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TERNARY INTERMETALLIC COMPOUNDS

B. K. Vul'f

Institute of Inorganic Chemistry,
Siberian Section of the USSR
Academy of Sciences.

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INTRODUCTION

A large number of binary intermetallic compounds have now been investigated. The scientific classification of such compounds has been based on Kurnakov's[1] treatment of berthollides and daltonides, and this also enables their precise position among binary metallic phases to be defined. The classification of binary intermetallic compounds according to the types of crystal lattices which they form has been dealt with in several monographs[2-4].

Recent reviews have analysed the general features of the structure, formation, and properties of particular groups of binary intermetallic compounds, and have clarified their role in industrial alloys and the possibilities of their practical utilisation. Data on binary metallic compounds have enabled binary equilibrium diagrams to be studied more completely and more thoroughly.

Three-component systems have received much less attention. Various phases, containing from one to three elements, can be formed in such systems; they are for the most part ternary metallic phases, since the pure components of ternary systems, as well as the binary metallic compounds which are often formed in these systems, are always able to dissolve the components present in excess, to some extent, forming ordinary and "metallide" solid solutions respectively.

The present author[5] has worked out a classification of ternary metallic phases based on a comparison of the nature and extent of the homogeneous regions of the ternary equilibrium diagram. Four of the eight types of ternary metallic phases, including ternary solid solutions based on one of the components of the system, cannot be included among intermetallic compounds.

Ternary phases which are metallide solid solutions of limited solubility are similar in structure and properties to

the binary intermetallic compounds on which they are based. Since, as was noted above, a great deal of work has been done on the investigation of binary intermetallic compounds, ternary phases of this type will not be examined here either.

The most interesting are the ternary phases which are represented on the ternary equilibrium diagrams by completely bounded regions of homogeneity, degenerating into points in the absence of ability to dissolve the excess of the components. These phases, usually distinguished by their own types of crystal lattices and their own special properties, represent independent chemical individuals in Kurnakov's sense, and should be termed "ternary intermetallic compounds".

Phases of this type form the main subject of the present paper.

Special note should be made of ternary phases formed by continuous solid solutions between two binary intermetallic compounds. Although these phases represent a particular case of metallide solid solutions, in several instances, especially at or near equimolar concentrations, they develop superlattice lines on the X-ray diffraction patterns and exhibit special properties, differing from those calculated on the basis of additivity, and therefore represent independent phases of the nature of ternary compounds. Such phases will also be discussed further together with typical ternary intermetallic compounds.

1. GENERAL FEATURES OF TERNARY INTERMETALLIC COMPOUNDS

Like the binary compounds, ternary metallic compounds can be formed in alloys as a result of the primary crystallisation, a peritectic transition, separation from solid solutions, or conversion of solid solutions into Kurnakov compounds. The stability of ternary compounds depends greatly on composition, generally increasing with increasing difference in chemical character between the component elements. Both the daltonide and berthollide type of phase is found among typical ternary intermetallic compounds.

An example of a daltonide is the compound $S(Al_2CuMg)$, which has been studied in detail (e.g. refs. 6 and 7). A berthollide character is shown by the ternary compounds T(Al, Cu, Mg)[6] and T(Al, Mg, Zn)[8]. One paper has been particularly concerned with the investigation of ternary berthollides[9].

The main factors governing the composition and crystal structure of ternary metallic compounds are the chemical nature of the component elements, the concentration of valency electrons, and the relative sizes of the atoms (ions). These factors will be examined in greater detail below.

The present author[10] was the first to classify data on the crystal lattices of ternary metallic compounds, describing in all about 250 compounds with an indication of their structural types. Some general rules linking the crystal structure of ternary metallic compounds with concentration of valency electrons and atomic radii have been discussed[11].

Analysis of existing data shows that the majority of ternary metallic compounds crystallise in close packed lattices with high coordination numbers characteristic of pure metals and binary intermetallic compounds. The most widespread among them are lattices with a high degree of symmetry, the cubic and hexagonal lattices.

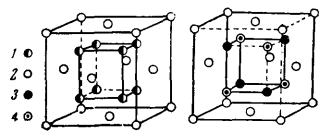


Fig. 1. Crystal lattices of LiMgN and LiZnN[12]: 1) $\frac{1}{2}$Mg + $\frac{1}{2}$Li; 2) N; 3) Zn; 4) Li.

Groups of isomorphous ternary metallic compounds exist, containing different elements from the same or neighbouring Groups of the Periodic System. This indicates the importance of the chemical nature of the elements composing the ternary compound. Some typical examples of such crystal-chemical analogues are examined below.

The character of the crystal lattices of similar ternary metallic compounds depends also on the chemical properties of their component elements. For example, comparison of the lattices of the ternary compounds LiMgN and LiZnN (Fig. 1) shows that they differ only in the distribution of the metal atoms, which is random in the former case (Mg and Li) and ordered in the latter (Li and Zn atoms). This may be explained by the fact that lithium and magnesium differ less in chemical character than do lithium and zinc.

When there is a continuous transition between two ternary compounds, the rearrangement of the crystal lattice is closely associated with a change in the nature of the chemical bond. Thus, in passing from NiMnSb to Ni_2MnSb[13] the lattice changes from the CaF_2 type to the Heusler close packed type (Fig. 2). This is accompanied by a strengthening of the metallic bond, which is confirmed by a corresponding change in magnetic properties and an increase in ductility. Binary and ternary metallic compounds, possessing similar chemical formulae and differing only in chemically analogous elements, often have the same crystal lattices. Typical examples are the pairs of compounds Co_2Al_5 and Fe_2NiAl_{10}, and Co_2Al_9 and $FeNiAl_9$; the members of each pair have very similar X-ray diffraction patterns[14].

Recently increased attention has been paid to research on the crystal structures of ternary intermetallic compounds. Reference must be made to Schubert's work[15] on the application of his theory of the spatial correlation of

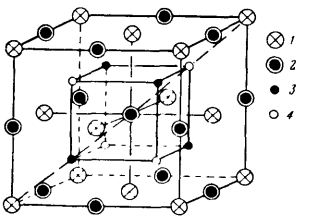


Fig. 2. Crystal lattices of NiMnSb and Ni_2MnSb[13]. Positions of atoms: for NiMnSb: 1) Ni; 2) Sb; 3) Mn; for Ni_2MnSb: O_h^5 type: 1) and 2) Ni; 3) Mn; 4) Sb; T_d^2 type: 1) and 3) Ni; 2) Mn; 4) Sb.

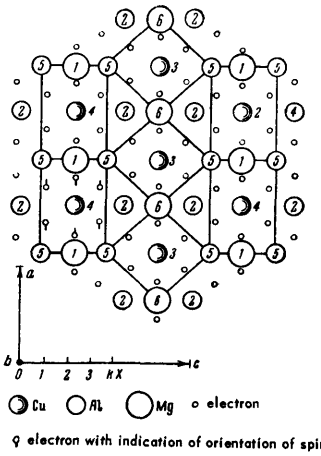


Fig. 3. Crystal lattice of $CuMgAl_2$ [15]. The distribution of atoms and electrons is shown (projection on b axis). The numerals indicate the heights at which atoms are located in multiples of b [14].

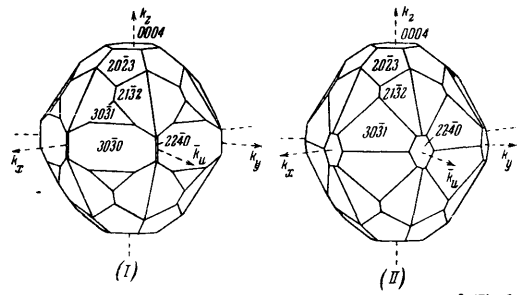


Fig. 4. First Brillouin zones for the structure of (I) the ternary intermetallic compound $MnSiAl_9$ and (II) the binary compound Co_2Al_5 [16].

electrons to explain the lattice structure of ternary compounds. Fig.3 is a diagram of such a model for the $S(Al_2CuMg)$ phase with an indication of the three-dimensional distribution of atoms and electrons.

The arrangement of the atoms has been established exactly, and the Brillouin zones have been constructed, for several ternary metallic compounds possessing complex crystal structures. Comparison of the three-dimensional models of the Brillouin zones for analogous binary and ternary compounds frequently shows a great similarity (see, for example, the models for the compounds Mn_3SiAl_9 and Co_2Al_5 [16] in Fig. 4).

The brief review of ternary metallic compounds given below shows that their composition and structure depend primarily on the chemical nature of the component elements, corresponding to the positions of the latter in the Periodic System. Among them are encountered all the types characteristic of binary compounds. This shows that binary and ternary intermetallic compounds have essentially the same nature.

2. TERNARY KURNAKOV PHASES

The literature hardly mentions the formation of ternary intermetallic compounds by transformations in ternary solid solutions. Reference can be made only to the work of Nemilov and Rudnitskii [17], which demonstrated the formation of a ternary intermetallic compound $CuFePt_2$ at ~1200° as a result of a transformation in a copper–platinum–iron solid solution (Fig. 5). But several investigators have established the influence of a third component on the conditions of formation of binary Kurnakov compounds. For example, the effect of Zn, Ni, Cd, Ti, Mg, Al, Mn, and Ag on the formation of the compounds AuCu and $AuCu_3$ has been ascertained [18–21]. Some of these elements (Zn, Ni, Mn, Ag) lower the temperature of formation of the binary compounds considerably, whereas the others have little effect in this respect. The effect becomes more marked as the quantity of the third element dissolved in the binary compounds is increased.

Extremely interesting and original methods of investigating the chemical bonds in solid solutions have been worked out by Grum-Grzhimailo and tested by him on a large number of experimental results [22–27]. To detect electron bonds between atoms, showing the characteristics of chemical interaction, he used methods based on the measurement of galvano-magnetic effects, the Hall effect, and values of the residual electrical resistivity.

In a study of solid solutions in the Fe–Cr, Fe–Co, Co–Ni, Cu–Ni, etc. systems, characteristic inflections, corresponding to intermetallic compounds of definite composition, were observed on the curves. These investigations

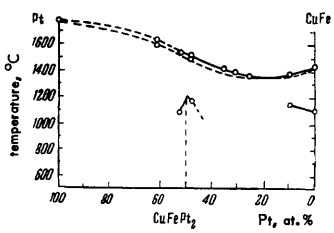


Fig. 5. Equilibrium diagram for Pt – CuFe alloys [17]; formation of the ternary intermetallic Kurnakov compound $CuFePt_2$ is shown.

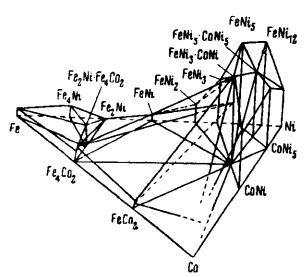


Fig. 6. Intermetallic compounds in the Fe – Co – Ni system [25].

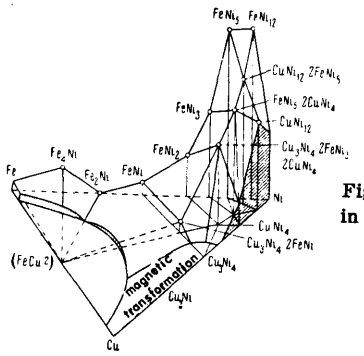


Fig. 7. Intermetallic compounds in the Cu – Fe – Ni system [25].

clearly confirm that a change occurs in the nature of the chemical bonds at concentrations corresponding to the composition of chemical compounds. Application of these methods enabled Grum-Grzhimailo to discover several new, and in particular some ternary, intermetallic compounds. For example, ternary compounds of the composition $Fe_2Ni \cdot Fe_4Co_2$, $FeNi_3 \cdot CoNi$, and $FeNi_5 \cdot CoNi_5$ were detected in the Fe–Co–Ni system (Fig. 6). Several ternary compounds were also found in the Cu–Fe–Ni system (Fig. 7).

The so-called σ- and μ-phases should be classed as Kurnakov phases. The isomorphism of the σ-phases and their related chemical nature suggest that they may form a continuous series of solid solutions. This has been demonstrated, for example, with the FeCr–FeV system [28], in which complete miscibility exists both below and above the temperature range in which the σ-phases are formed (Fig. 8).

Analogous solubility relationships exist for the interaction of μ-phases. For example, it has been confirmed [29] that the isomorphous phases $\mu(Fe_7Mo_6)$ and $\mu(Co_7Mo_6)$ give continuous solid solutions (Fig. 9).

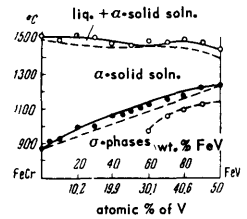


Fig. 8. Continuous solid solutions between the compounds FeCr and FeV (σ-phases)[23]: ○ arrests on the cooling curve; ● arrests on the heating curve.

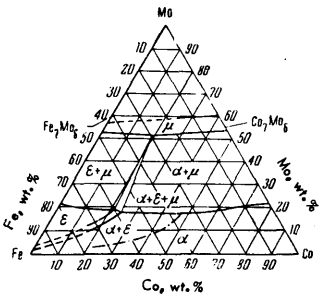


Fig. 9. Continuous solid solutions between the compounds μ (Co_7Mo_6) and μ (Fe_7Mo_6) at 1200° in the Fe – Co – Mo ternary diagram [29].

In several solid solutions of this kind ternary phases are sometimes formed with maximum or minimum values of various properties. In such phases the strength of the chemical bond between the interacting elements undoubtedly changes, and this serves as a criterion of the formation of association complexes, closely similar to typical ternary compounds.

3. TERNARY INTERMETALLIC COMPOUNDS OF NORMAL VALENCY

A large group of ternary compounds containing elements of Groups I and V of the Periodic System have now been studied, several examples being given in Table 1. The component elements of these compounds exhibit valencies corresponding to their positions in the Periodic System. Investigation of analogous compounds of this type shows that their structure and properties vary regularly with change in their chemical composition.

TABLE 1. Ternary valency compounds.

Analogues differing in elements of Group V		Analogues differing in elements of Groups II–IV	
compound	reference	compound	reference
LiMgN	12	LiMgP	30
LiMgP	30	LiZnP	30
LiMgAs	31	Li_3AlP_3	32
LiMgSb	31	Li_3GaP_3	33
LiMgBi	31	Li_5SiP_2	33
		Li_5TiP_2	33
		Li_5GeP_2	33

For example, compounds containing non-metals — LiMgN, Li_3AlP_2, Li_3AlAs_2, AgMgAs, etc. — have a well defined salt-like character, which is confirmed for the majority of them by high melting points, ready hydrolysability, low electrical conductivity, and other properties characteristic of compounds having an ionic bond [32]. On the other hand, analogous compounds formed solely from metals — CuMgBi, CuCdSb, etc. — exhibit more clearly metallic properties and the metallic bond predominates.

A detailed analysis [30,34,35] of the crystal structures confirms this difference in properties and nature of the interatomic bond.

4. ELECTRONIC TERNARY INTERMETALLIC COMPOUNDS

Very few electronic ternary intermetallic compounds satisfy Hume-Rothery's rules if the concentration of valency electrons is calculated in the usual way, and in particular if elements of Group VIII are given zero valency. For example, $MgSnNi_2$ [36] and $CuAuZn_2$ [37] have an electron concentration (electron : atomic ratio) of 1.5 and crystallise in

TABLE 2. Number of electron vacancies in certain metals (from magnetic measurements).

Element	Ni	Co	Fe	Mn	Cr
Number of electrons per atom in "atomic" orbitals	0.61	1.71	2.66	3.66	4.66

TABLE 3. Concentration of valency electrons and crystal lattices of some ternary intermetallic compounds.

No.	Group	Concentration of valency electrons, electrons per atom	Ternary compound	Crystal lattice	Reference
1		1.85	$T(Cu_2Al_{20}Mn_8)$	orthorhombic	41
2		1.85	$T(ZnAl_{24}Mn_5)$	orthorhombic	41
3	I	1.85	$\alpha(Al_3SiCr)$	cubic	39
4		1.85	$\beta(Al_9SiMn_2)$	hexagonal	16
5		1.85	$T(Al_{60}Mn_{11}Ni_4)$	orthorhombic	41
6		2.04	$N(Cu_2Al_7Fe)$	tetragonal	42
7		2.04	$\tau(Cu_3Al_6Ni)$	cubic	43
8	II	2.04	$T(Cu_5Al_{13}Co_2)$	—	44
9		2.04	$\alpha(Al_{12}SiFe_2)$	cubic	42
10		2.04	$\alpha(Al_{10}SiMn_2)$	cubic	42
11		2.37	$E(Mg_3Al_{25}Cr_2)$	cubic	45
12	III	2.37	$T(\sim Mg_2Al_{10}Mn)$	—	46
13		2.37	$\beta(Al_{4,5}SiFe)$	monoclinic	42
14		2.37	$\pi(Al_9FeNi)$	monoclinic	14

the β-brass structure. If the valency of manganese is taken as unity[11], such compounds as Cu_2MnAl, Cu_2MnIn, Co_2MnSn, Ni_2MnSn, etc. also can be included among electronic β-phases.

The majority of other electronic ternary compounds do not obey Hume-Rothery's rule. In order to explain their structure, Raynor and his collaborators[38,39] used Pauling's theory[40], based on the hypothesis of a "negative" valency for the transition metals with unfilled d-levels. According to this theory, when aluminium and silicon form ternary compounds with the transition metals of the Fourth Period, the Al and the Si give up their valency electrons to the common electron atmosphere, whereas the transition metals capture some of these electrons in order to complete their d-levels. The number of electrons which are thus captured depends on the position of the element in the Periodic System, and can be calculated from the magnetic properties of these elements. Thus the transition metals should not be assigned a zero valency, as in the binary Hume-Rothery phases, but some negative valency; according to Pauling this is equal to the number of electrons in the so-called "atomic" orbitals (Table 2).

TABLE 4. Number of electron vacancies in certain metals[38].

Element	Ni	Co	Fe	Mn	Cr
Number of electrons per atom in "atomic" orbitals	0	1	2	3	4

TABLE 5. Number of electron vacancies in certain metals.[28]

Element	Ni	Co	Fe	Mn	Cr
Number of electrons per atom in "atomic" orbitals	1.6	1.71	2.2	3.2	4.66

If the electron concentrations are calculated from these values for various ternary compounds, the latter can be divided into groups having the same ratios (Table 3 and Fig. 10).

In group I, compounds 1, 2, and 5 are isomorphous; they all contain 80 at.% of aluminium.

In group II, compounds 9 and 10 are isomorphous, and together form a continuous series of solid solutions[38].

In group III, compounds 13 and 14 have similar monoclinic lattices; it is interesting that the electron : atom ratio corresponding to this group is also reached in the isomorphous saturated solutions of silicon or nickel in the binary compound Co_2Al_9; Raynor and Pfeil[47] consider that this ratio is in general a limiting value for ternary intermetallic compounds.

It is possible to calculate the electron concentration by a different method[38], on the hypothesis that the transition metals take up an integral number of electrons per atom (Table 4).

However, results obtained by this method agree less well with the shape and size of the Brillouin zones, and do not give as good agreement with the values for the electron concentration in some solid solutions based on binary intermetallic compounds.

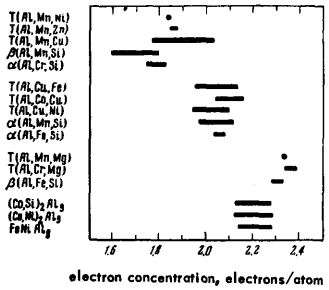


Fig. 10. Concentration of valency electrons in ternary compounds containing aluminium and transition metals [38].

The values of the number of electron vacancies adopted for the transition metals in these calculations are not actually encountered. Thus, a paper[29] on solid solutions between σ- and μ-phases in some ternary systems considers it expedient to assign to the transition metals the numbers of electron vacancies indicated in Table 5. In this case, for example, for solid solutions between μ-phases, the concentration of valency electrons remains constant at 2.95–3.24 electrons per atom.

The examples which have been quoted show a certain artificiality in the calculation of electron concentrations on

the basis of the theory of electron vacancies, which appears in a tendency to round off the values of this quantity for the separate groups of ternary metallic phases. Further, the data in Table 3 show that the relations between electron concentration and crystal structure, found by Hume-Rothery for binary intermetallic compounds, are not exhibited by ternary compounds, apart from rare exceptions. Thus the results of the study of ternary compounds of electronic type do not yet provide a satisfactory explanation of their structure. Only a more thorough investigation of the conditions of chemical interaction between the elements in the formation of these compounds will enable their nature to be ascertained and their inherent properties to be explained.

A much clearer idea has been obtained of the structure of ternary electronic phases which are solid solutions between binary electronic compounds. In the majority of cases, binary compounds which are Hume-Rothery phases, possessing the same electron concentration and the same types of crystal lattices, form continuous series of solid solutions; a few examples are given in Table 6*.

The formation of such continuous solid solutions is subject in the majority of cases to the conditions formulated by Kornilov[56]. In this case binary compounds which are chemically similar and are composed of analogous elements generally form continuous solid solutions characterised by a constant value of the electron concentration.

5. TERNARY LAVES PHASES

Among ternary intermetallic compounds phases have been found with the homeotectic structures $MgCu_2-MgNi_2-MgZn_2$, with ratios of atomic radii characteristic of binary Laves phases.

A systematic and detailed analysis of the crystalline structure of these phases, which are distinguished by high coordination numbers, has been given by Kripyakevich[59]. Another paper[11] has discussed several ternary Laves phases and has stressed their wide distribution.

Table 7 lists a few examples[60].

For these compounds R_A/R_B is on the average 1.206, which differs little from the ideal ratio (1.225).

The chemical similarity of compounds composed of analogous elements is noteworthy. This shows that the chemical nature of the elements composing a given group of compounds is important, in addition to the volume factor.

Binary Laves phases seldom form continuous series of solid solutions among themselves. Their interaction is typified rather by cases of successive transition from an $MgCu_2$ structure through $MgNi_2$ to $MgZn_2$, as observed in several ternary systems[61-65]. It is possible that the intermediate phases formed in this process may be ternary intermetallic compounds.

6. TERNARY NICKEL ARSENIDE PHASES

As yet, few ternary metallic compounds have been found to have the NiAs structure. Examples are the compound BeSiZr[66], and a few compounds containing germanium (MnFeGe, MnCoGe, MnNiGe, FeCoGe, FeNiGe), and some others, of which a systematic account has been given[67].

* More complete data have been given previously[5].

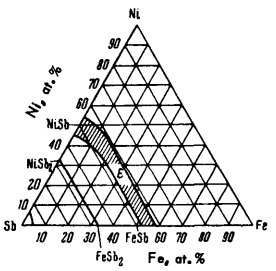


Fig. 11. Continuous metallide solutions in the Sb — Fe — Ni system[69].

However, many ternary phases which are continuous solid solutions of two binary compounds are known, several examples being given in Table 8. The range of solid solution between FeSb and NiSb is shown in Fig. 11[69]. This system is an interesting example of the formation of a continuous series of solid solutions between a daltonide (NiSb) and a berthollide (FeSb).

Chemically these phases are very similar, since they are formed from analogous elements of Group V and VIII.

TABLE 6. Continuous solid solutions between binary electronic compounds.

β-Brass type, 3/2 *		γ-Brass type, 21/13 *		ε-Phase type, 7/4 *	
system	reference	system	reference	system	reference
CuZn — AgZn	48	Cu_5Zn_8—Ag_5Zn_8	53	$CuZn_3$ — $AgZn_3$	57
AgMg — AgCd	48	Ag_5Cd_8—Ag_5Zn_8	48	$CuZn_3$ — $MnZn_7$	57
AgMg — AgZn	49	Cu_5Zn_8—Cu_9Al_4	54	$AgZn_3$ — Ag_5Al_3	58
AgCd — AgZn	48	Cu_5Zn_8—γ(Cu, Ga)	55	$AgZn_3$ — $MnZn_7$	57
AlFe — AlCo	50	Cu_5Zn_8—$Cu_{31}Sn_8$	56		
AlFe — AlNi	51				
AlCo — AlNi	52				

* Concentration of valency electrons, electrons/atom.

TABLE 7. Ternary Laves phases.

Crystal structure	Composition	Ratio of radii R_A/R_B	Crystal structure	Composition	Ratio of radii R_A/R_B
$MgCu_2$	CuCdZn	1.15	$MgZn_2$	$Cu_{1.5}MgSi_{0.5}$	1.24
				CuMgAl	1.18
	$Ag_{0.8}MgZn_{1.2}$	1.14		$Ag_{0.9}MgAl_{1.1}$	1.12
					1.37
	$MgZn_{1.3}Co_{0.7}$	1.21	$MgNi_2$	CuMgZn	1.21
				$Cu_{1.4}MgSi_{0.6}$	1.23
	MgNiZn	1.23		CuMgAl	1.18
				$Ag_{0.4}MgZn_{1.6}$	1.16
	$MgSi_{0.2}Ni_{1.8}$	1.30			

TABLE 8. Continuous solid solutions between binary compounds of the nickel arsenide type.

System	Reference	System	Reference
FeSb — CoSb	69	CoSb — NiSb	48
FeSb — NiSb	69	NiAs — NiSb	71
CoAs — NiAs	70	NiSb — NiBi	48

In addition, they provide a clear example of the rules established earlier[56], governing the formation of continuous metallide solid solutions.

7. TERNARY INTERSTITIAL PHASES

Borides. The formation of ternary compounds containing boron has been noted[72,73], and the compositions of the ternary borides which have been obtained are indicated in Table 9.

Comparison of the formulae for the ternary borides shows that chemically they are very similar, since within each of the columns in Table 9 they differ only in the analogous elements of Group VIII of the Periodic System.

TABLE 9. Ternary compounds containing boron.

Composition	Reference	Composition	Reference
Mo_2FeB_2	72	Mo_2FeB_4	72
Mo_2CoB_2	72	Mo_2CoB_4	72
Mo_2NiB_2	72	Mo_2NiB_4	72
		Cr_2NiB_4	73

TABLE 10. Continuous solid solutions between borides.

System	Reference	System	Reference	System	Reference
$TiB_2 - ZrB_2$	74	$TiB_2 - CrB_2$	75	$CrB_2 - MoB_2$	78
$TiB_2 - HfB_2$	75	$TiB_2 - MoB_2$	75	$CrB - MoB$	78
$ZrB_2 - HfB_2$	75	$ZrB_2 - MoB_2$	75		
$TiB_2 - VB_2$	75			$MnB_2 - FeB_2$	79
$TiB_2 - NbB_2$	76	$VB_2 - CrB_2$	75	$MnB_2 - CoB_2$	79
$TiB_2 - TaB_2$	75	$NbB_2 - CrB_2$	75		
$ZrB_2 - NbB_2$	75	$TaB_2 - CrB_2$	75	$FeB_2 - CoB_2$	79
$ZrB_2 - TaB_2$	77				

TABLE 11. Ternary compounds containing carbon.

Composition	Reference	Composition	Reference	Composition	Reference
Fe_2Mo_2C	80	Fe_3Mo_3C	85	Fe_4Mo_4C	80
Fe_2W_2C	81	Fe_3W_3C	81	Fe_4W_4C	88
Co_2W_2C	82	Co_3Mo_3C	86		
		Co_3W_3C	87	Fe_6Mo_6C	80
Fe_2Mo_4C	83	Ni_3Mo_3C	83	Fe_6W_6C	81
Co_2Mo_4C	84	Ni_3W_3C	85	Co_6W_6C	84
Co_2W_4C	83			Ni_6W_6C	89
Ni_2Mo_4C	83	Mn_3Mo_3C	83		
		Mn_3W_3C	83	$Fe_{21}Mo_2C_6$	90
				$Fe_{21}W_2C_6$	90

The formation of continuous solid solutions between binary borides (Table 10) has been established in several cases. Analysis of these systems shows that (1) the formation of continuous solid solutions follows the main rules[56]; (2) in many cases continuous solid solutions are formed between binary compounds composed of analogous elements*; (3) in all known cases (with the exception of three systems containing elements of Groups IV and VI) continuous solid solutions are formed between binary borides containing transition metals belonging either to the same Group or to adjacent Groups of the Periodic System.

These data indicate the closely similar chemical character and common structure within the separate groups of boron-containing solid solutions.

Carbides. Ternary compounds containing carbon form a particularly clear example of chemical analogy. Several groups of such compounds exist containing different analogous elements, and possessing the same molecular composition and isomorphous crystal lattices (Table 11).

The carbides which have been studied contain predominantly elements of Groups VI and VIII. Many of them can dissolve the excess of the components, and form homogeneous regions on the ternary diagrams. They all form interstitial phases.

Several ternary phases containing carbon represent solid solutions between isomorphous carbides (Table 12).

Here, too, chemical analogy is well developed. The systems included in Table 12 are composed of phases containing elements of either Group IV or Group V.

Silicides. Among ternary silicides the most thoroughly studied are ternary compounds containing aluminium or

TABLE 12. Continuous solid solutions between carbides.

System	Reference	System	Reference
TiC — VC	91	VC — NbC	91
TiC — NbC	92	VC — TaC	91
TiC — TaC	92	NbC — TaC	91
ZrC — NbC	92		
ZrC — TaC	92		
HfC — TaC	93		

TABLE 13. Ternary compounds containing silicon.

Compound	Reference	Compound	Reference
$NaAlSi_4$	94	TiFeSi	98
$MgAl_2Si$	95	$V_5Fe_4Si_4$	99
$\alpha(CrAl_2Si)$	39		
β(Cr, Al, Si)	39	$MoNi_4Si_2$	100
$\alpha(Mn_3Al_{21}Si_5)$	39	Mo_2Ni_3Si	100
$\beta(Mn_3Al_9Si)$	96	WFeSi	101
$\alpha(Fe_{1.5}Al_6Si)$	97	W_2FeSi	101
$\beta(FeAl_{4.5}Si)$	97	$MnCo_2Si$	102
$\gamma(Fe_{0.5}Al_{1.5}Si)$	97		

* In Table 10 such systems are grouped separately.

TABLE 14. Continuous solid solutions between silicides.

System	Reference	System	Reference
V_3Si—Cr_3Si	103	Ti_5Si_3—Zr_5Si_3	104
V_3Si—Mo_3Si	103	VSi_2—$NbSi_2$	105
		Cr_3Si—Mo_3Si	106
		$MoSi_2$—WSi_2	107

TABLE 15. Ternary compounds containing nitrogen.

Compound	Reference	Compound	Reference
$Ti_{0.7}Co_{0.3}N$	68	$Ta_3FeN_{2.5}$	108
$Ti_{0.7}Ni_{0.3}N$	68	$Ta_3CoN_{2.5}$	108
$Mo_{0.8}Co_{0.2}N$	68	$Ta_3NiN_{2.5}$	108
$Mo_{0.8}Ni_{0.2}N$	68		

TABLE 16. Continuous solid solutions between nitrides.

System	Reference	System	Reference
TiN—ZrN	109	TiN—VN	109
		TiN—NbN	109
ZrN—HfN	109	ZrN—NbN	109
		HfN—NbN(?)	109

elements of Group VIII. Several examples are given in Table 13. Ternary silicides which are electronic compounds have been discussed above (Table 3).

The limited experimental data available on complex silicides do not permit any generalisations to be made. Only a few representatives (e.g. Mn_3SiAl_9, see above) have been studied in detail. A few ternary silicides represent continuous solid solutions between binary compounds (Table 14).

The first two systems in Table 14 are chemically analogous. The remaining systems contain analogous elements of Groups IV–VI and agree well with the rule governing the formation of continuous solid solutions[48].

Nitrides. Ternary compounds of non-valency type containing nitrogen were discovered relatively recently. Several of them, summarised in Table 15, display a well defined similarity of chemical structure. Comparison of the continuous solid solutions formed by nitrides (Table 16) also shows the closely similar chemical nature of ternary phases containing nitrogen.

Analysis of the above data shows that, in all known groups of typical ternary intermetallic compounds and ternary phases formed by continuous metallide solid solutions of two binary compounds, the chemical factor has a strong influence, expressing itself in the chemical and structural similarity between ternary phases of a given group. The role of the chemical factor is predominant also in the formation of ternary phases of classes other than ternary compounds[11], e.g. metallic solid solutions of limited solubility or ternary solid solutions based on one of the components of the ternary system. In many cases this enables us to predict the formation of certain ternary phases in systems not yet investigated, and thus greatly facilitates the construction of the equilibrium diagrams for such systems.

8. PROPERTIES AND PRACTICAL APPLICATION OF TERNARY METALLIC COMPOUNDS

Very little work has been done on the properties of ternary metallic compounds. But even the existing experimental data enable a relation to be established between the properties and the chemical nature of such compounds.

Table 17 gives the colours of "valency" compounds. It is readily seen that in each triad of compounds with two elements in common the intensity of the colour increases regularly with increase in the atomic number of the third element (Group V).

Numerous investigations on the so-called "Heusler alloys" [111-123] have proved their magnetic properties to be closely linked with the formation of the ternary compounds Cu_2MnAl, Cu_2MnGa, Cu_2MnIn, and Cu_2MnSn. The first three are chemical analogues, and the fourth differs from them only in a single element which is similar in chemical character.

TABLE 17. Colours of some "valency" ternary compounds.

Composition	Colour	Reference	Composition	Colour	Reference	Composition	Colour	Reference
LiMgN	light reddish brown	33	Li_3GaN_2	light grey	110	Li_5GeN_3	yellowish	33
LiMgP	brown	30	Li_3GaP_2	medium brown	33	Li_5GeP_3	brown	33
LiMgAs	—	33	Li_3GaAs_2	blackish brown to black	33	Li_5GeAs_3	greyish black	33
Li_3AlN_2	white to light grey	110	Li_5SiN_3	greyish yellow	33	Li_5TiN_3	yellow	33
Li_3AlP_2	yellowish brown	32	Li_5SiP_3	brown	33	Li_5TiP_3	brown	33
Li_3AlAs_2	reddish brown	32	Li_5SiAs_3	greyish black to black	33	Li_5TiAs_3	black	33

This type of relationship is displayed also in other ternary systems. For example, the ternary compounds Co_2MnGe, Ni_2MnGe, Co_2MnSn, and Ni_2MnSn, which are similar in chemical character and have the same crystal lattices, all show magnetic properties[124]. Chernov and the author[125] have determined the electrode potentials of

TABLE 18. Electrode potentials of some ternary intermetallic compounds containing magnesium or aluminium.

Ternary compound	Electrode potential at 20°, V*	Reference	Ternary compound	Electrode potential at 20°, V*	Reference
MgLiZn	—1.199	—	$Al_9Si_3Mn_4$	—0.557	125
$Mg_5Ca_2Zn_5$	—1.129	—	$Mg_2Al_{12}Cr$	—0.470	125
$Mg_4Zn_3Al_3$	—0.826	125	MgCuZn	—0.459	—
$MgLiAl_2$	—0.689	—	$MgCu_4Sn$	—0.019	—

* The values given represent the steady potentials in 3% NaCl solution relative to the hydrogen electrode.

TABLE 19. Microhardness of some ternary compounds containing magnesium.

No.	Ternary compound	Microhardness at 20° $H_{□}$, kg/mm²	Reference	No.	Ternary compound	Microhardness at 20° $H_{□}$, kg/mm²	Reference
1	MgLiZn	239	—	5	Mg_2Cu_4Sn	445	—
2	$MgLiAl_2$	297	—	6	$Mg_5Ca_2Zn_5$	322	—
3	MgCuZn	381	—	7	$Mg_4Zn_3Al_3$	345	125
4	$MgCuAl_2$	380—400	7	8	$Mg_2Al_{12}Cr$	461	125

several ternary intermetallic compounds containing magnesium or aluminium (Table 18).

Comparison of ternary compounds having two elements in common shows that, in the majority of cases, with increasing difference in chemical properties between each of these two elements and the third element, the potentials become more positive.

Quantitative values have been determined for the microhardness of individual ternary intermetallic compounds[7,125-127]. The present author has determined the microhardness of several ternary compounds containing aluminium and magnesium, of interest as light aircraft alloys. The results of these investigations are set out in Tables 19 and 20.

In the majority of cases the microhardness increases with increasing difference in chemical character between the elements forming the ternary compounds. This type of regularity can be observed on comparing ternary compounds containing two elements in common, e.g. Nos. 1 and 2, 3–5, 6 and 7, and 7 and 8 (Table 19). Also, in this

TABLE 20. Microhardness of some ternary compounds containing aluminium.

No.	Ternary compound	Microhardness at 20° $H_{□}$, kg/mm²	Reference	No.	Ternary compound	Microhardness at 20° $H_{□}$, kg/mm²	Reference
1	Al_6LiMg	297	—	9	T(Al,Cu,Mn)	628	127
2	$Al_3Mg_4Zn_3$	345	125	10	T(Al,Si,Mn)	880	127
3	$Al_3Mg_3Zn_3$	422	127	11	Al_6Cu_3Ni	740	125
4	Al_2CuMg	380—400	7	12	Al_9FeNi	860	125
5	Al_6CuMg_4	414	127	13	Al_9FeNi	987	127
6	$Al_{20}Cu_2Mn_3$	421	125	14	α(Al,Si,Fe)	1097	127
7	$Al_{12}Mg_2Cr$	461	125	15	Al_4Si_2Fe	1147	127
8	T(Al,Si,Mn)	589	125				

TABLE 21. Microhardness at 300° of ternary compounds containing aluminium.*

Ternary compound	Microhardness, kg/mm², after		Ternary compound	Microhardness kg/mm² after	
	30 sec	60 min		30 sec	60 min
$Al_{60}Mn_{11}Ni_4$	307	231	$Al_6Mn_4Si_3$	458	361
$Al_3Mg_4Zn_3$	225	101	Al_6Cu_3Ni	585	316
$Al_{20}Cu_2Mn_3$	404	302	Al_9FeNi	719	414
$Al_{12}CrMg_2$	402	358			

* Load on indenter 50 g.

series of ternary compounds containing magnesium, the hardness is greater when the magnesium is combined with elements which are well removed from it in the Periodic System (Nos. 5–8 have $H_{□}$ = 445 and 461 kg/mm²) in comparison with ternary compounds composed of more closely related elements (Nos. 1–4, and 6 and 7, with a hardness $H_{□}$ = 239–345 kg/mm²).

A similar regularity is in general observed in a group of ternary compounds containing aluminium (Table 20). Thus the hardness of compounds 1–5 in Table 20, which contain only elements of Groups I and II of the Periodic System, apart from aluminium, lies in a comparatively low range ($H_{□}$ = 297–414 kg/mm²); compounds 6–10, containing elements of Groups VI and VII, are harder ($H_{□}$ = = 421–880 kg/mm²); finally the last five compounds (Nos. 11–15 in Table 20), containing elements of Group VIII, have the greatest hardness ($H_{□}$ = 740–1147 kg/mm²).

Thus, the hardness of ternary metallic compounds depends to some extent on the position of the component elements in the Periodic System, increasing with increasing difference between the chemical properties of the elements.

Several papers[125,126,127] have been concerned with the determination of the hardness of ternary metallic compounds at elevated temperatures. The microhardness at 300° of several ternary compounds containing aluminium is shown in Table 21 [125].

At a sufficiently high temperature the majority of intermetallic compounds pass into a plastic condition, becoming easily deformable. This was first demonstrated for binary compounds by Savitskii. He carried out a great amount of experimental work[128-131], published in an extensive monograph[132], which showed the possibility of pressing intermetallic compounds at high temperatures and examined in detail the accompanying changes in structure and properties.

Our experiments on the pressing of ternary intermetallic compounds also show that those which are brittle at ordinary temperatures pass into a plastic condition on heating and can undergo considerable deformation. In particular, it was found that the possibility of deforming certain ternary compounds (e.g. $Ca_2Mg_5Zn_5$) enables us to impart a more favourable structure to them, and to alter the ductility of the alloy as a whole favourably.

In conclusion it must be noted that the experimental data are still insufficient to establish definite quantitative relations between the composition of ternary compounds and their properties. However, the investigations which have been carried out indicate the existence of certain regularities in this respect, determined by the chemical nature of

the elements forming the ternary compound: with increasing difference in chemical properties between the elements, the strength of the chemical bond linking them increases correspondingly, and the resulting ternary compounds become more stable; owing to this, their hardness is increased, their melting points are raised, and their electrode potentials become more noble. In several cases these properties can be successfully exploited to improve the mechanical properties, heat resistance, and corrosion resistance of alloys.

Ternary compounds are encountered in the structure of many alloys of practical importance. In this connection, most work has been done on aluminium alloys[133-142]. Ternary compounds are present in these alloys both in the structurally independent state as eutectics or solid solutions. The properties of ternary compounds and the conditions in which they react with the metal on which the alloy is based, enable the following general principles to be laid down for their practical exploitation:

1. Hardening of solid solutions by dissolving ternary intermetallic compounds in them. The formation of such ternary solid solutions involves more complex interatomic bonds than in binary solid solutions, with greater distortion of the crystal lattice, which makes it stronger.

2. Hardening of alloys by forming structurally free ternary intermetallic compounds in them, distinguished by improved mechanical properties. Several such ternary compounds possess greater hardness than the binary compounds, and therefore the hardening effect may also be more strongly marked. A typical example is the increase in the hardness of tool steels as a result of the formation of ternary carbides of the type Fe_2W_2C, Fe_6W_6C [81,143], Ti_2W_2C [144], etc.

3. Hardening of alloys by ternary compounds containing relatively more of the metal on which the alloy is based than in binary compounds. In this case the influence of alloying elements on the structure and properties of the alloy is considerably greater than in the formation of binary compounds.

Thus Dudzinski et al.[145,146] have shown that the formation of ternary compounds in several aluminium alloys can raise appreciably their normal moduli of elasticity. Pointing out that in isolated cases the modulus of aluminium alloys is increased by ~20%, they note the great and practically important effect of ternary intermetallic compounds on the properties of industrial, and in particular aircraft, alloys.

4. Utilisation of the temperature variation of the solubility of ternary compounds in the main metal to achieve hardening by heat-treatment, consisting in a quenching process followed by ageing. It has been found with several ternary systems that solid solutions may be in equilibrium with various ternary intermetallic compounds; with many alloys which form "metal–ternary intermetallic compound" systems, it has been proved that the solubility of the ternary compound increases on heating. Thus by quenching certain alloys of this type it is possible to obtain supersaturated solid solutions, which can be hardened by subsequent ageing.

The possibility has been noted of using ternary compounds for the age-hardening of aluminium alloys[16,138,147,148]. Special reference must be made to a series of papers by Bagaryatskii[149-152], in which a detailed analysis is given of the role of the ternary phase $S(Al_2CuMg)$ in the ageing of aluminium alloys. The ternary compound T(Al, Mg, Zn)

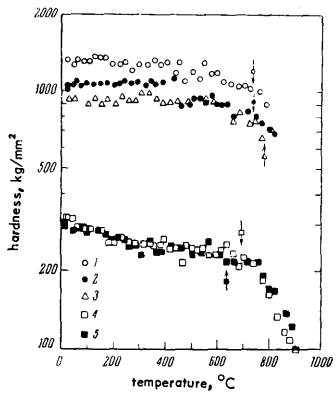


Fig. 12. Effect of temperature on the hardness of some intermetallic compounds and heat-resistant alloys [163]; the arrows indicate 0.6 × m.p.: 1) η_1 — Fe_4Mo_2C; 2) η_2 — Fe_2Mo_4C; 3) Fe_7Mo_6; 4) S-816 alloy; 5) "Jetalloy 1650" alloy.

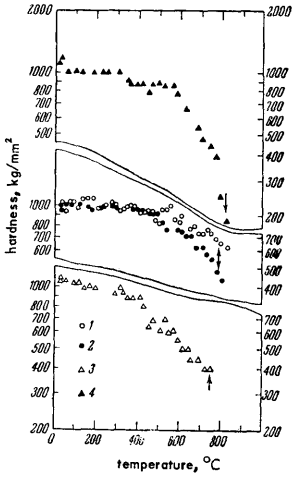


Fig. 13. Effect of temperature on the hardness of some intermetallic compounds [163]; the arrows indicate 0.6 × m.p.: 1) σ - $Fe_{36}Cr_{12}Mo_{10}$; 2) χ - $Fe_{36}Cr_{12}Mo_{10}$; 3) σ - CoCr; 4) σ - FeCr.

has a similar role[153-156]. Our investigations[157-159] of cast and extruded alloys based on aluminium and on magnesium have demonstrated the possibility of hardening these alloys with ternary intermetallic compounds.

5. Improvement of the heat-resistance of alloys containing ternary intermetallic compounds by producing a favourable structure which will as far as possible prevent plastic deformation on heating. As Kornilov[160-162] and others have shown, at certain temperatures such a structure corresponds to saturation of a solid solution. In this case solid solutions which are saturated with ternary intermetallic compounds are formed. In view of the greater complexity of the crystal lattice, ternary solid solutions should possess greater resistance to deformation at high temperatures, as compared to binary solid solutions. The breakdown of

ternary solid solutions with the incipient precipitation of ternary intermetallic compounds, or their separation in a state of dispersion, may also produce an increase in the resistance to plastic deformation on heating, and hence raise the heat-resistance.

The great hardness and thermal stability of several ternary metallic compounds can also be utilised in developing heat-resistant alloys. Some ternary compounds[163] considerably surpass modern heat-resistant alloys (Fig. 12) and binary compounds (Fig. 13) in their hardness at ordinary, and especially at elevated, temperatures.

We have demonstrated the possibility of improving the heat-resistance of aluminium alloys by means of ternary intermetallic compounds[164,165].

6. Improvement in the corrosion resistance of alloys by the introduction and appropriate structural distribution of ternary compounds possessing suitable electrode potentials in given operational environments. A special investigation has been made to determine the effect of ternary intermetallic compounds on the corrosion resistance of pressed aluminium alloys[166].

7. Production of alloys having definite physical properties by utilising the appropriate properties of ternary intermetallic compounds. An example is provided by the work on Heusler alloys already cited[111-123].

8. Employment of ternary intermetallic compounds to impart predetermined technological properties to alloys. Reference must be made to work on the effect of ternary compounds on the modification of Silumins[167-170], on the ductility of cast aluminium alloys[133,171] and of chromium–manganese alloys[172], and also on metal-refining processes for refining metals, e.g. the decarbonisation of uranium[173]. The influence of ternary compounds on the properties of aluminium and magnesium alloys has been discussed in greater detail elsewhere[174].

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Zhukovskii Air Force
Engineering Academy

CONSTRUCTIONAL PLASTICS, THEIR PRODUCTION AND APPLICATION

B. A. Kiselev

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The outstanding success of polymer chemistry has enabled new types of plastic materials to be produced, possessing a remarkable combination of properties, especially great mechanical strength. These plastic materials are being more and more widely employed in the national economy as constructional materials, competing with metals and often replacing them.

1. GLASS-REINFORCED PLASTICS

Among constructional materials a special position is occupied by plastics reinforced with glass. This type covers a group of materials with different physical and mechanical characteristics, technological properties, and fields of application.

Glass-reinforced plastics can be conventionally divided into four main groups according to the type of reinforcement and the technical properties: (1) glass fabrics, (2) oriented glass fibres, (3) plastics based on preformed unoriented glass fibre or mat, and (4) cast or moulded materials incorporating glass fibre.

The problem of using glass-reinforced plastics in different branches of technology covers a complex of questions associated with the production of the glass-fibre reinforcement, the synthesis of binders, the processing and production of the plastic, and the design, manufacture, and application of articles made from it.

The wide use of glass-fibre materials as reinforcing agents is connected with the great mechanical strength of glass fibres, which depends on the chemical composition of glass, the diameter of the fibres, and the technical process by which they have been manufactured.

Glass-reinforced plastics are based mainly on fibres made of an aluminium borosilicate glass containing no alkali, and much more rarely on an alkali glass. The latter contains a large amount of sodium or potassium oxide, and the resulting fibres undergo an irreversible diminution in strength when subject to the action of moisture and temperature. A non-alkali glass fibre is comparatively unaffected by moisture, can be employed without appreciable diminution in strength at temperatures up to 300°–400°, and possesses good electrical insulating properties.

The great merit of fibres based on an alkali-containing glass is the availability and cheapness of the raw materials, and the ease of manufacture of the fibres. Such fibres possess good stability to the action of acids, and therefore with appropriate choice of binder they can be employed in the chemical industry. In this connection, more work must be carried out on the application of glass-fibre fillers based on an alkali glass in the production of plastics and articles made from them.

In several cases a more heat-resistant fibre, which retains its mechanical properties at 1000° and above, is required. These demands have stimulated work in different countries on recipes for more thermostable glass suitable for fibre production, and on practical methods for manufacturing quartz fibres. Information has been published[1] on the production of fibres containing copper oxides, which are then reduced. The presence of a film of copper or other metal on the fibre tends to increase the adhesion, especially of epoxy binders, to the fibre. The mechanical properties of glass plastics can thus be improved.

In the USSR until recently glass cloth has been mainly employed as reinforcement in constructional plastics. In countries such as the USA, England, Italy, and several others, the volume of production and demand for glass mat and rovings are growing. The use of these cheaper reinforcing materials, which do not require to be woven, allows