# Founding properties of non-ferrous liquid metals

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**SYNOPSIS**

*The paper evaluates the important physical properties of some non-ferrous liquid metals in terms of their application in the foundry. The properties discussed are: viscosity, surface tension, density and volume contraction on solidification, etc. Wherever possible the paper correlates them with the structure in the liquid state and particularly in terms of interatomic cohesion.*

ALTHOUGH the liquid state is the first step of all founding operations no fundamental measure is available to evaluate the capacity of liquid metals to flow adequately into intricate moulds. Whilst a consideration of viscosity and surface tension is natural in any discussion of the flow of liquid metals, it is not adequate to describe their founding characteristics. In this paper an attempt has been made to evolve a fundamental basis of viscosity and surface tension and their impact on casting fluidity.

## Viscosity

The concept of viscous flow is based on the correlation of the external force producing displacement of adjacent layers of the liquid with the force tending to return them to a position of equilibrium. The relationship is expressed by the following relation:

$$F = \eta S \frac{dv}{dy}$$

where

$F$ = external force, $\text{g. cm/sec.}^2$

$S$ = area of the displaced layer, $\text{cm}^2$

$\frac{dv}{dy}$ = velocity gradient of displacement of the layers, 1/sec.

$\eta$ = dynamic viscosity, g/cm. sec.

The force of restitution naturally arises from the interatomic cohesion which is a periodic function of atomic number. Fig. 1 shows that viscosity (at 50°C super heat) of metals bears the anticipated periodic relationship[1] with atomic number and is highest for the most strongly bound transition metals and lowest for the alkali metals.

## Effect of temperature

Reynold[2] empirically stated that viscosity decreases exponentially with absolute temperature due to the weakening of inter-atomic cohesion which is simultaneously accompanied by volume expansion. An Arrhenius type of rate process equation was suggested by Andrade[3]:

$$\eta = Ae^{-E_n}/RT$$

$\eta$ = viscosity

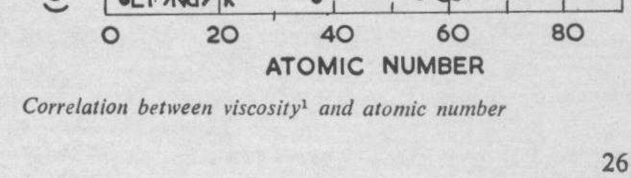
$A$ = constant

$E_n$ = activation energy of viscous flow

$R$ = gas constant

$T$ = absolute temperature

In metals like silicon, germanium, gallium and indium[4]



1 *Correlation between viscosity[1] and atomic number*

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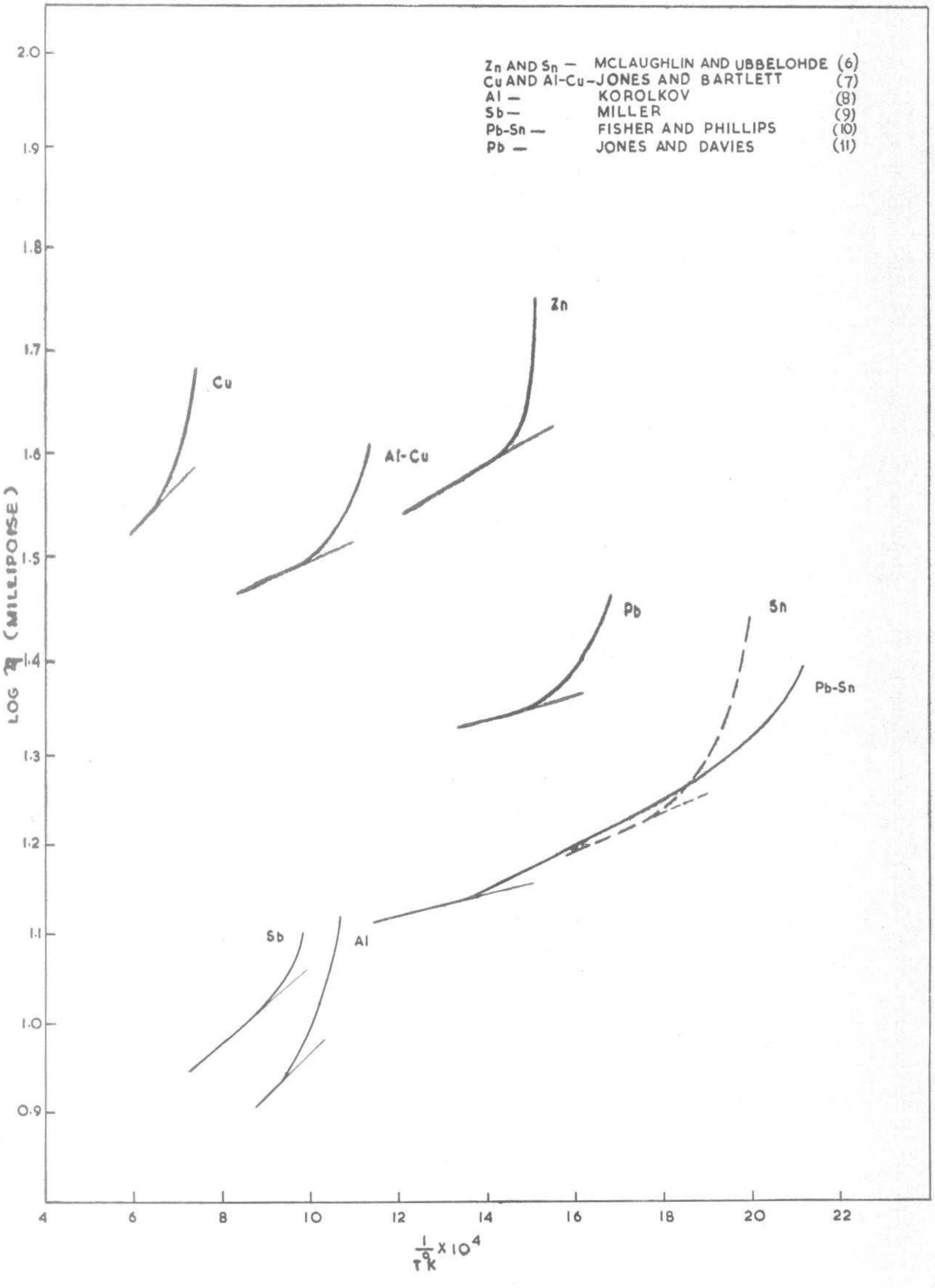
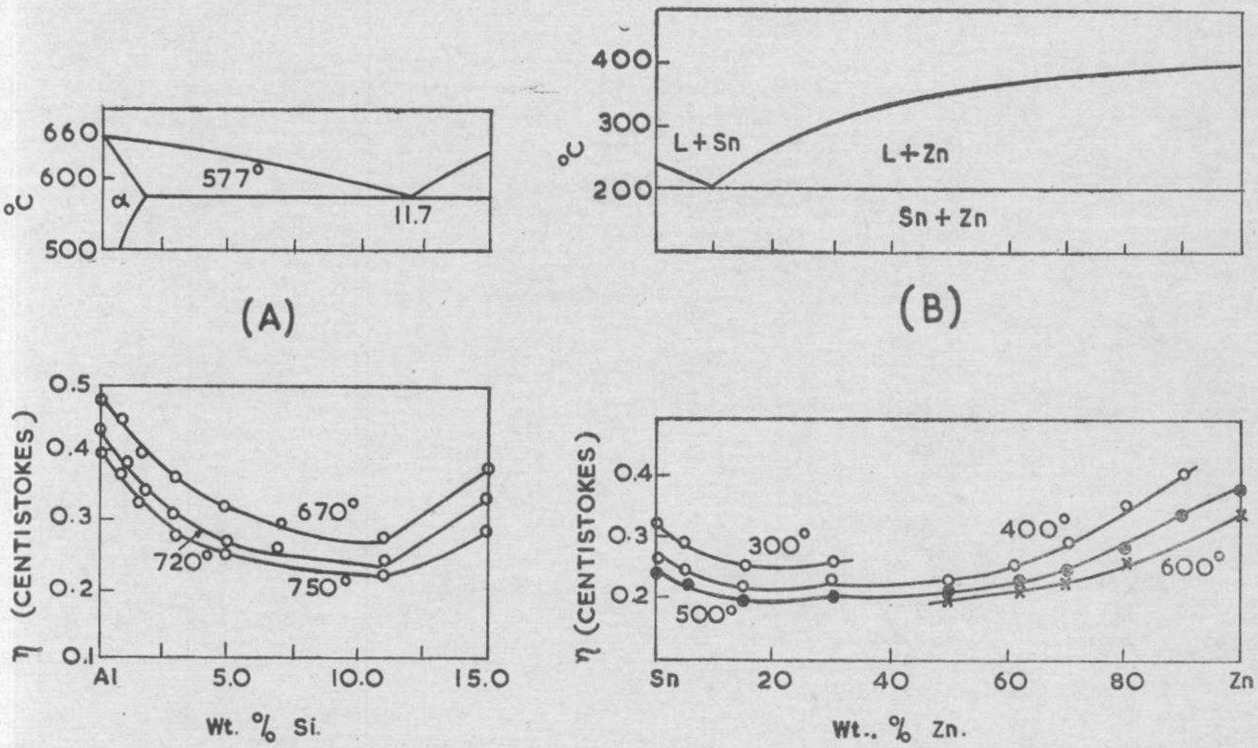


2 *Viscosity of metals and alloys*



3 *Viscosity composition diagrams*[8] *for Al–Si (A) and Sn–Zn (B) systems*

where solid-liquid transformation is marked by volume contraction and change of bonding from homo-polar to closely packed metallic, there is at first significant increase in viscosity on heating above the melting point followed by the usual decrease as temperature is further raised in liquid state. Similar behaviour has been reported for their arsenides.[5]

Whereas a linear relationship between log$\eta$ and $1/T$ is usually observed in the case of monomeric liquids, metallic liquids[6-11] (tin, zinc, aluminium, lead) generally show deviations particularly near freezing temperature (Fig. 2). McLaughlin and Ubbelohde[6] attributed such deviations to 'pre-freezing phenomenon' in liquid state. The deviations can also be due to the presence of insoluble oxide and other impurities ; but their disappearance at higher temperatures where the insoluble impurities are still present, is suggestive of a more fundamental operative mechanism particularly as the deviations are observed in a number of non-metallic solutions[12] as well.

## *Nature of the 'pre-freezing phenomenon'*

Regarding liquid metals structurally as consisting of clusters of atoms where the aggregation is a close derivative of that in the crystalline state, dispersed in atoms, which behave like pure liquids in respect to degrees of freedom and having an excess number of vacancies, Kumar and his co-workers[13-17] demonstrated the existence of clusters and determined the average cluster size with the help of the Kumar-Samarin technique of centrifuging liquid metals.

The volume fraction of the clusters suspended in atoms of true liquid can be determined if the Einstein equation relating viscosity of colloidal solution with the volume fraction of suspended particles is applicable :

$$\frac{\eta_1}{\eta_{s1}} = 1 + \alpha\phi_1 + \beta\phi_1^2$$

where $\phi_1$ = volume fraction of suspended particles/milliliter at temperature Ti,

$\eta_1$ = actual value of viscosity in millipoise,

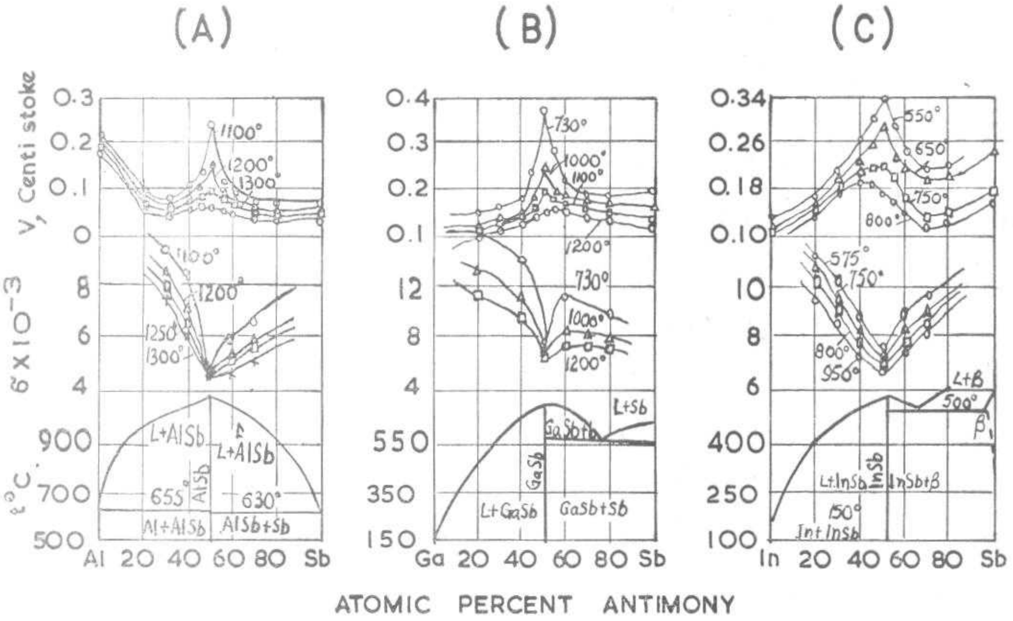
$\eta_{s1}$ = value the viscosity would have if Arrhenius expression is extrapolated to Ti ; i.e. the viscosity of monomeric liquid.

$\alpha, \beta$ = constant equal to 2·5 and 7 respectively.

When published values of viscosity are used, the volume fraction of clusters is about 10 per cent in liquid tin and zinc,[9] about 7 per cent in aluminium-copper eutectic melt and 9 per cent in Pb-62% Sn alloy immediately above their melting points.[15]

## *Viscosity alloys*

Since the viscosity of pure liquid metal is related to



4 *Viscosity and electrical conductivity isotherms*[19] *in the Al–Sb (A) Ga–Sb (B) and In–Sb (C) systems*

their inter-atomic cohesion and temperature, the viscosity of liquid alloys bear relationship with the liquidus (hence composition and the degree of superheat, △T). In eutectic systems the viscosity isotherms show minima at the eutectic composition.[10,18]

Typical results for the Al-Si and Sn-Zn systems[8] are shown in Fig. 3.

The presence of liquidus maximum (Al-Sb, Ga-Sb, In-Sb) due to intermetallic compounds in solid state gives rise to a pronounced increase in viscosity at corresponding composition near the liquidus temperature.[19] The viscosity isotherms shown in Fig. 4 in conjunction with the phase diagrams of Al-Sb, Ga-Sb and In-Sb suggest that a strong atomic interaction is retained on transformation to liquid state. On increasing the temperature, the viscosity maximum shows a gradual flattening indicating a progressive weakening of the atomic cohesion and thus the true melt features become prominent through randomization of atoms of the clusters.

It is evident that the viscosities of molten metals are (i) low (ii) do not vary much from one metal to another and (iii) very much affected by temperature.

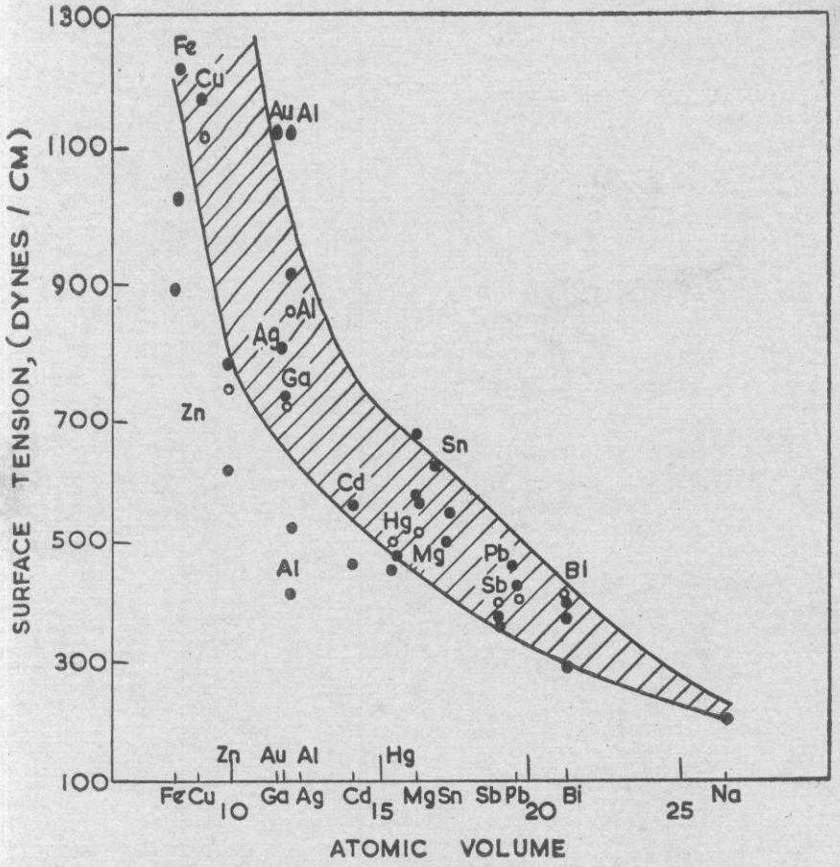
## Surface tension

The condensed states of matter—solid and liquid—possess an unique property of minimising their surface area; whether or not this would occur at a noticeable rate depends upon the atomic mobility. Surface tension is usually ascribed to the net imbalance of cohesive forces between the atoms at the surface and those in the interior. On a fundamental plane, it should be related to the inter-atomic cohesion. In the absence of any precise measure of inter-atomic cohesion, attempts have been made to correlate it with other cohesive properties. It has been observed[8,20,21] that the surface tension (i) varies periodically with the atomic mumber, (ii) is inversely proportional to the atmoic volume (Fig. 5), (iiii) is related to the heat of vaporization by the relationship shown in Fig. 6 and (iv) gradually decreases with increasing temperature (there are a few exceptions which increase).

Although values of the surface tension of almost all metals, except mercury, are not precisely known, their surface tensions (dynes/cm) is numerically equal to the melting point (°C) of the respective metals.[22] In general, liquid metals are characterised by high surface tension. Measurements of the surface tension of alloys are more uncertain and varied. Solid solution systems may either exhibit a linear variation with composition or show slight negative deviations.[23,24] Eutectic systems have minimum surface tension at the eutectic composition[25]—Pb-Sn, Pb-Bi and Bi-Sn.

In systems with intermetallic compound in the solid state, discontinuity is observed in surface tension in the liquid state at the composition of the intermetallic compound, indicating that the dissociation of the compound is incomplete on melting. The discontinuity in surface tension isotherms may exhibit: (i) minima: when the compound is surface active to alloy constituents, eg. Al-Mg, Mg-Sn systems[26], (ii) maxima: when the compound is not surface active, e.g. Ni-Al, Ni-Be systems[27,28] and (iii) an inflexion: when the compound is surface active to only one of the alloy constituents as in Cd-Sb[29], Zn-Sb[30], Cu-Sb[31] systems. As for the viscosity isotherms, the surface tension isotherms of liquid gold-tin alloys at different temperature[32] show that the minima disappear on increasing temperature.

In general, the surface tensions of metals and alloys are substantially greater than water, whereas their viscosities are of the same order of magnitude as that of water.



5 *Dependence of surface tension*[8] *of liquid metals on their atomic volumes*

**Role of viscosity and surface tension in foundry**

*Nature of flow of liquid metals*

The nature of flow of fluids in pipes or channels can be divided into types: Laminar in which all the particles of the liquid move smoothly and parallel to the direction of flow without creating any turbulence and (ii) turbulent: in which the 'particles' of the fluid move irregularly and their velocity can be resolved into more than one direction. It has been found[33] that the same liquid tends to flow in turbulent manner at high velocities and the transition between laminar and turbulent flow occurs when the Reynold's number (Re) defined by the following relation

$$\mathrm{Re} = \frac{DV\rho}{\eta}$$

where

$\rho$ = density of liquid metal

$V$ = average velocity along a runner

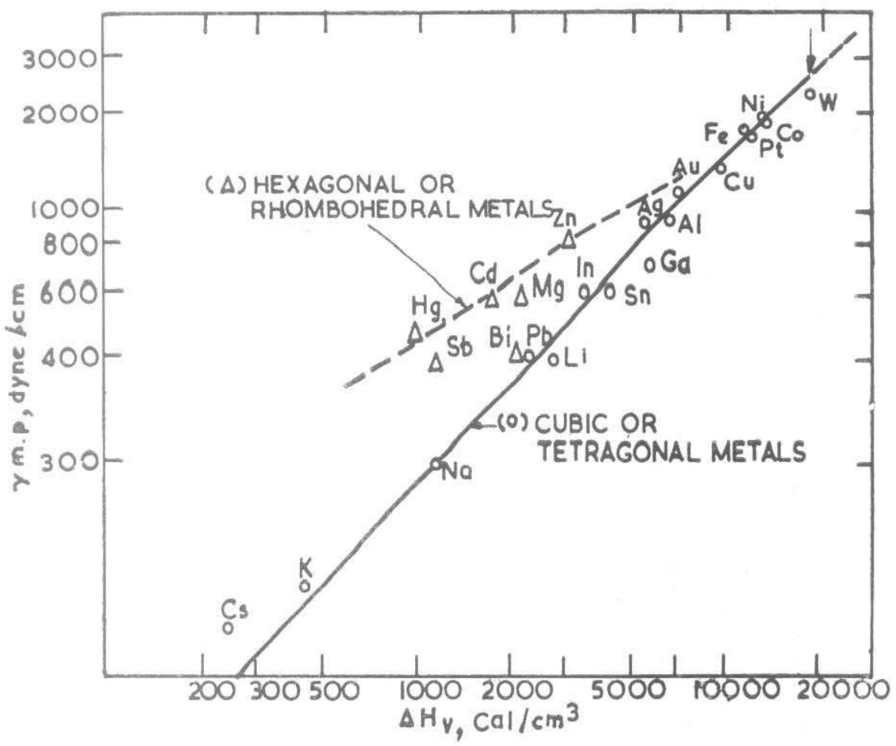
$D$ = diameter of runner

$\eta$ = viscosity

passes through the range 2 000 to 3 000. Any disturbance in flow, introduced by vibrations, unflared inlet tubes, obstructions, entrapped oxides and abrupt changes in flow direction or channel dimensions, promotes turbulent flow. From the point of view of a foundry metallurgist, the flow should ideally be laminar but in practical conditions of founding Reynold's number mostly exceeds the critical range. This indicates that although a foundryman's ideal is laminar flow, a certain amount of turbulence can be permitted in the gating systems. Since a certain amount of turbulence is tolerated, Eastwood[34] classified turbulence into (i) harmful kind and (ii) indifferent which merely causes agitation in the the melt. When the Reynold's number is about 20 000 the turbulence is so violent that it breaks down the oxide film around the periphery of the flowing stream and causes entrapment of the oxides.

*Solidification*

To a foundry metallurgist, the process of solidification is of great importance. On cooling, a melt may transform either discontinuously into a crystalline solid as in metallic liquids or continuously pass into the solid, amorphous or glassy state so characteristic of silicate melts. One important difference between the two kinds of melts can be established in terms of the temperature dependence of viscosity; in the former viscosity



6 *A correlation between surface tension and heat of vaporization (Grosse)*[81]

decreases abruptly near the melting point but in the latter falls gradually as temperature drops.

The kinetics of crystallization from melts is usually discussed in terms of the classical nucleation and growth theory. The driving energy for the process is derived from Gibb's concept of bulk thermodynamic behaviour of phases. Since the process of crystallization from the melt involves the simultaneous creation of a liquid/solid interface and the transfer of atoms, one by one, across the interface, the process of spontaneous solidification below equilibrium freezing temperature is inhibited (i) by the energy requirements of the liquid/solid interface and (ii) by the decrease in the mobility of the atoms. If crystallization is to occur, it is not sufficient to have only potential centres of nucleation, the atomic mobility between the phases must be high enough. A measure of atomic mobility is the activation energy for growth ; this parameter is very low for metals but high for complex organic crystals.

### *Inhibition of crystallization*

In the initial stages of its growth, the high surface to volume ratio precludes any stability of the nucleus of the phase otherwise thermodynamically stable. However, there exists a critical size of the embryo for which the surface to volume ratio is such that there is a net decrease in the free energy. As the growth of such critical embryos decreases the free energy of the system, they readily grow into crystallites at some degree of super-cooling where the driving energy surmounts the restrictive factors. Thus, there exists a region of temperature below the equilibrium melting temperature over which crystal nuclei do not form at a detectable rate (because the restriction imposed by the requirements of surface energy is not overcome by the low available driving energy).

### *Nucleation catalysis*

Bulk metallic liquids seldom super-cool more than a few degrees. The absence of much super-cooling in bulk metals may be due to the presence of external surfaces which promote nucleation. Since nucleation depends on the existence of receptive foreign surfaces for the crystallizing phase, it is termed heterogeneous nucleation. It is obvious that all foreign surfaces will not be equally active for nucleation. Metallurgists would like to promote solidification of their castings into fine grains and would be prepared to introduce suitable inoculants. Development of suitable inoculants is usually discussed in terms of the interfacial energies.

### *Effect of high surface tension*

The high surface tension of liquid metals exercises various effects on foundry processes. It makes liquid metals reluctant to wet most other surfaces ; the reluctance is more pronounced in the presence of tenacious oxide films which apparently increase the surface tension several folds : examples are the formation of zinc oxide on brass, alumina on aluminium and aluminium-bronze, chromic oxide on stainless steel and other grades of heat resisting steels, etc. Any entrapment of the oxide reduces the castability of the liquid metal but if the oxide is soluble in the liquid metals as in copper or nickel, surface tension is not much influenced. Another consequence of the high surface tension is that appreciable pressure is required to cause the flow of liquid metals through narrow channels in moulds and runners. It may also prevent splashing of the metal in mould cavity and reduce agitation and vortex formation.

**Fluidity**

Foundry metallurgists are primarily concerned with the production of satisfactory castings for which the ability of a melt to fill the mould and to reproduce the surface details is as important as sub-surface soundness. Considerations of viscosity and surface tension of the melts either individually or jointly are unable to give an adequate indication of whether or not the metal will flow in the mould satisfactorily. It is well-known that the castability of various metals are vastly different despite the similarities of their viscosity. Although castability is a related property of fluidity which is fundamentally defined as the inverse of viscosity, it is so sharply influenced by extraneous factors – surface tension, surface film, gas and presence of solid phase in the melt on the one hand and the nature of the mould/metal interface and mould temperature on the other, so as to make nonsense of the fundamental criterion of fluidity ; yet the term fluidity is widely used by the foundry metallurgists to define castability. Since the fundamental relation of fluidity with viscosity is a factor of only secondary importance in determining the casting fluidity of metals and alloys, foundry fluidity is evaluated by empirical tests in which the length of the casting is measured when the molten metal is made to run along a channel, usually of a spiral form, in horizontal metal or sand moulds under standard conditions of temperature and hydrostatic head. Good fluidity additionally assists in (i) the formation of concentrated shrinkage cavity and (ii) removal of non-metallic inclusions and gases.
The following general conclusions can be drawn :[33,35]

(i) Metallic phases which solidify at constant temperature—pure metals, eutectics or inter-metallic compounds—have higher fluidity than those which solidify over a range of temperature.

(ii) In a number of binary systems— Al-Si, Mg-Al, Sn-Zn and Pb-Zn, fluidity first decreases with increasing percentage of solute and then increases again as the eutectic composition is approached. A general rule is that elements showing little mutual solubility cause large changes in fluidity. Theoretical interpretation of the effect of solidification interval on casting fluidity has aroused controversy because of no established criterion of fluidity. If metal flow till the completion of solidification is considered, the fluidity of such melts appears to decrease when compared with pure components because the formation of dendrites obstructs the metal flow. However, if the flow of metal above the liquidus temperature is adopted as the criterion, alloys with wide solidification range give higher values of fluidity ; such a treatment obviates any involvement of the mechanism of solidification in the criterion of fluidity.

(iii) Oxide films, dissolved gases and impurity affect the fluidity value. Thus, fluidity drops rapidly at first if molten zinc is held in atmospheric air or covered with $NH_4Cl$ or ZnO. Small additions of titanium to aluminium decrease its fluidity markedly.

(iv) Casting fluidity is increased by high mould temperature.

(v) Since one manifestation of inter-facial tension is to make liquid metals reluctant to wet surfaces (mould/metal interface), mould washes excercise influence on fluidity.

(vi) Fluidity increases linearly as temperature is raised above the melting point but beyond a certain temperature range, further super-heat has little effect upon fluidity.

(vii) High heat content of the metal increases the fluidity and vice-versa ; in practice the heat content is controlled by the pouring temperature. The amount of super-heat applied to a melt varies with the nature of the alloy and the casting.

The following super-heat is usually suggested for casting non-ferrous alloys with sections :

| | | |
|---|---|---|
| $< 0{\cdot}5$ | in. | 15% |
| 0·5–1·5 | in. | 10% |
| $> 2$ | in. | 7% |

Unnecessary super-heating of the melt should be avoided as it leads to oxidation losses, gas pick-up and increased refractory costs.

**Density : volume change**

*Pure metals*

Density measurements on pure metals indicate that in most of the metals the average density change and thus the volume change on melting is about 3-4%.[36,37] The atomic volume and volume change on melting of the different liquid metals at their melting points are given in Table I.

The variation of atomic volume near the melting point with the atomic number is identical both in the solid and liquid states. The transition metals having lower atomic volume than alkali metals in liquid state thus exhibit stronger atomic interaction than the alkali metals. The loosely packed metals like bismuth, antimony, gallium and silicon[38] show contraction on melting (increase in density), due to the tendency towards closer packing in the liquid state.

The temperature dependence of the volume of liquid is expressed as :

$$V_T - V_O\,(1+\alpha\,T)$$

where
$\alpha$ = bulk co-efficient of thermal expansion. The value of

TABLE I Atomic volume, volume change on melting, co-efficient of expansion of the liquid metals near their melting points[1]

| Metal | At. volume Cm³/g. atom | Volume change on melting, % of solid volume | ∝Solid cm³/g. | ∝Liquid atom. deg. 10³ |
|---|---|---|---|---|
| Li | 13·68 | 1·65 | 0·17 | — |
| Na | 24·74 | 2·5 | 0·22 | 0·275 |
| K | 47·15 | 2·55 | 0·25 | 0·29 |
| Mg | 15·29 | 3·1 | 0·078 | 0·166 |
| Al | 11·38 | 6·0 | 0·070 | 0·122 |
| Si | 11·12 | −9·6 | 0·23 | 0·145 |
| Cu | 7·95 | 4·15 | 0·051 | 0·100 |
| Ag | 11·59 | 3·8 | 0·057 | 0·097 |
| Au | 11·50 | 5·1 | 0·042 | 0·069 |
| Zn | 9·95 | 4·2 | 0·093 | 0·150 |
| Cd | 14·05 | 4·0 | 0·093 | 0·151 |
| Ga | 11·54 | −3·2 | 0·037 | 0·126 |
| Sn | 17·03 | 2·6 | 0·070 | 0·088 |
| Pb | 19·58 | 3·5 | 0·087 | 0·127 |
| Sb | 18·80 | −0·95 | 0·033 | 0·096 |
| Bi | 20·90 | −3·35 | 0·040 | 0·11 |

TABLE II Volume changes on mixing for solid solution and eutectic systems[1]

| System | Temperature °K | VM % |
|---|---|---|
| Ag-Au | 1350 | +Ve, V. Small |
| Au-Cu | 1300 | −0·5 |
| Cu-Ni | — | ±0 |
| Al-Zn | 950 | ±0 |
| Bi-Sn | 608 | +1·1 |
| Sn-Zn | 700 | +1·5 |
| Cd-Pb | 773 | +0·8 |
| Cd-Zn | 800 | +0·6 |

∝ in the solid and liquid state for the different metals is also given in Table I. The ratio ∝ solid/∝ liquid varies approximately between 0·75 and 1·0 for most of the metals.

### *Density of alloys and volume change on mixing*

When the density of liquid alloys is related with the densities of their component metals, slight (1–5%) deviation from the linear relationship is usually observed due to the preferential association between either like or unlike atoms.

The volume changes on mixing are dependent upon the type of alloy system and are given in Table II for some of the solid solution and eutectic systems. It is seen that the changes are very small and usually positive for eutectic systems.

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