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RESEARCH ON PHASES CONTAINING TRANSITION METALS
AND NON-METALS

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Research on phases containing transition metals
and non-metals

This report deals with accurate determinations of basic properties of phases in systems of transition metals and non-metals. These studies are mainly confined to the borides, silicides and phosphides of transition metals from Groups VI, VII and VIII. Comprehensive and detailed reviews of the binary transition metal borides, silicides and phosphides have been given in Technical Notes No. 13 and 34. The present report is therefore confined to general aspects only, which are presented in two main paragraphs: "Phase analyses" and "Crystal chemistry". Some further comments are made on very recent results not included in the Technical Notes mentioned above.

Phase analyses

In spite of very intense basic research on binary transition metal borides, silicides and phosphides, the characterisation of these phases is in many cases incomplete. This is particularly true for phases containing rare earth metals, but also for phases containing e.g. Group IV and V transition metals. In many systems, the number and approximate composition of the phases may be known, but the lack of quantitative information about homogeneity ranges and melting points prevents the construction of the complete equilibrium diagrams.

Our phase-analytical work has been devoted to the solid regions of some 35 binary and 15 ternary systems. The alloys have been prepared by heating weighed amounts of the component elements at high temperatures under carefully controlled conditions. Special efforts have been made to ensure high purity and equilibrium conditions of the products. The X-ray powder diffraction technique and chemical analytical methods have been the chief research tools.

Borides. Binary borides of the following metals have been investigated: Cr, Mn, Re, Fe, Ru, Os, Co, Rh, Ir, Ni, Pd and Pt. Detailed reports have been given in Technical Notes No. 1, 5, 6, 8, 11, 13, 16, 17, 20, 25 and 32. The phase relationships in the systems Cr-B, Mn-B, Re-B, Fe-B, Ru-B, Os-B, Co-B and Ni-B are fairly well clarified. However, the compositions of the boron-rich phases in the Re-B, Ru-B, Os-B (and also Mo-B and W-B¹) systems are still somewhat uncertain. It was first pointed out by La Placa and Post² that only a fraction of the available crystallographic positions for the boron atoms are occupied in the structure of the most boron-rich phase in the Re-B system, and similar results have recently been obtained by Roof and Kempter³ in the Ru-B and Os-B systems. Further studies seem desirable.

○ In re-investigations of binary boride systems, inconsistencies between the old and the more recent results have frequently been encountered. This is certainly in many cases caused by the high impurity content in the old boride preparations. For instance, heating metal and boron powder in evacuated and sealed silica tubes may lead to serious contamination of silicon and oxygen, and ternary boro-silicides may even be formed (see Technical Notes No. 2, 5, 6, 13 and 35). With the high-purity chemicals and good high-vacuum furnaces now available, much more accurate determinations of the Me-B phase diagrams can be made, which appears to be an important task for future research.

In recent studies the electrical properties of lanthanum boride have been investigated⁴. A number of investigations have been published on the mechanical properties of some borides, which may be useful as high-temperature construction materials⁵. In this connection a recent study of boron-containing titanium alloys may be mentioned⁶.

Few systematic studies of the chemical properties of borides seem to have been made. A better knowledge about oxidation of borides should be of great theoretical and practical interest.

Silicides. Binary silicides of the metals Mn, Fe, Ru, Co, Rh, Ni and Pd have been investigated as reported in Technical Notes No. 3, 5, 9, 15, 16, 18, 23 and 35. Although some recent studies ⁷⁻¹³ have added to our knowledge of the silicides, a large number of Me-Si systems, in particular those containing platinum metals, are still very incompletely elucidated. However, as was mentioned in the case of borides, the experimental difficulties in determining the equilibrium diagrams are now largely overcome.

Some silicides have semi-conducting properties and high thermo-electric force, which has stimulated an intense research on these materials ¹⁴⁻¹⁹. Few studies seem to have been devoted to the mechanical properties of silicides in "bulk form".

Phosphides. Binary phosphides of the following metals have been studied: Ti, V, Cr, Mo, W, Mn, Re, Fe, Ru, Os, Co, Rh, Ir, Ni, Pd and Pt. The results have been reported in Technical Notes No. 2, 4, 7, 10, 12, 19, 21, 22, 24, 26, 28, 30, 31 and 33. The phase relationships have been well established in the solid regions of the systems Mo-P, W-P, Mn-P, Fe-P, Ru-P, Os-P, Co-P, Rh-P, Ir-P and Ni-P, while the conditions in the remaining systems need further clarification. In general, the homogeneity ranges for the phosphides investigated are very narrow. However, extended homogeneity ranges have been observed for some phases with the ideal composition Me_2P . Careful single-crystal investigations indicate that the extended homogeneity ranges can be interpreted in terms of metal atom vacancies in the structures (see Technical Notes No 12 and 30).

Recently, the occurrence of mono-phosphides of hafnium ²⁰ scandium and yttrium ²¹ has been demonstrated. However, the information regarding the phosphides of Groups III, IV and V transition metals is still rather scanty.

The physical properties of transition metal phosphides have hitherto been very little explored. Some data for mono-

phosphides of Ti, V, Nb, Ta, Cr, Mo, W and Mn were recently reported²². All these phosphides are hard materials (comparable with hardened high-carbon steel) and resistivity measurements indicate metallic behaviour.

Ternary systems. A number of ternary systems containing transition metals and the non-metals boron, silicon and phosphorus have been investigated. In some cases more detailed studies have been made and phase-relationships and homogeneity ranges have been determined over large parts of the systems (the Fe-Si-B, Fe-P-B and Co-Si-B-systems as reported in Technical Notes No. 3, 15, and 24). In other cases the work has been confined to explorations of selected smaller regions of the systems (the Mn-Si-B, Ni-Si-B, Cr-P-B, Mn-P-B, Co-P-B, Ni-P-B, Cr-Co-P, Mn-Co-P, Fe-Co-P, Fe-Si-P, Co-Si-P and Cr-Ni-P systems, reported in Technical Notes No. 2, 12, 15, 24, 26 and 28).

The interest has been largely devoted to systems containing one transition metal and two non-metals. The Me-Si-B and Me-P-B systems have many features in common, and several ternary isomorphous boro-silicides and boro-phosphides with the composition Me_5XB_2 occur. A notable feature is the large solubility of boron in the phosphides. The solubility of silicon and phosphorus in the borides is, however, very limited except in borides of the cementite type ($Fe_3(B, Si)$, Co_3B , Ni_3B). The behaviour of phosphorus and silicon in the stabilisation of sigma-phases has been found to be very similar (see Technical Note No. 26).

Crystal chemistry

The main effort in our work on transition metal borides, silicides and phosphides has been devoted to studies of the crystal chemistry of these compounds. Some 70 crystal structures have been determined. In most cases the single-crystal

technique has been employed, and interatomic distances and scattering parameters have been determined to a high degree of accuracy.

The results of these studies have been collected and discussed in a general way in Technical Notes No. 13, 29 and 34. The main observations are as follows.

The structural similarities between metal-rich borides, silicides and phosphides are pronounced. Isostructural compounds occur frequently, especially in systems containing Group VII and VIII transition metals. Boron and silicon substitute to a large extent for phosphorus in several phosphide structures, and isomorphous Si/P replacement has been observed in silicide structures. Several isomorphous ternary boro-phosphides and boro-silicides occur.

In correlating and classifying these structures, the size-factor concept has proved very useful. In particular, the ordered distribution of the non-metal atoms observed in the ternary boro-phosphide and boro-silicide structures is understandable from the size-factor point of view; the boron atoms occupy the smaller, and silicon and phosphorus atoms the larger voids in the metal lattices. Furthermore, it has been shown that simple geometrical and topological arguments can explain particular trends in interatomic distances observed in various series of isomorphous phases.

There are, however, notable structural features, which can hardly be explained in terms of the size-factor. In metal-rich phosphides there seems to be a tendency for the phosphorus atoms to avoid short P-P contacts. The near environment of the phosphorus atoms thus consists of metal atoms only. In silicide, and particularly in boride structures, short non-metal contacts occur frequently. The difference in this respect between phosphides on the one hand, and borides and silicides on the other becomes more pronounced in phases with high non-metal content, where the number of short P-P contacts is very restricted while short B-B and Si-Si contacts form infinite two- or three-dimensional networks in the structures.

The metal—non-metal distances are generally in close agreement with the sums of the Goldschmidt metal radii and the tetrahedral covalent radii for the non-metals. However, it has been found that when the group number of the transition metal increases there is a tendency for the formation of progressively shorter metal—non-metal distances in comparison with the above mentioned radius sums. Extremely short distances occur in phases containing nickel, palladium and platinum.

These examples illustrate the shortcomings of the size-factor concept and emphasize the need of a more fundamental approach in the structural discussion. Unfortunately, the present state of the chemical bond theories for compounds between transition metals and non-metals is very unsatisfactory (a brief résumé is given in Technical Note No. 13). The hypotheses put forward provide very little material for detailed structural discussions and are very far from giving an account of the various physical and chemical properties of the compounds. The task of formulating a quantitative theory of the chemical bond in these compounds is indeed formidable, and little success is expected in the near future. At present, it seems desirable to collect accurate data for the electric, magnetic, thermodynamic and other important physical properties. While such knowledge can be expected to lead to a better foundation for theoretical speculations, it would be invaluable in developing materials for future technical applications.

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