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TERNARY METAL COMPOUNDS

BY: V. K. Vul'f

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TEMETARY METAL COMPOUNDS

By B. K. Vol'f

Introduction

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2. Ternary Kurnakov phases
3. Valant ternary metal compounds
4. Electronic ternary metal compounds
5. Ternary Laves phases
6. Ternary nickel-arsenide phases
7. Ternary interstitial phases
8. Properties and practical application of ternary metal compounds

Introduction

At the present time study has been made of a great number of metal compounds formed with two elements, i.e., binary compounds.

Kurnakov's teaching on bertholides and daltonides has become the
basis of the scientific classification of these compounds, and has made it possible
to determine their exact place among the binary metal phases. There are monographs
devoted to the classification of binary metal compounds according to their crystal
lattice /2-4/.

In recent years a whole number of surveys have been published on analysis of the
structure, formation and properties of certain groups
of binary metal compounds, and also on clarification of the part played by the latter
in industrial alloys and their potential application. Data on binary metal compounds
has made possible a fuller and more profound study of binary diagrams of state.

three-component systems have been studied to a considerably smaller extent,
however. These systems may contain diverse phases with from one to three elements;
for the main they are ternary \textit{complex} phases, since the pure components of
ternary systems, as well as the metal compounds frequently forming in these systems,
are always able to some extent to dissolve the excess components, forming either
normal or metalide solid solutions, accordingly.

The author /5/ has devised a system of classification for ternary metal phases
based on the comparison of the nature and extent of the homogeneous areas in the
ternary diagram of state.
Out of the eight types of ternary metal phases there are four different types, including ternary solid solutions based on one of the system components, which cannot be classed as metal compounds.

Ternary phases, which are limited metalide solid solutions, are close in structure and properties to the corresponding binary metal compounds on which they are based.

Since, as noted above, a great deal of research has been devoted to binary metal compounds, ternary phases of this type will not be considered here.

The most interesting are ternary phases which are characterized in their diagram of state by areas of homogeneity limited on all sides and degenerating into points when they lack the power to dissolve excess components. These phases, which usually have their own kind of crystal lattice and properties, are independent chemical compounds in the sense established by Kurnakov, and should be termed ternary metal compounds.

The phases of this type are the main concern of this article.

We should note in particular the ternary phases which are continuous solid solutions between two binary metal compounds. Although these phases are a particular case of metalide solid solutions, in a number of cases — usually in equimolecular and similar concentrations — they show superstructural lines in x-rays and manifest
particular properties different from those worked out according to the additivity principle, and hence constitute independent phases of the nature of ternary compounds.

In view of this we will later consider such phases along side the typical metal compounds.

1. General Features of Ternary Metal Compounds

Like binary compounds, ternary compounds may occur in alloys as a result of primary crystallization, peritectic transition, precipitation from solid phases or transition of solid phases into Kurnakov's compounds.

The stability of ternary compounds depends greatly on their composition, and, generally speaking, increases with the difference in the chemical nature of the component elements. Among the typical ternary metal compounds we find phases of the bertholide and daltonide type.

An example of a daltonide is the compound \( \text{S(Al, Cu, Mg)} \), which has been studied in detail in /6, 7/ and other work.

A bertholide nature is possessed, for example, by the ternary compounds \( \text{T(Al, Cu, Mg)} /6/ \) and \( \text{T(Al, K', Zn)} /6/ \). The research /9/ is devoted in particular to the investigation of ternary bertholides.

The principle factors which determine the composition and crystal structure of
ternary metal compounds are: the chemical nature of the elements forming them, the
valence electron concentration and the dimensional relationships of the atoms (ions).
These factors will be considered in more detail below.

The author /10/ was the first to give systematized data on the crystal lattice
of ternary metal compounds. In all, approximately 250 compounds have been described
and their structural types indicated.

Some of the general laws governing the relationship between the crystal structure
of ternary metal compounds, and the valence electron concentration, and the atomic
radii are considered in /11/.

An analysis of available data shows that most ternary metal compounds
..crystallize in close-packed lattices with high coordination numbers typical of
pure metals and binary metal compounds. The commonest lattices among them are ones
with a high degree of symmetry — cubic and hexagonal.

There are groups of isomorphic ternary metal compounds differing in the elements
contained in the same or neighboring groups in the periodic table. This is an
indication of the great part played by the chemical nature of the elements making
up the ternary compound. Below we consider some typical examples of this
crystallo-chemical analogy.
The nature of the crystal lattice of similar ternary metal compounds also
depends on the chemical properties of the constituent elements. For example, a
comparison of the crystal lattices of ternary compounds LiMgN and LiZnN (Fig. 1)
shows that the only difference between them is that in the case of the former
lattice the arrangement of metal atoms (Mg and Li) is statistical, while for the
latter it is systematized (Li and Zn atoms). This can be explained by the fact
that Li and Mg differ in their chemical nature to a lesser extent than Li and Zn.

Fig. 1. Crystal lattices of LiMgN and LiZnN (12); 1) Li + Mg; 2) N; 3) Zn; 4) Li.

Fig. 2. Crystal lattices of NiMnSb and Ni2MnSb (13); Arrangement of atoms for
NiMnSb: 1) Ni; 2) Sb; 3) Mn; arrangement for Ni2MnSb: type C2/m (13); 1) and 2) Ni;
3) Mn; 4) Sb; type P2_1/ (13); 1) and 3) Ni; 2) Mn; 4) Sb.

If there is a continuous transition between two ternary compounds, the rearrangement
of the crystal lattice is closely linked with a change in the nature of the chemical
bond. Thus, when going from NiMnSb to Ni2MnSb (13), the lattice changes from the
CaF type to the Heusler close-packed type (Fig. 2). At the same time there is an
intensification of the metal bond, which is confirmed by the corresponding change in the magnetic properties and an increase in plasticity.

Identical crystal lattices are often possessed by binary and ternary metal compounds which have similar chemical formulae, but differ chemically, having analogous elements. Typical examples of this are the pairs Co Al - Fe Ni Al , and Co Al - which produce Fe Ni Al , which have very similar x-ray photographs /14/.

More and more attention has been given of late to the study of the crystal structure of ternary metal compounds. We should point out the work of Schubert /15/ on the application of his own theory of the spatial correlation of electrons to the explanation of the structure of ternary compound lattices. Fig. 3. shows a model of this kind for the phase S(Al Cu Mg) with indication of the spatial distribution of atoms and electrons.

In the case of a number of ternary metal compounds with complex crystal lattices the arrangement of the atoms has been worked out and Brillouin zones have been constructed. When spatial models of the Brillouin zones for similar binary and ternary compounds are compared, a great similarity is often detected (see, for example, the models in Fig. 4 for the compounds Mn Si Al and Co Al according to /16/),
Below we give a brief systematic survey of metal compounds, showing that their composition and structure depend first and foremost on the chemical nature of the constituent elements, in accordance with their position in the periodic table; moreover, all the types characteristic of binary compounds can be found among them. This is a manifestation of the single nature of binary and ternary metal compounds.

Fig. 3. Crystal lattice of CuMgAl/15/. It shows arrangement of atoms and electrons (projection with respect to b axis). Figures indicate height of atom arrangement in values b/4a.

Fig. 4. First Brillouin zones for structure of ternary metal compound MnSiAl (I) and binary compound CoAl (II).

2. Kurnakov Ternary Phases

There are hardly any references in scientific literature to the existence of ternary metal compounds formed during the transition of ternary solid solutions. One can only mention the work of Nemilov and Rudnitskiy/17/, in which proof is given of the formation of a ternary metal compound CuFePt at \( \sim 1200^\circ \) as a result
of the transition of the solid solution copper-platinum-iron (Fig. 5).

Nevertheless, a number of works have established the effect of the third component on the conditions for the formation of Kurnakov's binary compounds. It has been brought to light that these elements Zn, Ni, Cd, Ti, Mg, Al, Sn and Ag, for example, affect the formation of the compounds AuCu and AuCu /18-21/.

Some of these elements (Zn, Ni, Mn, Ag) greatly reduce the formation temperature of binary compounds, while others have little effect in this sense. The reduction of the formation temperature of binary compounds increases with an increase in the third element dissolved in them.

Fig. 5. Diagram of state for Pt-CuFe alloys /17/;

Here is shown the formation of the ternary Kurnakov metal compound CuFePt

Of great interest are the unusual methods of investigating the chemical bonds in solid solutions, devised and tested with a great deal of experimental material by Grum-Grzhinaylo /22-27/. To detect the electron bonds expressing the nature of the chemical interaction between the atoms, Grum-Grzhilaylo used the method of
measuring the magneto-thermoelectric effects, the Hall effect and the residual electric resistance.

Study of the solid solutions in the systems Fe-Cr, Fe-Co, Co-Ni, Cu-Ni, etc., revealed characteristic inflexions in the curves corresponding to metal compounds of a certain composition. This research clearly confirms the change in the nature of chemical bonds in concentrations corresponding to the composition of the chemical compounds. The use of this method enabled Grum-Grzhilaylo to discover a number of new metal compounds, among them ternary compounds. For example, in the ternary system Fe-Co-Ni there were discovered ternary compounds of the composition FeNi-FeCo, FeNi-CoNi and FeNi-CoNi (Fig. 6). A number of ternary compounds were also discovered in the system Cu-Fe-Ni (Fig. 7).

Fig. 6. Metal compounds in the system Fe-Co-Ni /25/.

Fig. 7. Metal compounds in the system Cu-Fe-Ni /25/.

The so-called $\sigma$- and $\mu$-phases should also be counted among Kurnakov phases. The isomorphism of the $\sigma$-phases and their related chemical nature suggest the possibility of their forming together continuous solid solutions. This has been
proved, for example, in the case of the system FeCr-FeV /28/, in which there is unlimited mutual solubility both below and above the zone of the formation temperatures of the $\sigma$-phases (Fig. 8).

Similar solubility relationships exist when the $\mu$-phases interact. For example, the existence has been confirmed /29/ of continuous solid solutions for the isomorphous phases $\mu_{2}(Fe\%Mo)\) and $\mu_{1}(Co\%Mo)\) (Fig. 9).

Fig. 8. Continuous solid solutions between compounds FeCr and FeV ($\sigma$-phases) /23/:

1. Liquid + $\sigma$-solid sol.
2. Solid solution
3. $\sigma$-phases
4. Weight FeV in % weight
5. V axis in weight

Fig. 9. Continuous solid solutions between compounds $\mu_{2}(Co\%Mo)\) and $\mu_{1}(Fe\%Mo)\) at 1200 $^\circ C$ in the ternary diagram Fe-Co-Mo /29/:

1. Fe in % weight
2. Co in % weight
3. Ni in % weight
In a number of similar solid solutions there sometimes form ternary phases with extreme property values. There is no doubt that in such phases the magnitude of the chemical bond between the most interacting elements changes, which is a sign of the formation of associations close to typical ternary compounds.

3. Valence Ternary Metal Compounds

At the present time study has been made of a large group of ternary compounds containing elements from the I and V/periodic groups; Table 1 gives some examples. The constituent elements in these compounds show valence corresponding to their position in the periodic system. The investigation of similar compounds of the same kind has shown that their structure and properties change systematically as their chemical composition changes.

Table 1

Valent Ternary Compounds

<p>| | | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
</table>

1) Analogs differing in elements of V/ group
2) Compound
3) Literature reference
4) Analogs different in group II, III and IV elements
a) analogs differing in elements of II, III and IIB groups

b) compound

c) literature reference

For example, compounds containing the nonmetals LiMgN, LiAlP$_3$, LiAlAs$_2$, and so on, have a strongly marked salt-forming nature, which is confirmed in the majority of cases by high melting points, low electrical conductivity, low hydrolyzability and other characteristics of compounds with an ion bond /32/.

On the other hand, in similar compounds formed solely from the metals CuMgBi, CuCdSb etc, metal properties show up more clearly, and the metal bond predominates.

A similar analysis of crystal structures confirming the difference in properties and nature of the interatomic bond of certain groups of these compounds is given in /30, 34 and 35/.

4. **Electronic Ternary Metal Compounds**

Very few electronic ternary compounds satisfy the Hume-Rothery rules if the valence electron concentration (VEC) is reckoned by the general rules, and in particular, if the elements in the VIII group are given zero valence. For example,
according to /36/, and CuAlZn according to /37/, have a VEC = 3/2 and crystallize in the \( \beta \)-brass structure. If it is assumed that, according to /11/, the valence of manganese is equal to unity, then among the electronic \( \beta \)-phases we can also class such compounds as Cu MnAl, Cu \( \text{MnIn} \), Cu MnSn, \( \text{Ni MnSn} \), and so on.

Fig. 10. Valence electron concentration of ternary metal compounds containing aluminum and transitional metals /28/.

1) electron concentration el/at.

Few of the other ternary electronic compounds conform to the Hume-Rothery rule. To explain their structure Raynor and his coworkers /39, 40/ made use of Pauling's theory, which is based on the idea of the "negative" valence of transition metals with incomplete \( d \)-levels. According to this theory, when aluminum and silicon form metal compounds with the transition metals of the 4th period, Al and Si give up their valent electrons to the common electron 'collective' \( \text{Al}_{63} \text{Si}_{63} \text{Ni}_{63} \text{Mn}_{63} \text{Cu}_{63} \) while transition \( \text{MnSn} \) metals \( \text{CuAl} \) capture some of these to complete their own \( d \)-levels. The number of captured electrons depends on the element's position in the periodic table and can be calculated on the basis of the magnetic properties.
as inphase-Fothey with binary phases, of the elements. Thus, the transition elements are not given a zero valence, but rather a negative valence which, according to Pauling, is equal to the number of electrons in the so-called "atomic" orbits (Table 2).

Table 2

<table>
<thead>
<tr>
<th>1</th>
<th>Number of &quot;Vacant&quot; electrons for certain metals (from magnetic measurement)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>Element</td>
</tr>
<tr>
<td>3</td>
<td>Number of el/atom in the &quot;atomic&quot; orbits</td>
</tr>
</tbody>
</table>

If we work out the \( \frac{C}{C} \) for various ternary compounds from these values, we can single out several groups with identical \( \frac{C}{C} \) values (Table 3 and Fig. 10).

In group I the compounds 1, 2 and 5 are isomorphous; they all contain 33\text{\%} \text{at.} \text{aluminum}.

Table 3

<p>| 1 | No. | 2 | Group | 3 | ( \text{VE}^c \text{e} ) &amp; \text{atom} | 4 | Ternary compound | 5 | Crystal lattice | 6 | Lit. ref. |</p>
<table>
<thead>
<tr>
<th>---</th>
<th>---</th>
<th>---</th>
<th>---</th>
<th>---</th>
<th>---</th>
<th>---</th>
<th>---</th>
<th>---</th>
<th>---</th>
<th>---</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>orthorhombic</td>
<td>8</td>
<td>hexagonal</td>
<td>9</td>
<td>cubic</td>
<td>10</td>
<td>tetragonal</td>
<td>11</td>
<td>monoclinic</td>
<td></td>
</tr>
</tbody>
</table>
In group II the compounds 9 and 10 are isomorphic and form continuous solid solutions together /38/.

In group III compounds 13 and 14 have close monoclinic lattices; it is interesting that the electronic concentration for this group is attained in the isomorphic maximum-saturated solutions of silicon or nickel in the binary compound Co Al; Raynor and Pfeil consider that this electron concentration is generally speaking the maximum for ternary metal compounds.

A calculation of the electron concentration can also be made by another method, if it is assumed that transition metals acquire a whole number of electrons per atom (Table 4).

Table 4

1) Number of "vacant" electrons for certain metals according to /38/
2) Element
3) Number of el/atoms in "atomic" orbits

The data obtained by this method, however, tally to a lesser extent with the shape and volume of the Brillouin zones, and do not show such a close correspondence in the electron concentrations for certain solid solutions based on binary metal compounds.
The number of "vacant" electrons for transition metals in these calculations is not the only one possible. For example, the research [29] on solid solutions between the $\sigma$- and $\mu$-phases in certain ternary systems recognizes the advisability of giving transition metals the values for the number of vacant electrons shown in Table 5.

In this case, for example, for solid solutions between the $\mu$-phases, the electron valence concentration maintains a constant value ranging from 2.95 to 3.24 el/atom.

### Table 5.

<table>
<thead>
<tr>
<th>$\frac{z}{Z}$</th>
<th>Number of &quot;vacant&quot; electrons for certain metals according to [29]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1) Element</td>
<td>2) Number of el/atom in &quot;atomic&quot; orbits</td>
</tr>
</tbody>
</table>

The examples given show that a certain artificiality in the VEC calculation based on the vacant electron theory, which shows up in the tendency to level out this value for certain groups of ternary metal phases. Moreover, the figures in Table 3 demonstrate that the laws governing the link between electron concentration and crystal structure, discovered by Hume -Rothery for a number of binary metal compounds, do not apply to the case of ternary compounds, with rare exceptions.
Thus, the results of the study of ternary electron-type compounds do not make it possible at the present time to find a satisfactory explanation for their structure. A more detailed study of the conditions for chemical interaction between the elements during the formation of these compounds will alone help to bring their nature to light and explain their inherent properties.

Considerably clearer is the structure of ternary electron phases which are solid solutions between binary electronic compounds. It has been established that in most cases the binary compounds relating to the Hume-Rothery phases, which possess an identical electron concentration and identical types of crystal lattice, form continuous solid solutions together; some examples are given in Table 6.

Table 6

<table>
<thead>
<tr>
<th>Continuous solid solutions between binary electronic compounds</th>
</tr>
</thead>
<tbody>
<tr>
<td>1) ( \beta )-brass type; VEC = 3/2; 2) ( \gamma )-brass type VEC = 21/13; 3) ( \epsilon )-phase type; VEC = 7/6</td>
</tr>
</tbody>
</table>

In most cases the formation of these continuous solid solutions conforms to conditions formulated in by Kornilov /56/. In the given case binary compounds with a close chemical composition consisting of analogous elements usually form continuous solid solutions together with a constant VEC value.

*Described in more detail in /5/.
5. Ternary Laves Phases

Among the ternary metal compounds were found phases with homotectic structures

\[ \text{MgCu -MgZn} \] which satisfied the condition of volume relationships for the
toxic radii typical of the Binary Laves phases.

A detailed analysis of the crystal structure of these phases, which are marked
by high coordination numbers, and their systematics are given in the research /59/.

A number of ternary Laves phases is also given in /11/ with the stress on their
abundance.

Table 7 gives some examples on the basis of data contained in /60/.

Table 7

<table>
<thead>
<tr>
<th>Ternary Laves Phases</th>
</tr>
</thead>
<tbody>
<tr>
<td>1)</td>
</tr>
<tr>
<td>2)</td>
</tr>
<tr>
<td>3)</td>
</tr>
</tbody>
</table>

1) Type of crystal structure; 2) composition; 3) ratio of radii $R/A$; index $R/B$

For these compounds $R/A$ is as an average equal to 1.206, which is only slightly
different from the ideal ratio (1.225).
There is a notable chemical similarity in a number of compounds composed of analog elements. This shows that the chemical nature of elements making up a given group of compounds is of great importance in addition to the volume factor.

The binary Laves bonds rarely form continuous solid solutions among themselves. More characteristic during their interaction are cases in which there is a successive transition from the structure MgCu to MgZn via MgNi, observed in certain ternary systems /61-65/.

It is possible that the intermediate phases forming in the process can be related to the ternary metal compound group.

6. Ternary Nickel-Arsenide Phases

So far few ternary metal compounds have been found with a NiAs structure. Examples are the compound BeSb /66/, and also certain compounds containing germanium (MnFeGe, MnCoGe, MnNiGe, FeCoGe, FeNiGe) and others systematized in /67/.

We know, however, of many ternary phases which are continuous solid solutions between two binary metal compounds, some examples of which are given in Table 8.

The solid solution area between FeSb and NiSb is shown in the diagram (Fig. 11) /69/.
This system is interesting as an example of the formation of continuous solid solutions between a daltonide (NiSb) and a bertholide (FeSb).

In a chemical sense these phases are very close to each other, since they are formed by analog elements of groups V and VIII. At the same time, they are a clear example of the appearance of the earlier established regularities governing the formation of continuous metallide solid solutions /56/.

Table 8

Continuous solid solutions between binary nickel-arsenide metal compounds

1) system; 2) literature reference

7. Ternary Laves Phases

Borides. The formation of ternary compounds containing boron /72, 73/ has already been noted. The ternary borides found have the composition shown in Table 9.

Fig. 11. Continuous metallide solutions in the system Sb-Fe-Ni /69/.

1) Ni atom %; 2) Fe atom %.

Translator's note: In the list of contents at the beginning of the article this section (7) is entitled 'Ternary Interstitial Phases.'
Ternary metal compounds containing boron

Comparison of the formulae for ternary borides enables us to establish a profound similarity in their chemical nature, since their only difference in the corresponding columns (Table 9) is in the analog-elements of VIII group in the periodic system.

A number of cases have also been established in which there is formation of continuous solid solutions between binary borides (Table 10).

Table 10

Continuous solid solutions between borides

1) system; 2) literature reference.

An analysis of these systems shows that 1) the formation of continuous solid solutions conforms to basic laws /55/, 2) there are a large number of cases of the formation of these solutions between binary compounds composed of analog-elements, and that 3) in all known cases (with the exception of three systems containing the elements of IV and VI groups), these solutions form between binary systems. In Table 10 these systems are grouped separately.
borides containing transition metals of either the same group or adjacent groups in the periodic system.

These data show the close chemical nature and similar structure of certain groups of continuous solid solutions containing boron.

Table 11

<table>
<thead>
<tr>
<th>Ternary metal compounds containing carbon</th>
</tr>
</thead>
<tbody>
<tr>
<td>Composition: 2) Literature references.</td>
</tr>
<tr>
<td>Ternary metal compounds containing carbon</td>
</tr>
<tr>
<td>Homogeneous areas on the ternary diagram.</td>
</tr>
<tr>
<td>They are all interstitial phases.</td>
</tr>
<tr>
<td>A number of ternary phases containing carbon are continuous solid solutions.</td>
</tr>
<tr>
<td>Carbides, ternary compounds containing carbon constitute a clear example of chemical analogy. Each phase is composed of elements in the V, VI, and VII periodic groups. Many of them can dissolve excess component elements and form isomorphous crystal lattices (Table 12).</td>
</tr>
<tr>
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</tbody>
</table>

Table 12

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</tr>
<tr>
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</tr>
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</tr>
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</tr>
<tr>
<td>These data show the close chemical nature and similar structure of certain groups of continuous solid solutions containing boron.</td>
</tr>
</tbody>
</table>
Table 12

Continuous solid solutions between carbides

1) system; 2) literature reference.

The chemical analogy also shows up well here. The systems in Table 12 are composed of phases containing either elements of the group IV or V of the periodic table.

Silicides. The which have studied most among the ternary silicides are those containing aluminum or elements in the group VIII of the periodic system. Some examples are given in Table 13.

Ternary silicides related to electronic compounds are considered on p. 761.

The limited nature of experimental data on the complex silicides makes it impossible to make any generalizations. Only a few representatives have been more studied in detail (for instance, MnSiAl; see above).
Some ternary silicides are continuous solid solutions between binary compounds (Table 14).

The first two systems are chemically analogous. The other systems contain analog elements of groups IV, V and VI of the periodic system and closely conform to the rule for the formation of continuous solid solutions /46/.

Table 14

<table>
<thead>
<tr>
<th>Table 14</th>
</tr>
</thead>
</table>

| 1) compound | 2) literature reference |
|------------------|

Continuous solid solutions between silicides

1) system; 2) literature reference.

Nitrides. Non-valent ternary compounds containing nitrogen were discovered only comparatively recently. Some of the ones grouped in Table 15 show clearly-marked chemically analogous in structure.
Table 15

Ternary metal compounds containing nitrogen

1) compound; 2) literature reference.

Table 16

Continuous solid solutions between nitrides

1) system; 2) literature reference.

Comparison of the continuous solid solutions formed by nitrides (Table 16) also shows the close chemical nature of ternary phases containing nitrogen.

An analysis of the data given above makes it possible to lay down that in all the groups, known so far, of typical ternary metal compounds and ternary phases relating to continuous metal solid solutions between two binary metal compounds, the effect of the chemical factor shows up clearly in the chemical and crystallochemical similarity of the ternary phases in this group.
The part played by the chemical factor is also a dominant one in the formation of the ternary phases of other groups unrelated to the ternary compounds /1/, for example, limited organic metal solid solutions or ternary solid solutions based on a component of the ternary diagram. This makes it possible in many cases to predict the formation of ternary phases in systems as yet uninvestigated, and thereby greatly facilitates the construction of the latter.

8. Properties and Practical Application of Ternary Metal Compounds

There has been very little investigation of the properties of ternary metal compounds. But even the experimental data to hand enables us to establish the relationship between the properties and chemical nature of the ternary compounds.

Table 17 gives data on the shade of color of compounds classed as "valent". It is easy to see that in each triad which has two common elements the intensity of the shade increases with the atomic number of the third element (group V) according to a law.
<table>
<thead>
<tr>
<th>Composition</th>
<th>Color</th>
<th>Lit. Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>light red-brown</td>
<td></td>
<td></td>
</tr>
<tr>
<td>red-light brown</td>
<td></td>
<td></td>
</tr>
<tr>
<td>brown</td>
<td></td>
<td></td>
</tr>
<tr>
<td>white to light gray</td>
<td></td>
<td></td>
</tr>
<tr>
<td>to red brown</td>
<td></td>
<td></td>
</tr>
<tr>
<td>to dark brown</td>
<td></td>
<td></td>
</tr>
<tr>
<td>light gray</td>
<td></td>
<td></td>
</tr>
<tr>
<td>light brown</td>
<td></td>
<td></td>
</tr>
<tr>
<td>black-brown to black</td>
<td></td>
<td></td>
</tr>
<tr>
<td>yellow-gray</td>
<td></td>
<td></td>
</tr>
<tr>
<td>brown</td>
<td></td>
<td></td>
</tr>
<tr>
<td>gray-black to black</td>
<td></td>
<td></td>
</tr>
<tr>
<td>yellow</td>
<td></td>
<td></td>
</tr>
<tr>
<td>brown</td>
<td></td>
<td></td>
</tr>
<tr>
<td>gray-black</td>
<td></td>
<td></td>
</tr>
<tr>
<td>yellow</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Numerous investigations of the so-called "Heusler alloys" have proved that their magnetic properties are closely associated with the formation of ternary metal compounds CuMnAl, CuMnGa, CuMnIn and CuMnSn. The first three of these are chemical analogs and the last differs in one element close in chemical nature.

A similar connection shows up in other ternary systems. For example, magnetic properties are possessed by a number of other ternary compounds with a common chemical nature and identical crystal lattices, namely CoMnGe, NiMnGe, CoMnSn and NiMnSn.

Working in collaboration with Chernov the author has determined the electrochemical potentials of certain ternary metal compounds containing magnesium or aluminum (Table 16).

Table 18
Electrochemical potentials of certain ternary metal compounds containing magnesium or aluminum.

<table>
<thead>
<tr>
<th>Composition of ternary compound</th>
<th>Electrochemical potential at 200 °F</th>
<th>Lit. Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
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</tr>
</tbody>
</table>

*We give the steady-state values of the potentials in a 3% NaCl sol. from hydrogen electrodes.*
A comparison of ternary compounds with two common elements shows that in most cases the greater the difference in chemical composition between each of the two elements and the third, the more positive the potentials become.

The quantitative values of the microhardness of certain ternary metal compounds were determined. The author determined the microhardness of some ternary compounds containing aluminum and magnesium of interest from the standpoint of developing light alloys for aviation. The results of this investigation are given in Tables 19 and 20.

Table 19

<table>
<thead>
<tr>
<th>No</th>
<th>Composition of ternary compound</th>
<th>Microhardness at 20°C H</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2</td>
<td>3</td>
<td>4</td>
</tr>
</tbody>
</table>

1) No; 2) composition of ternary compound; 3) microhardness at 20°C H kg/mm²; 4) literature reference.

By comparing the values for microhardness it is possible to see that in most cases the latter increases with an increase in the chemical difference in the elements forming the ternary compound. A similar regularity can be observed if we compare ternary compounds with two elements in common, for example, (Table 19),...
Nos. 1-2; 3-5; 6-7; 7-2. Moreover, in this series of ternary compounds containing magnesium, the hardness is greater in cases where the magnesium combines with elements along way away from it in the periodic system (Nos. 5-8 have $H = 145-161 \text{ kg/mm}^2$) compared with those composed of closer-lying elements (Nos. 1-4 and 6-7 with a hardness $H = 239-305 \text{ kg/mm}^2$).

Table 20

<table>
<thead>
<tr>
<th>No;</th>
<th>composition;</th>
<th>microhardness at $20^\circ H_\omega$ $\text{kg/mm}^2$;</th>
<th>literature ref.</th>
</tr>
</thead>
</table>

A similar regularity is observed, generally speaking, in the group containing aluminum (Table 20). Thus, the hardness of compounds 1-5 in Table 20 containing, apart from aluminum, elements of periodic groups I and II varies over a range of fairly small values ($H_\omega = 297-111 \text{ kg/mm}^2$); compounds 6-10, which include group VI and VII elements, show increased hardness ($H_\omega = 521-880 \text{ kg/mm}^2$); finally, the last five compounds (Nos. 11-15 in Table 20) containing group VIII elements have the greatest hardness ($H_\omega = 740-1117 \text{ kg/mm}^2$).

Thus, the hardness of ternary metal compounds is a known function of the
position of the constituent elements in the periodic table, that is to say, it increases as the chemical properties of the elements differ.

A number of publications /125, 126/ are devoted to determination of the hardness of ternary metal compounds at elevated temperatures.

The microhardness of certain ternary compounds containing alumini at 300° is shown in Table 21 /125/.

Table 21

Microhardness at 300° of ternary metal compounds containing aluminum

<table>
<thead>
<tr>
<th>Composition</th>
<th>1) Microhardness in kg/mm², soaking for</th>
<th>2) 30 sec; 3) 60 min</th>
</tr>
</thead>
</table>

* Indentor load 50 g

1) composition; 2) microhardness in kg/mm², soaking for; 3) 30 sec; 4) 60 min;

It should be pointed out that when the temperature is sufficiently high, most metal compounds change to a plastic state and acquire a property of easy deformation.
This was first proved for the case of binary metal compounds by Savitskiy. He carried out a great deal of experimental work/128-131/ which has been generalized in an extensive monograph showing the possibility of pressing metal compounds during heating, and investigating in detail the structural and microscopically changes taking place during the process.

Our own experiments on pressing ternary metal compounds also enable us to establish that ternary compounds fragile at normal temperatures change to a plastic state when heated and become liable to considerable deformation. It was established, in particular, that the possibility of deforming certain ternary compounds (for example Ca Mg Zn) enables us to give them a more favorable structural shape and thereby have an positive effect on the alloy's plasticity indices as a whole.

It should be pointed out in conclusion that there are as yet too few experimental data to establish the definite quantitative relationships between the composition of ternary compounds and their properties. But the investigations carried out indicate the existence of certain natural laws in this respect determined by the chemical nature of the elements forming the ternary compound.
the greater the difference in the chemical properties of the elements, the stronger their chemical bond, and the more stable the compounds formed become; their hardness increases, the melting point is raised and electrochemical potentials improve. In a number of cases these properties can be successfully applied in alloys for improving the mechanical properties, heat resistance and corrosion resistance.

Metal ternary compounds are met with in the structure of many alloys of practical importance. The greatest amount of research in which this is demonstrated is devoted to aluminum alloys. The ternary compounds are present in these both in a free state as well as in the form of solid solutions containing these compounds.

The properties of ternary metal compounds and the conditions under which they interact with the base metal of the alloy make it possible to note the following general principles for their use:

1). Hardening of solid solutions by dissolving ternary metal compounds in them. When such ternary solid solutions form, the interatomic bonds which occur are more complex than in binary compounds, and there is considerably more distortion of the crystal lattice, giving rise to greater hardening.
2). Hardening alloys by forming in them structure-free ternary metal compounds marked by greater mechanical properties. Some of these ternary compounds have greater hardness than the binary ones, hence the hardening effect may also be more clearly marked. Typical in this respect are cases of the improvement in the hardness of instrument steels by through the formation of ternary carbides of the type Fe W C, Fe W C /61, 113/, Ti W C /144/, and so on.

3). The hardening of alloys through the formation in them of ternary metal compounds containing a relatively greater quantity of metal as the base than in binary compounds. Here the effect of the alloying elements on the structure and properties shows up more strongly than in the formation of the binary compounds.

Thus Dudzinskiy /115, 116/ and his coworkers have shown that the formation of ternary metal compounds in aluminum alloys can in certain instances appreciably increase the modulus of normal elasticity of the latter. While stressing that in certain cases the modulus of aluminum alloys increases 20%, the authors note the great effect, of great practical importance, of ternary metal compounds on the properties of industrial alloys, particularly those used in aviation.

4). The use of the temperature-variable solubility of ternary metal compounds in the base metal in order to bring about hardening through heat treatment, which consists in quenching with subsequent aging. It has been established that in a
number of ternary systems solid solutions with metal bases may be in a state of equilibrium with different ternary metal compounds; for many alloys the system "metal-ternary metal compounds" it has been demonstrated that there is an increase in the solubility of the ternary compound during heating. Thus, as a result of the tempering of certain alloys of this type we can obtain supersaturated solid solutions capable of hardening during subsequent aging.

The possibility is noted of using ternary compounds for hardening aluminum alloys /16, 138, 147, 148/. In particular we should point out a number of investigations by Bagaryatskiy /149-152/ in which he gives a detailed analysis of the role of the ternary phase \( \delta(\text{Al CuMg}) \) during the aging of aluminum alloys.

From some other investigation /153-156/ the similar role of the ternary compound \( \Gamma(\text{Al Mg Zn}) \) is obvious.

We made a special investigation /157-159/ of cast and pressed aluminum- and magnesium-base alloys during which we demonstrated the possibility of hardening these alloys with ternary metal compounds.

5). Improving the heat resistance of alloys containing ternary metal compounds by creating a structure which prevents plastic deformation to the maximum extent during heating. At certain temperatures this structure, as shown by Kornilov in
a number of investigations /163-162/, corresponds to a state in which the solid solution is saturated to the maximum. In the given case there form solid solutions saturated with ternary metal compounds. By virtue of their more complicated crystal lattice, ternary solid solutions should have greater resistance to deformation at elevated temperatures compared with binary solutions.

Fig. 12.
Influence of temperature on hardness of some metal compounds and heat-resistant alloys /163/; arrows indicate 0.6 T

\[
\begin{align*}
(1) & \quad \text{FeMoCr} & & \text{FeMoCr} & & \text{FeMoCr} \\
(2) & \quad \text{FeCrMo} & & \text{FeCrMo} & & \text{FeCrMo} \\
(3) & \quad \text{CoCrMo} & & \text{CoCrMo} & & \text{CoCrMo} \\
(4) & \quad \text{FeCrMo} & & \text{FeCrMo} & & \text{FeCrMo} \\
(5) & \quad \text{Tantalum} & & \text{Tantalum} & & \text{Tantalum} \\
\end{align*}
\]

Fig. 13.
Influence of temperature on hardness of certain metal compounds /163/; arrows show 0.6 T:

\[
\begin{align*}
(1) & \quad \text{FeCrMo} & & \text{FeCrMo} & & \text{FeCrMo} \\
(2) & \quad \text{FeCrMo} & & \text{FeCrMo} & & \text{FeCrMo} \\
(3) & \quad \text{CoCrMo} & & \text{CoCrMo} & & \text{CoCrMo} \\
(4) & \quad \text{FeCrMo} & & \text{FeCrMo} & & \text{FeCrMo} \\
(5) & \quad \text{Tantalum} & & \text{Tantalum} & & \text{Tantalum} \\
\end{align*}
\]

decomposition

The decomposition of ternary solid solutions with precipitation of particles of ternary metal compounds, in a state of dispersion or with pre-precipitation of the particles, may also cause greater plastic strength during heating, and consequently, may increase heat resistance.
It is also advisable to use the high degree of hardness and oxidation resistance of a number of ternary metal compounds when developing heat-resistant alloys. Some ternary compounds are considerably greater in hardness than modern heat-resistant alloys (Fig. 12) and binary metal compounds (Fig. 13) at normal, and particularly, elevated temperatures.

The possibility of increasing the heat resistance of aluminum alloys with ternary metal compounds was demonstrated by us in earlier research (164, 165).

(6) The improvement of corrosion resistance in alloys by the introduction and suitable structural distribution in them of ternary metal compounds with favorable electrochemical potentials in the given operational media.

The investigation is devoted to the special study of the effect of ternary metal compounds on the corrosion resistance of pressed aluminum alloys.

7) The production of alloys with definite physical properties by using the corresponding properties of ternary metal compounds. This includes, for example, the above-quoted work on Heusler alloys (p. 787).

8) The use of ternary metal compounds in order to impart technological properties to alloys. In this connection we should point out investigations
concerned with the effect of ternary compounds on modified silicides, on the
plasticity of castings of aluminum alloys /133, 171/ and chromo-manganese /172/;
and also on refining metals, for example, the decarbonization of uranium /173/.

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