50 | ~ 10 |
| CrSi–FeSi | css | | $Mn_5Si_3$–"$Co_5Si_3$" | 15 | — |
| $Cr_5Si_3$–$Fe_5Si_3$ | ~ 30 | ~ 25 | $Mn_3Si$–$Co_3Si$ | < 5 | < 5 |
| CrSi–CoSi | css | | MnSi–NiSi | 35 | < 5 |
| CrSi–NiSi | ~ 70 | < 5 | FeSi–CoSi | css | |
| $MnSi_2$–$FeSi_2$ | ~ 5 | ~ 10 | FeSi–NiSi | 30 | < 5 |
| MnSi–FeSi | css | | CoSi–NiSi | 25 | < 5 |
| $Mn_5Si_3$–$Fe_5Si_3$ | css | | $V_5Si_3$–$Mo_5Si_3$ | css | |

*According to data in [7], between the metallic compounds $Mn_3Si$ and $Fe_3Si$, there is a narrow region of inhomogeneity, the solid solution $(Mn, Fe)_3Si$ extends to 42 at. % Fe and the solid solution $(Fe, Mn)_3Si$ to 24 at. % Mn.

TABLE 3. Characteristics of Ternary Systems Containing Two Transition Metals and Silicon




metal having the smallest atoms (Fe, Co or Ni). All the other ternary systems not containing Fe, Co or Ni form the second group.

In these systems and also in the systems Cr(Mn) – Fe – Si and Re – Fe(Ni) – Si, ternary metallic compounds of the above-mentioned class have not been found; these systems, there are continous solid solutions of isostructural binary compounds, or there is limited solubility in binary silicides.

The metals Fe, Co and Ni, having atoms similar in size to silicon atoms, form silicides of structure types which have almost no representatives among the silicides of other transition metals, except some silicides of Cr, Mn and Re. In ternary systems containing Fe, Co or Ni as one component, therefore, there are no isostructural silicides, which could form continuous solid solutions. At the same time, the considerable difference in the sizes of the atoms of the transition metals creates favorable conditions for the formation of ternary intermetallic compounds.

## SUMMARY

Phase equilibria in ternary systems of two transition metals and silicon have been investigated.

In systems containing iron, cobalt or nickel, ternary phases with closest packing of atoms have been found; in some systems, there are continuous solid solutions of isostructural binary compounds, or there is limited solubility in binary silicides.

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# PROSPECTS OF UTILIZING REFRACTORY COMPOUNDS FOR MANUFACTURE OF HIGH-TEMPERATURE THERMOCOUPLES

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Materials to be employed in the manufacture of thermocouple junctions must meet several special requirements as regards mechanical, chemical and physical properties. To get accurate measurements, thermoelectrodes must be homogeneous both in chemical composition and in structure, and their properties must not change during use. The chemical composition of metallic thermocouple electrodes is homogenized by melting and subsequent annealing; homogenization of the structure is achieved by repeated broaching and recrystallization.

Many metallic thermocouples possess reproducible standard calibration characteristics and are employed in mass production of industrial apparatus. In industrial applications, metallic thermocouples are not used above 1300° in air (PG10/0), or above 1800° in a neutral medium or in vacuo (VR5/20), notwithstanding that a large variety of thermocouples consisting of either noble or refractory metals have been developed (Table 1).

As can be seen in the table, temperatures of 1800-1900° evidently constitute the limits of stable operation of metallic thermocouples, because at these temperatures recrystallization and growth of the grains take place even in refractory metals such as tungsten and rhenium, resulting in a change of the thermo-emf. Since noble and refractory metals cannot be used in the various aggressive media employed in practice today, a new type of thermocouples on the basis of nonmetals must be developed.

It is known that the properties of refractory compounds do not change at high temperatures in various aggressive and nonaggressive media. Many of them are stable up to 1700° in oxidizing media, molten salts, metals, steel and slags, and even up to 2500-3000° in protective, neutral or carburizing gases.

Tests have proved the relatively high stability of titanium and zirconium carbide in a hydrogen atmosphere at temperatures up to 2350-2400°, in converted natural gas up to 2500°, in protective and carburizing media up to the melting points (the stability during operation was determined from the change in weight and thermo-emf of the samples forming a couple with platinum and being annealed for ten hours at the maximum temperature). The results reported in Table 2 indicate that the thermoelectric properties hardly changed at all under these conditions.

Tests on the stability of refractory materials in molten steel, cast iron and slags showed that silicides and carbides are completely unsuited for these purposes, and that some borides are highly stable in the above melts [1]. Silicides were found to be stable in molten salts (NaCl + $BaCl_2$) at 900-1100°.