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THE VOLUME CHANGE DURING SOLIDIFICATION

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16. Abstract The liquid-solid phase transformation of solidifying metallic melts is accompanied by a volume change ΔV_m . This volume change produces a gravity-independent microscopic flow near the solidification front in a ground-based laboratory. Solidification processes are also affected by convection due to temperature and concentration gradients. A quantitative evaluation of the effects of these flows on the formation of structure requires reproducible values of ΔV_m . Alloys with $\Delta V_m = 0$ would be best suited for such an evaluation, while alloys with a constant value for ΔV_m are still usable. Another requirement is related to a solidus-liquidus interval which is as small as possible. One-phase alloys, which would be particularly well suited, could not be found. For these reasons, alloys which solidify in two phases, as for example eutectics, have been considered, taking into account the Al-Ge system. Attention is given to the volume change at the melting point, the measurement of this change, the volume change at solidification, and applications to terrestrial technology.			
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THE VOLUME CHANGE DURING SOLIDIFICATION

M. Rittich*

1. SUMMARY

The liquid-solid phase transformation of solidifying metallic **/135 melts is accompanied by a volume change $\Delta V_{\text{r}} = 0$. This volume change produces a gravity-independent microscopic flow near the solidification front. In a ground-based laboratory, solidification processes are also affected by convection due to temperature and concentration gradients. A quantitative evaluation of the effects of these flows on the formation of structure requires reproducible values of ΔV_{r} . $\Delta V_{\text{r}} = 0$ alloys would be best suited for such an evaluation, while alloys with a constant value for $\Delta V_{\text{r}} = 0$ are still usable. Another requirement is related to a solidus-liquidus interval which is as small as possible. One-phase alloys, which would be particularly well suited, could not be found. For these reasons alloys which solidify in two phases, as for example eutectics, have been considered, taking into account the Al-Ge system. Most metallic alloys do not crystallize in a plane but in a cellular or dendritic solidification front.

Since distinct ΔV_{r} data cannot be found in the literature, ΔV_{r} values should be measured with the help of a self-built laboratory apparatus. The method chosen was the pressure change of argon above the solidifying melt. The experience gained has led to a measuring device of the second generation. The volume

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**Numbers in the right margin indicate foreign pagination.

changes during solidification are the cause of many mistakes in the field of casting. ΔV_m measurements and basic analysis of the volume change would have great effects on practical procedure.

2. THE VOLUME CHANGE AT THE MELTING POINT

The liquid-solid phase transformation of metallic melts can be accompanied by macroscopical flows. Due to the gravity of the earth, the driving forces behind these flows are found in the temperature and concentration differences trying to reach equilibrium. Also, during the solidification of metallic alloys, a volume change occurs and leads to a density change. This causes a microscopical flow at the phase-borderline. The temperature and concentration caused flows are gravity dependent, whereas the flow produced by the volume change is gravity independent. Ground-based laboratory experiments about solidification processes are affected by convection due to temperature and concentration gradients. For a quantitative evaluation of these flows and the flow due to volume change on the formation of structure, a μ -g experiment, that is, an experiment under space conditions, can be useful since the g-dependent flow components can be eliminated.

Knowing the volume increment ΔV_m is fundamental when experimenting with alloys, when trying to determine the effect of volume change caused flow or the absence of μ -g dependent flows on structure formation. Volume change data have been available in the literature for a long time. Table 1 shows data from several reference books and the specific literature as well. Table 2 shows the range of data in a selection of elements. Noticeable are the values for antimony with a ΔV_m varying between +1.4 and -0.95. Its ΔV_m can be looked at as a "volumeshrinker" as well as a "volume-expander".

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3. MEASUREMENT OF THE VOLUME CHANGE

The ΔV_m data found in the literature are based on various measuring methods.

To gain genuine experience, a laboratory apparatus was built. In order to exclude the influence of probes and measuring detectors, the measuring device was constructed as follows. By means of a liquid or gas barrier in the closed furnace system, it was possible to obtain a continuous reading of the volume change of the melted and controlled solidifying alloy. The installation was built under the influences of an apparatus used by Clyne and Davis in 1978. Fig. 1.

The sample is melted in an open crucible in the furnace under protective gas. Then the crucible is closed vacuum-tight with a cooled lid. The lid has built-in thermo-couples and gas-conduits. To remove gas residuals in the melt, the crucible is evacuated for half an hour. To measure pressure changes, the installation is filled with 0.8 bar argon and kept in a steady state. A water cooled ingot-mould is brought to the bottom of the crucible and the heat is turned off to obtain a controlled solidification. This results in a change of the level of the melt and thus in a pressure change indicated at the compensation pressure-gauge. Adjusting this manometer to zero yields a reading at the measuring manometer of the actual pressure change taking place in reference to the atmospheric pressure. The appropriate temperature can be registered at the same time. The established values, that is, pressure and temperature, plotted down on a time axis, Fig. 2, show the connections sought for. The linear decline of the pressure near the stopping point is used to calculate ΔV_r by means of

$$P \cdot V = n \cdot R \cdot T$$

Fig. 2 shows that the change of the slope of the pressure curve does not coincide with the solidification interval, that is, the point of stability of the temperature. There seems to be no connection between the solidification period of the metallic melt and the break of the pressure curve. The problem of measuring gas in a dynamic state requiring a continuous pressure measuring device still remains to be solved. The apparatus was improved by installing a piezo-pressure tube but local changes of the gas temperature during the experiment can still not be registered in a sufficiently accurate way. Therefore, the gas problem has to be optimized in a new installation.

4. THE VOLUME CHANGE DURING SOLIDIFICATION

During liquid-solid phase transformation a volume change occurs. The sequence of pictures in Fig. 3 shows the volume change starting at casting temperature down to room temperature. For undisturbed examination of flows at and just near the phase borderline during solidification, a sample with controlled reproducible values of ΔV_r , at best $\Delta V_r = 0$, is feasible. Also suited are alloys with a known, and during experimentation constant value of ΔV_r . Due to physical and crystallographical conditions, pure substances not showing a change in density during liquid/solid phase transformation do not exist.

Therefore, in experimenting with alloys having a $\Delta V_m = 0$ or $= \text{constant}$, certain conditions have to be met. In the phase diagram at the point where the concentration compound is calculated $\Delta V_r = 0$, the compound of the alloy containing a substance with $\Delta V_m > 0$ and a substance with $\Delta V_m < 0$ should show a rather small solidus-liquidus interval. In bivalent alloys with one phase preceding the other, one can find microscopical turbulent flows at the phase border line even though the alloy compound possesses a summary $\Delta V_m = 0$. Fig. 4

Therefore, single-phased $\Delta V_m = 0$ systems would be better suited for the tests mentioned above. The Bi-Sb system has such qualities: formation of mixed crystals within the whole compound, Figure 5.

author	A. R. Ubbelohde	G. V. Samsonov	P. J. Flory	A. Abell	G. Felsing	Metals Rev.	D. Audisichewski	L. D. Lucas	I. V. Gavrillina	L. J. Wittenberg	P. Hicter	A. Schneider	H. Lindner
Element	1930	1975	1974/75	1957	1950	1967	1945	1964	1974	1972	1965	1950	1972
Al	6.0	6.37	7.14	6.4	6.26	6.5	6.0	6.37	6.0	6.9	6.37	6.0	6.26
Bi	-3.35	-2.9	-3.32	-3.3	-3.3	-3.35	-3.35	-2.9	-3.9	-3.87	-2.9	-3.35	-3.32
Co	4.7	4.0	4.0*	4.7	4.72	4.0	4.7	4.0	4.7	3.4	4.0	4.0	4.74
Ce	-	-	-	-	-	-	-	-	-1.0	-1.0	-	-	-
Cu	-	1.3	5.26	-	-	3.5	-	5.69	-	-	5.69	-	-
Cr	4.51	4.33	5.3	4.1	4.25	4.2	4.15	4.33	4.51	3.96	4.33	4.15	4.05
Fe	-	1.4	3.16	-	-	3.5	4.4	3.58	2.2	3.6	3.58	3.0	-5.50
Ge	-3.2	-3.33	-	-3.4	-3.24	-3.2	-3.2	-3.13	-3.2	-2.9	-3.13	-3.2	-
Ga	-	-5.1	-	-	-	-5.1	-	-5.1	-	-5.1	-5.1	-5.0	-
Hg	-	3.7	-	3.5	-	3.7	3.7	3.7	-	3.64	3.7	3.7	3.75
In	2.7	1.90	1.90*	2.7	-	2.0	2.7	1.90	-	2.6	1.90	2.0	-
K	2.55	2.81	-	2.5	2.55	2.55	2.55	2.83	-	2.54	2.83	2.55	2.81
Mg	3.05	4.12	-	4.2	4.1	4.12	4.1	4.12	-	2.95	4.12	4.1	-
Ni	2.5	2.59	-	2.5	2.5	2.5	2.5	2.59	-	2.6	2.59	2.5	2.53
Pb	-	3.3	5.11	-	-	4.5	-	6.34	4.6	6.3	6.34	-	-
Pt	-	3.50	3.22	3.4	3.30	3.5	3.5	3.50	3.5	3.81	3.50	3.5	3.44
Sn	-	-	-	-	-	-2.5	-	-	-	-2.4	-	-	-
Sb	-0.95	-0.95	0.64	-0.95	-0.95	0.8	-0.95	-0.95	-0.95	-0.95	-0.95	-0.95	1.4*
Si	-	-9.5	-2.9*	-	-10.0	-10.0	-	-9.5	-	1.1	-9.5	-9.6	-
Te	-	3.0	2.5	2.7	2.6	2.3	2.8	3.0	-	-2.9	3.0	2.8	2.6
Zn	4.7	4.00	4.00*	6.5	4.7	4.7	4.2	4.00	4.2	4.00	4.00	4.2	6.5*

Table 1 Volume increment-data, taken from various sources show a great range of the measured values; positive values mean shrinkage, negative values mean expansion during solidification.

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metal	$(\Delta V_m)_{\min}$	$(\Delta V_m)_{\max}$
Si	- 9,5	- 10,0
Ge	- 4,75	- 5,5
Bi	- 2,9	- 3,9
Ga	- 2,9	- 3,4
Sb	- 0,95	+ 1,4
Sn	2,3	3,0
Pb	3,22	3,85
Fe	1,4	4,4
Cd	3,4	4,74
Mg	2,95	4,2
Cu	3,96	5,3
Al	7,14	6,0

$$\Delta V_m = \frac{V_l - V_s}{V_s} \cdot 100 [\%]$$

Table 2 The range of ΔV_m data is very distinct with the element Sb. During solidification Sb shrinks and expands as well.

- A: Ni-crucible
- B: Furnace
- C: Fireblock
- D: High-grade steel lid system
- E: Extension for measuring current
- F: Joint of steel parts
- G: Fire protection shield
- H: Vacuum stopcocks
- I: Fire-proofed plate
- J: Pressure equalizing manometer
- K: Measuring manometer
- L: Extension to safety container
- M: Extension for Argon
- N: Extension for vacuum

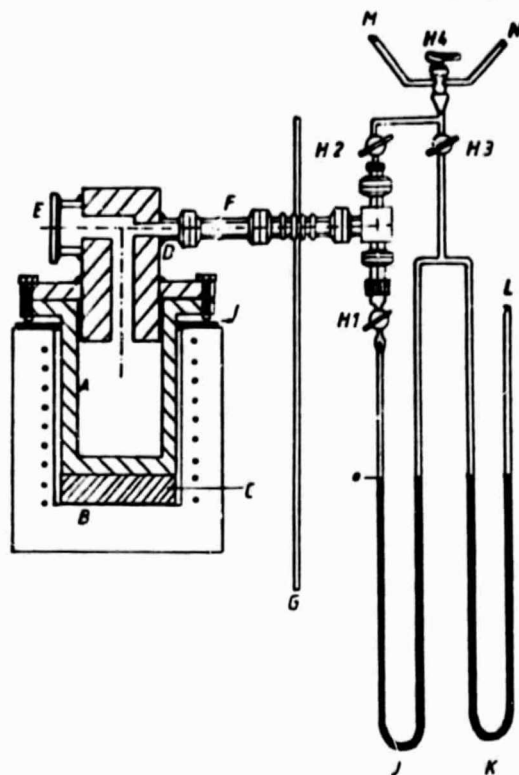


Fig. 1 The measuring device functions according to the method of discontinuous pressure measuring. In the closed furnace system, the set pressure changes, e.g. through lowering the level of the melt in the crucible. The column of mercury in the compensation pressure-gauge rises. For compensating, a vacuum is pumped through H3 until the manometer reads zero. By then, the column in the measuring manometer has adjusted itself against the atmospheric pressure. Now, a definite value can be obtained. The sum of these singular values is linearized in the P-t diagram thru a compensator straight line.

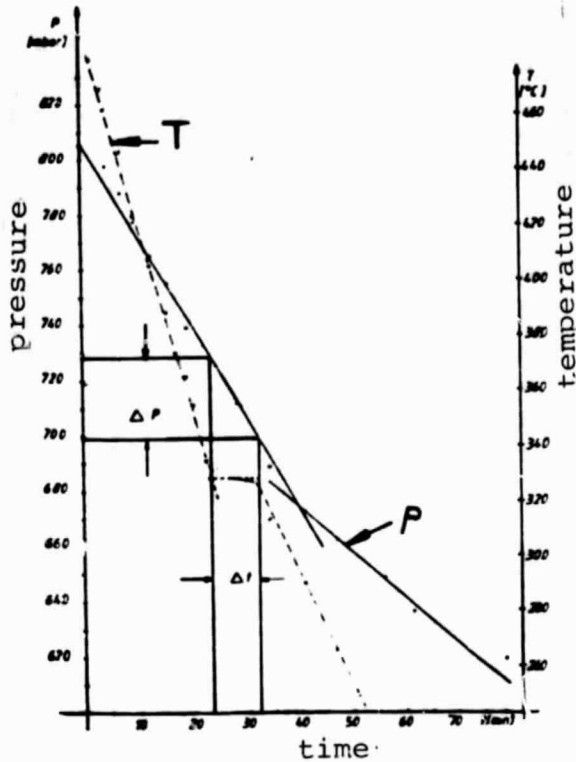


Fig. 2 Pressure-Time-Temperature Diagram
 From the temperature-time curve of the solidification process, the solidification time $\Delta-t$ is determined. Transference of $\Delta-t$ onto the pressure-time curve enables one to assign $\Delta-t$ to the corresponding pressure difference $\Delta-p$. By means of the general law of gases, the volume increment ΔV is calculated. Measuring conditions: Amount of gas is constant. The change of the pressure should take place near the thermal "stopping point". Only then can a satisfactory reproducible measurement be expected. Using Pb led to a $\Delta V_m = +3.5\%$, comp. table 2.

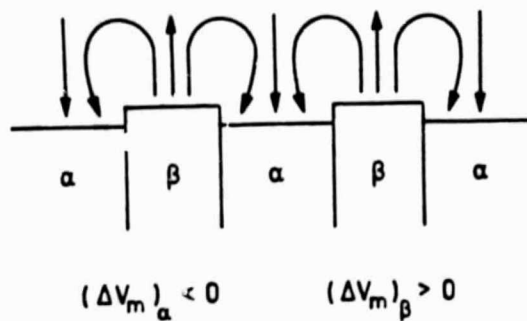


Fig. 4 Eutectic alloys, e.g. Fe-C, Al-Si (with Fe Alpha phase and / or Si as Beta phase) will produce strong micro-convective flows at the phase border line depending on the strongly diverging volume increments. The sum $\Delta V_m = 0$. P.R. Sahn and M. Rittich 1982.

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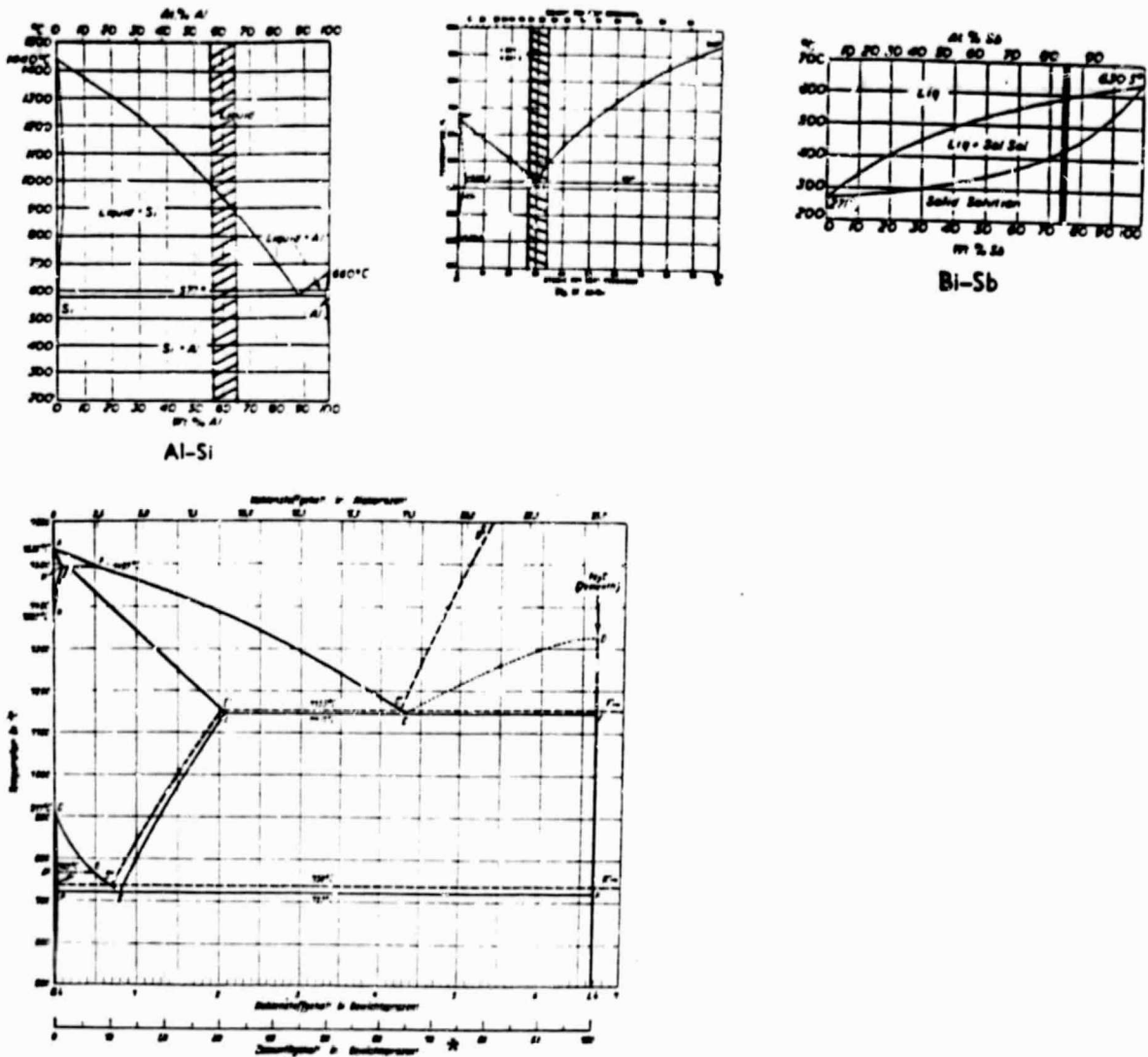


Fig. 5 Using the rule of compounds, alloys with $\Delta V_m = 0$ are determined. The search for binary systems comes especially into play in alloys with a $\Delta V_m = 0$ point just near the eutectic, that is, bivalent alloys without a primary solidification area. The single-phased alloy system Bi-Sb plotted at $\Delta V_m = 0$ is not very realistic since the calculated data for Sb with $\Delta V_m = +1.6$ are apparently not correct.

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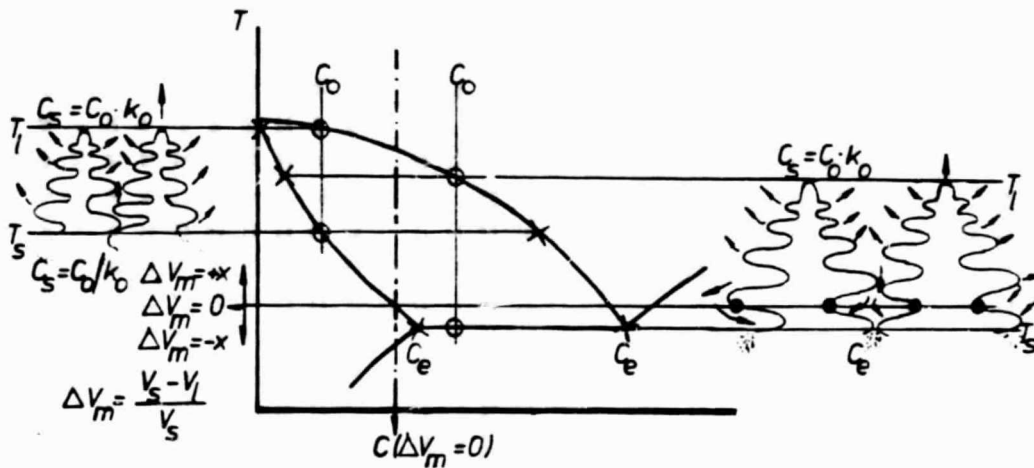
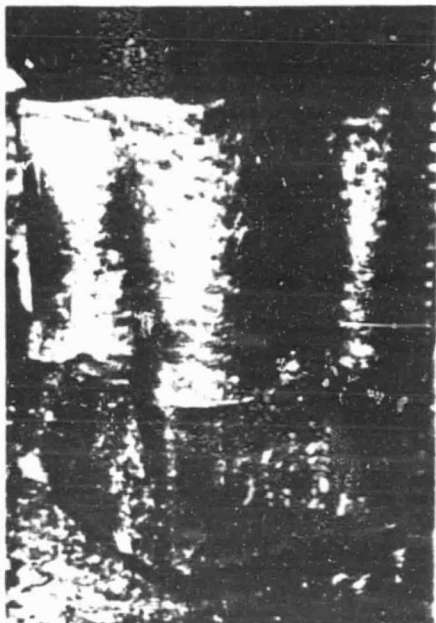


Fig. 6 The schematic graph of a section of a phase diagram with a distinct solidus-liquidus interval shows that if the solidification front grows dendritically, there is only one level where $\Delta V_m = 0$ ist. All the rest solidifies with either a positive or negative volume increment. In such alloys, opposite volume change compensator flows are induced above and beneath the $\Delta V_m = 0$ level. P.R. Sahn & M. Rittich 1982.



b

Fig. 7 a) Large feeders are necessary for this piece of cast-steel to obtain a dense casting (even though in this case it was a bit exaggerated). R. Wlodawer, Controlled Solidification of Cast-steel, Giesserei Verlag, Duesseldorf 1967
b) In contrast to that, a piece of cast-iron, which was cast without feeder. By using $\Delta V_m \sim 0$ in cast-iron, one can work without a feeder, making a clean-up unnecessary.
S. Karsay, Ductil Iron III Q II-Per et Titan. INC 1981 (courtesy: Vulcan Foundry, USA)

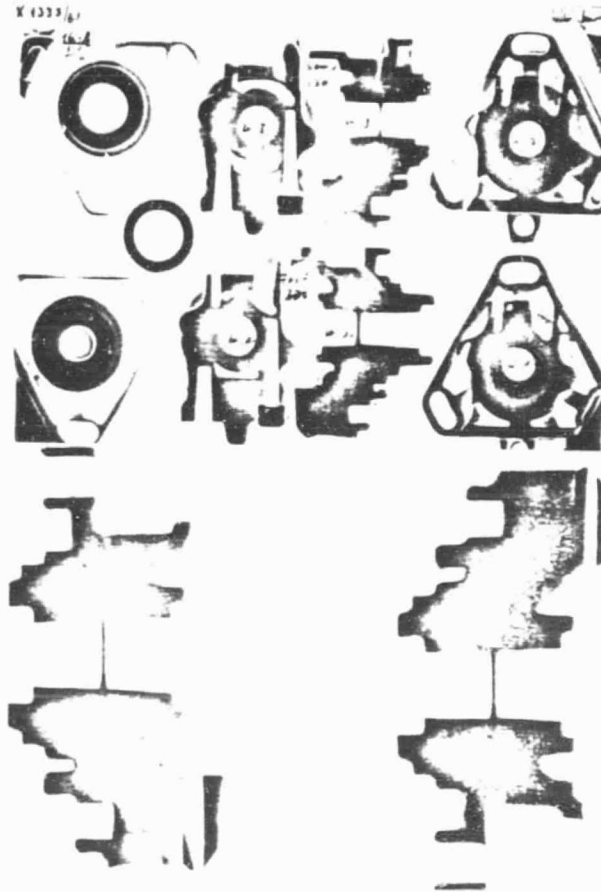


Fig. 8 Xerographs showing micro-porosity in aluminum (pressure casted) caused by solidification shrinkage. Bosch Group 1981

Research in the literature about volume change data of antimony /142 gives reason to doubt if an alloy with $\Delta V_m=0$ is synthesizable at all. Compare Table 1 and 2. Other single-phased alloy systems cannot be found in the literature so the analysis was restricted to poly-phased systems.

Bivalent solidifying alloys with $\Delta V_m=0$ do exist. The $\Delta V_m=0$ -point should be located near the eutectic since the eutectic does not possess a primary solidification area. Fe-C or Al-Ge are two possible systems, Fig. 5. The melting point of Fe-C TE-1147 degrees Celcius is higher than the melting point of Al-Ge TE 423 degrees Celcius.

Most metallic alloys do not solidify as a plane smooth solidification front but rather crystallize, depending on the morphology cellularly or dendritically. Conditions for $\Delta V_m=0$ or constant at the phase borderline are in accordance with the theoretical derivations as shown in Fig. 6. The graph indicates that constant ΔV_m conditions are only applicable to specific areas of the expansion front. The expansion speed of the controlled solidifying samples, the temperature gradient and the concentration distribution just ahead of the solidification front are the biggest influences. By cooling the solidification front and freezing the sample, one can expect, with the help of micro-sections of the solidification morphology and micro-probe analysis of the concentration distribution, results reflecting the influence of the volume change compensator flow on the solidification front.

5. APPLICATIONS TO TERRESTRIAL TECHNOLOGY

The volume change is the cause for many failures e.g. micro-porosity, shrink-holes and interior deficit.

In the casting industry strong efforts are made to solve these problems. Fig. 7 shows a piece of steel where the volume compensation was achieved by using larger feeders. At this time, technology makes use of the alloy compound $\Delta V_m=0$ in cast-

iron, leading to feederless casting. Micro-porosity in aluminum alloys very often leads to throw-out. Fig. 8. The light areas in Fig. 8 represent micro-porosity. Little has been done in basic research to solve this problem. Investigations about this and Delta-Vm measurements of the volume change phenomenon would have positive influences on the practical work.

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