Solidification of Intermetallic Compounds at High-rate Cooling of Melts

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Introduction and Methods

According to BEVER and ROBINSON[1] intermetallic compounds may be characterized by their bonding forces. These can be metallic, covalent or partially ionic or there are superpositions of them.

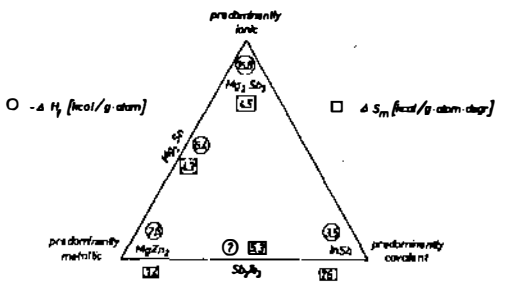


fig.1: Compound-triangle

Fig.1 describes the predominent bonding forces in the compounds $MgZn_2$ (metallic), Mg_3Sb_2 (ionic) and InSb (covalent) and, between them, characteristic transition compounds. There are given the figures of the enthalpy of formation and the entropy of fusion.

It seemed of special interest to investigate the behaviour of some mostly intermetallic compounds of different bonding characteristics with high rate cooling from the melts. The cooling method applied in these investigations has been described by K.LÖHBERG and H.MÜLLER[2]. The molten alloy is shooten by high pressure against a silverplate and reaches it, yet fluid. It may solidify with a rate of nearly 10^4 to 10^6 degr.sec^{-1}. Unfortunately it was not possible to measure the temperature because of not knowing the emission coefficients of these alloys. The intermetallic compounds were molten as one-phase alloy or as one of the phases of binary eutectic alloys.
The tables I and II show the compositions of all compounds and eutectic alloys.

The melts solidified as platelets of a thickness of 30 µm, in some spots of 5 µm. These were investigated by metallographic and X-Ray methods. For the X-Ray probe the slowly cooled samples were powdered, the rapidly cooled samples were X-rayed as such. For the metallographic observation the rapidly cooled thin platelets were fastened on a substrate, grinded, polished and etched.

Table I — One-phase compounds

Intermetallic compound	bonding force	T_m degr.K	S cal/g-atom.degr.
$Cu_9 In_4$ (HUME-ROTHERY)	metallic	955	
Cu Zn_3 (HUME-ROTHERY)	"	973	
Cu_2 Mgn (fcc LAVES)	"	1o92	
Zn_2 Mg (hcP LAVES)	"	863	3,9
Ge Te	predom.ionic	998	
Sn Te	"	1o63	
Pb Te	"	119o	
In Te	metallic-ionic	969	4,5
In_2 Te_3	"	94o	4,1
In Bi	"	383	
In_2 Bi	metallic-ionic - covalent	362	
Cu_2 In	"	94o	
In Sb	covalent	8o3	7,6

Table II — Eutectic alloys

System A-B	At.% B	Eutectic phases	T(eut) °C
Cu - Te	71	Cu Te + Te	34o
Al - Te	9o	Al_2Te_3 + Te(+Te,pr)	42o
In - Te	89	In_2Te_5 + Te	427
Si - Te	81	Si_2Te_3 + Te	4o9
Ge - Te	85	Ge Te + Te	375
Sn - Te	84	Sn Te + Te	4o5
Pb - Te	85,5	Pb Te + Te(+PbTe,pr)	4o5
Sb - Te	89	Sb_2Te_3 + Te	424
Bi - Te	9o,3	Be_2Te_3 + Te	413
Mg - Ge	86	Mg_3Sb_2 + Sb	579
In - Sb	68,3	InSb + Sb	5oo
Cu - Sb	63	Cu_2Sb + Sb	526
Pb - Bi	56,3	Pb_3Bi + Bi	125

Results and Discussion:

One-phase intermetallic compounds

The slowly cooled as well as all rapidly cooled one-phase intermetallic compound crystallized with solidifying and every one with its own, wellknown structure: the equilibrium phase had been formed. In our opinion this means, that only the compounds, with their structures refered here, are the stable phases in that composition range. The undercooling may not have been the highest possible; but the mechanical shock in the moment when the undercooled melt reaches the silver plate, may favour the nucleation. In the same manner also pure elements bonded by metallic or covalent-metallic forces crystallize with their structure also with highest cooling rates.
According to JACKSON and CHALMERS[3] the ratio of the accomodation coefficients of the atoms in the melt (Am) and in the crystal surface (A_f) can be reduced to

$$Lm\ (A_m/A_f) \propto \Delta S/R$$

with ΔS = entropy of fusion (cal.(gr.at.degr.)$^{-1}$ and R = gas-constant. Let us assume $A_m = 1$, then A_f is the higher the lower the entropy of fusion of an element is. For Cu : A_f = o,32 for Ge : A_f = o,o42, for AuZn : A_f = o,12 and for InSb : A_f = o,o22. Therefore the crystallization of a covalent bonded element as Si or Ge may be hindered with highest cooling rates of the melt much more than a normal metal.
But, indeed, there is no difference in the solidification of metallic or covalent bonded elements or compounds. In both cases the jumping rate of one atom from the melt to the surface of the crystal may be much higher than the cooling rate. Let us assume, the distance of a jump be s = 2 Å and the coefficient of the self-diffusion in the melt be D = $4.1o^{-5}$ cm^2 sec^{-1} in the supercooled melt; the jumping time is then

$$\tau = s^2/4\,D \approx 1o^{-11}\,\text{seo}.$$

If the critical radius of a nucleus be $r_K = 1o.1o^{-8}$ cm and the radius of the atom be d = $1,5.1o^{-8}$cm, the number of atoms in the critical nucleus is nearly N = 3oo and the total time for building up the critical nucleus by jumping of the atoms one after

the another is $t_\gamma = 3.10^{-9}$sec, whereas the time, the melt being in the critical range of supercooling (T_- 200°), with a cooling rate of 10^5 grd.sec^{-1} is $t_c = 2.10^{-3}$sec. The ratio of t_γ to t_c may be nearly the same for elements or compounds.

Eutectic alloys

In every case the typical eutectic structure has formed with slow cooling rate but with higher cooling rate, after supercooling one of the eutectic phases crystallises primarily and the spacing of the eutectic phases is smaller after rapid cooling as very well known.

Only some eutectic melts with Te as the one phase solidified without any crystal structure; they seem to be glassy as shown by X-Ray investigation. (Fig.2a u.2b).

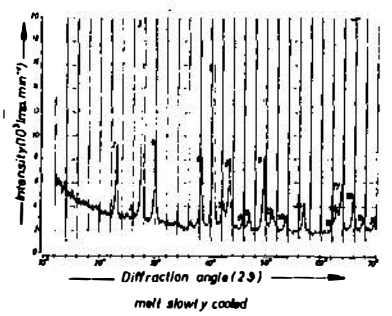
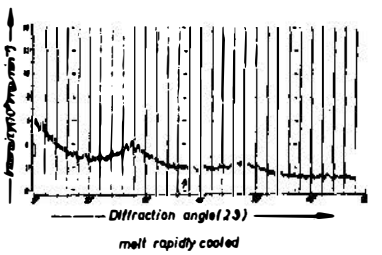


fig. 2: Debyeograms of Ge-Te 85



The fracture of these samples was brittle. According to other authors and to our own observations, the following eutectic melts showed an anomalous behaviour with rapid, Si-Te also with slow cooling:

Al - Te Ga - Te In - Te Si - Te G e - Te

whereas all other eutectics with Te as the one phase (Cu-Te, Sn-Te, Sb-Te, Pb-Te and Bi-Te) crystallised. So far as known, there is no distinct difference between the bonding characters in the compounds of Te with Cu, Sn, Pb, Al, Ga, In, Si and Ge. KREBS[4] and his collaborators have suggested a correlation between glassy solidifacation of ternary melts of e.g Sb - Te - Ge or As - Te - Ge, and their electrical resistance. Melts solidifying glassy also with slow cooling are comparable to semiconductors, those crystallizing are metallic. It seems further, that

melts tending to form glasses have a higher viscosity - indeed, the eutectic melt of the system $Si_2 Te_3$ - Te is strongly viscous and this melt solidifies glassy also with slow cooling rate.

These references are badly abbreviated, but the tendency seems clear. In the opinion of KREBS et al. the anomalous behaviour may be caused by special bonding forces. It seems to be essential for melts of metallic character, that the bonding electrons are not directed (arranged by p σ - electrons). On the other hand, if the electrons are unilaterally directed by (sp)-bonding, the mobility of electrons is reduced and a glass is formed.

It seems also to us, that the chemical or bonding character of glassy solidifying melts may be changed by Al, Ga, In, Si or Ge in another manner than by Sn or Pb and so on. But beside this in our opinion it seems necessary to keep in mind that eutectic melts tend to form glasses. With crystallization the Te-atoms must separate from the (Te-X) groups in the melt. If the viscosity of the melts is very strong, the separating of the Te-atoms is hindered and so the melt may solidify without changing the arrangement of the atoms. For testing this it seems important to measure the coefficient of diffusion of the constituents in eutectic $Te\text{-}Te_X X_Y$ melts.

L i t e r a t u r e

(1) ROBINSON, P.M. and M.B. BEVER: Intermetallic Compounds (Edited by J.H.WESTBROOK) John WILEY, New York 1967

(2) LÖHBERG, K. and H. MÜLLER: Paper to International Conference on Metastable Metallic Alloys

(3) JACKSON, K.A. and B. CHALMERS: Canad.J.Physics 34 (1956) p.473

(4) KREBS, H.: Journ.of Non-Crystalline Solids 0 (1969), S.455-473

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DISCUSSION

P. Duwez (Comment) : It is true that intermetallic compounds melting congruently cannot be quenched into the amorphous state. Some compounds, however, may crystallize into a metastable crystal structure. This is the case of Te_2Au (monoclinic) which after quenching is simple cubic with one atom per unit cell.