

The Surface Tension of Tin and its Alloys with Particular Reference to Solders

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ABSTRACT.

Literature data for the surface tension of tin and tin-based alloys, have been collated and are discussed.

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PART 1

Preamble

INTRODUCTION

Although tin is a very well-known metal and is widely used throughout industry, it is nevertheless, a fairly rare element with respect to the relative abundance in the earth's crust. World-wide, there are only a few commercially viable sources of tin ore (principally the oxide, cassiterite), and as a consequence, the pure metal is a comparatively expensive commodity. For example, based on the 1993 figures from the London Metal Exchange, the market value for tin, is on a par with that for nickel and is about twenty times greater than that for lead. The aim of any industrial process is to utilise the most economic operating conditions commensurate with the production of a good quality end-product. It follows, that in view of the relatively high cost of the metal, it would always be sound practice to fully establish the optimum operating parameters for any process involving the use of substantial quantities of tin or tin-based alloys.

The major industrial application for molten tin alloys is in the field of joining technology eg assembly of electronic packages and devices; production of capillary joints in plumbing. Recently, studies⁽¹⁾ have shown that activated tin alloys (eg Sn+Ti) could prove to be suitable materials for brazing metals to ceramics using no fluxing agent. The intrinsic ductility of the alloys should minimise the residual stress at the interfaces of the join.

Conditions of use of solders in plumbing are well established, and pose no particular problems for routine production of good quality joins. In contrast, modern industrial processes for the large-scale production of multicomponent electronic devices require the use of highly sophisticated soldering techniques. With the continuing trend towards the use of surface-mounted components coupled with improvements in the miniaturisation of circuits, the criteria for producing reliable joints have become increasingly more stringent and soldering technology has had to be continually upgraded to keep abreast of developments. Since the solder alloys are applied in the liquid state, and must rapidly form a satisfactory bond with the substrate, pertinent physicochemical properties such as surface (or interfacial) tension¹, wettability and interfacial adhesion will all play an important role in ensuring the integrity of a soldered joint. In order to produce good wetting conditions and strong adhesion at the solid/liquid interface, industrial soldering techniques almost invariably entail the presence of fluxing agents, and in such circumstances, the interfacial tension between the molten metal and flux (γ_{LF}) would be of more relevance than the surface tension of the metal (γ_{LG}). The magnitude of (γ_{LF}) will depend upon both the composition of the alloy and the particular type of flux used. Figure 1⁽²⁾ shows the effect of two types of flux on the interfacial tension with Sn+Pb alloys at 400 °C, and it can be seen that values for (γ_{LF}) are markedly lower than the corresponding values for (γ_{LG}). However, it has been found that with the modern electronic assembly techniques, the presence of flux may introduce problems with respect to chemical attack on the conductor leads and to final 'clean-up' of the joint.

In view of this, a significant amount of research effort has been directed, in recent years, towards the development of fluxless soldering techniques, which it is claimed⁽³⁾, could result in substantial savings for the electronics industry.

Few details of the new technology have been revealed, but it is known, that in one instance⁽³⁾, soldering operations were conducted using fluorine-based gas (eg F₂ or CF₄) in the open air. In this case, the relevant surface property of the solder would be the surface tension in the particular gaseous environment. To date, the effect of halogens on the surface tension of tin alloys is not known, although some work has been carried out to study the influence of dry Cl₂ and dry HCl on the surface tension of pure tin. (See Part 2 of this

¹throughout this report, the term "surface tension" refers to a liquid/vapour or gas interface and "interfacial tension" pertains to either a liquid/liquid or a liquid/solid interface. Also, surface/interfacial tension and surface/interfacial energy will be assumed to be numerically equivalent

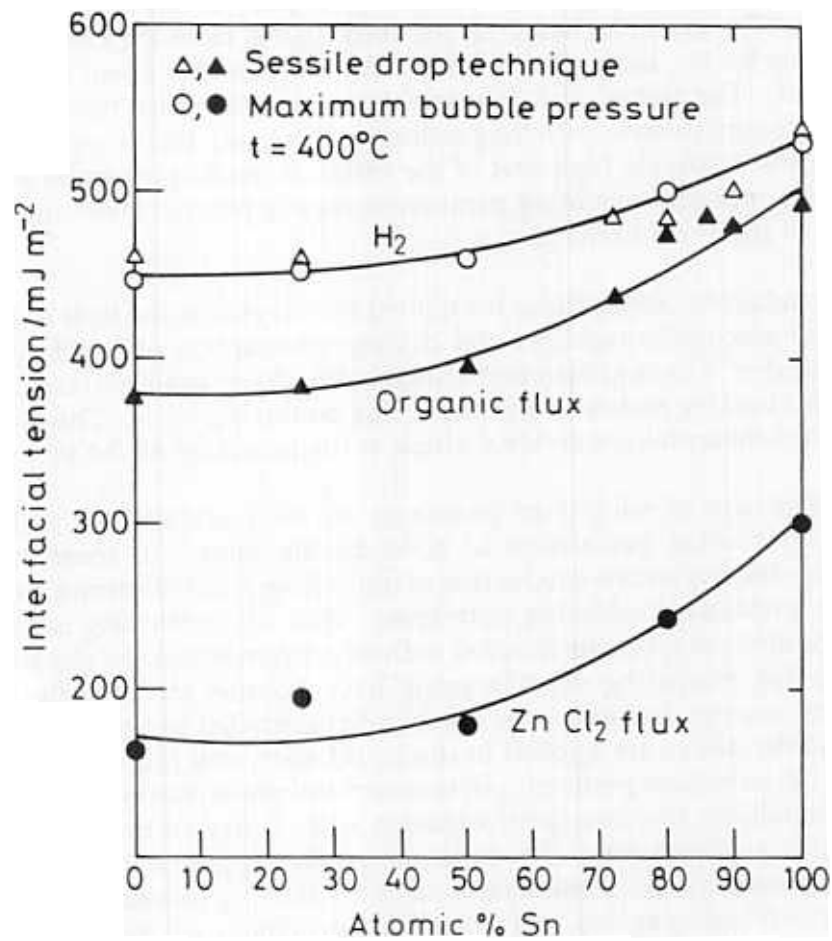


Figure 1 Comparison of the interfacial tension between two different fluxes and Sn+Pb alloys with the surface tension of these alloys under hydrogen (Ref 2).

report). In both instances, it was found that at a relatively high partial pressure of the gas, the (γ_{LG}) of the metal would be reduced substantially. Coffman and Parr⁽⁴⁾ also observed a marked reduction in (γ_{LG}) of two Sn+Pb alloys (40% and 60% Sn) in the presence of HCl gas (reductions in (γ_{LG}) of ~12% and ~19% respectively).

To determine the optimum operating conditions for any industrial process, it is normal procedure to compile mathematical or computer models of the system so that the effects of changes in any particular process parameter can be readily established. However, the relevance of any prediction must be critically dependent upon the reliability of the data used in the model. Although any model for modern soldering techniques would generally require data for the alloy/flux interfacial tension (γ_{LF}) , there is nevertheless, a strong current interest in development of fluxless soldering technology for which the surface tension of the alloy (γ_{LV}) would be of greater relevance. In addition, one of the experimental methods commonly used to determine the interfacial tension (γ_{LF}) of liquid/liquid systems (viz profile of a floating liquid lens), would require knowledge of the surface tensions of the respective liquids in order to calculate a value for (γ_{LF}) . Part 2 of this report collates the literature data pertaining to the surface tension of tin-based alloys.

RELEVANT THERMODYNAMIC RELATIONS FOR SURFACE ENERGY

In this section, a series of important equations relating surface energy to other thermodynamic properties is given. The treatment present here is to simply quote the relevant relations without recourse to the fundamental bases for their derivation, details of which can be found in many of the large number of text books devoted to the subject.

(a) Single component system

The free energy per unit area of surface $(G^s)_{T,P} = \gamma$

The surface entropy $(-S^s) = \frac{d\gamma}{dT}$

The total surface energy $(E^s) = G^s + TS^s$

ie $(E^s) = \gamma - T \frac{d\gamma}{dT}$ (1)

Since $\left(\frac{d\gamma}{dT} \right)$ should always be negative for pure single components, then:-

$$E^s > \gamma$$

In many instances, $\left(\frac{d\gamma}{dT}\right)$ is constant over a limited temperature range, and it follows from (1) that in these circumstances, (E^s) is invariant with temperature. The variation of (E^s) with (T) is termed the surface specific heat (C^s) ie

$$C^s = \frac{dE^s}{dT}$$

(b) Binary and multicomponent systems

The thermodynamic relations for systems containing more than one component are more complex, since account has to be taken of the chemical potentials (μ) of the respective species.

The general Gibbs relation for a multicomponent system is:

$$-\left(\frac{\delta\gamma}{\delta\mu_1}\right)_{V,T,\mu_2,\dots,\mu_n} = \Gamma_1 \quad (2)$$

(where Γ_1 is the surface excess of component 1)

It is important to note that equation (2) is expressed in terms of partial differentials, and strictly, would only be applicable to those systems in which any change in the chemical potential of one component would have no effect on the chemical potentials of the other components. Such a condition is rarely fulfilled in practice.

For a binary system, consisting of a solute (2) in a solvent (1) equation (2) gives:

$$d\gamma = -\Gamma_1 d\mu_1 - \Gamma_2 d\mu_2 \quad (3)$$

Now, based on the Gibbs' convention, it is permissible to arbitrarily select a specific plane in the surface layer, such that $\Gamma_1 = 0$, and thus (relative to this plane)

$$\Gamma_2^1 = \left(\frac{d\gamma}{d\mu_2}\right)_{T,V} \quad (4)$$

(The superscript (1) on the adsorption (Γ) means that the reference dividing surface was selected such that $\Gamma_1 = 0$.)

Since, $\mu_i = \mu_o + RT \log_n a_i$ (where a_i = activity of the solute, (i)) then:-

$$d\mu_i = -\frac{RT}{a_i} \cdot da_i$$

and from (4):-

$$\Gamma_2^1 = \frac{1}{RT} \cdot a_2 \cdot \frac{d\gamma}{da_2} \quad (5)$$

For very dilute solutions $a_2 \approx$ concentration (C_2), and thus:-

$$\Gamma_2^1 = \frac{1}{RT} \cdot C_2 \cdot \frac{d\gamma}{dC_2} \quad (6)$$

In a similar manner, it is possible to define an analogous relation for (Γ_1^2), for which the reference dividing surface is such that $\Gamma_2 = 0$.

The arbitrary plane surface conceived by Gibbs is difficult to visualise in terms of the surface molecular structure and the treatment by Guggenheim and Adam⁽⁵⁾ is easier to comprehend, in that a small but finite thickness is assigned to the surface layer. Based on this premise, it is possible to express the surface excess of a solute in several ways, eg in terms of volume concentrations or mole fractions. In view of the fact that the densities of many molten metals are not accurately known, expression of Γ_2 in terms of mole fraction (x_2) is more reliable. The Guggenheim adsorption (Γ_2^x) is related to the Gibbs' adsorption Γ_2^1 by the relation:-

$$\Gamma_2^1 = \Gamma_2^x \left[1 + \frac{x_2}{x_1} \right] \quad (7)$$

Combining equations (5) and (6) with (7) gives:-

$$\Gamma_2^x = -\frac{a_2}{RT} \cdot (1 - x_2) \frac{d\gamma}{da_2}$$

which for dilute solutions, gives:-

$$\Gamma_2^x = \frac{C_2}{RT} (1 - x_2) \frac{d\gamma}{dC_2}$$

For solutes which exhibit surface-activity in the solvent, the $\Gamma([x])$ curves usually show an increase in (Γ) with increase in $[x]$ until a maximum value ($\Gamma_{\max}$) is attained. At ($\Gamma_{\max}$) it is generally assumed that the surface layer is saturated with surfactant. Then, based on the supposition of monomolecular layer at the surface, it is possible to calculate the area (A) occupied by individual adsorbed species from the relation

$$A = \frac{1}{\Gamma_{\max} \cdot N} \quad (\text{where } N = \text{Avogadro's Number}).$$

However, the work of Semenchenko⁽⁶⁾ demonstrates that the assumption of complete surface coverage at ($\Gamma_{\max}$) is not always valid and will depend upon the relative magnitude of a factor (F), which is defined by:-

$$F = \frac{f_1 f_2^s}{f_1^s f_2}$$

(where (f) represents the activity coefficients of species in the bulk, and (f^s) represents the activity coefficients at the surface.)

Semenchenko showed that:-

$$\frac{[C_{TP}]^s}{[C_{sat}]^s} = \frac{1}{(1 + 1/\sqrt{F})} \quad (8)$$

where $[C_{TP}]^s$ = surface concentration at the turning point on the adsorption curve.
 $[C_{sat}]^s$ = surface concentration equivalent to surface saturation.

Equation (8) shows that only for relatively large values of (F), (eg with a highly surface-active solute for which (f_2^s) is large), will the concentration at the turning point equate to surface saturation. It follows, that for small values of (F), the difference between $[C_{TP}]^s$ and $[C_{sat}]^s$ could be substantial. The value of (F) also determines the sign of the adsorption ie

$F > 1$, then $\Gamma > 0$ and the curve passes through a maximum
 $F < 1$, then $\Gamma < 0$ and the curve passes through a minimum.

SURFACE TENSION, ADHESION AND WETTING

When a liquid drop is in equilibrium on a smooth horizontal surface (Figure 2), then the Young equation gives:-

$$\gamma_{SV} = \gamma_{LV} \cos \theta_e + \gamma_{LS} \quad (1)$$

where

γ_{SV} = surface tension at solid/vapour interface
 γ_{LV} = surface tension of the liquid
 γ_{LS} = interfacial tension at liquid/solid interface
 θ_e = equilibrium contact angle

On initial contact between the liquid drop and the solid, then, provided no chemical interaction occurs, the respective interfacial properties are invariant and the liquid will spread across the surface until the equilibrium contact angle is attained in accord with equation (1). The adhesion tension (A) is a term which is widely used as a direct measure of the wettability of a solid by a liquid. (A) is defined by the relation

$$A = \gamma_{SV} - \gamma_{LS}$$

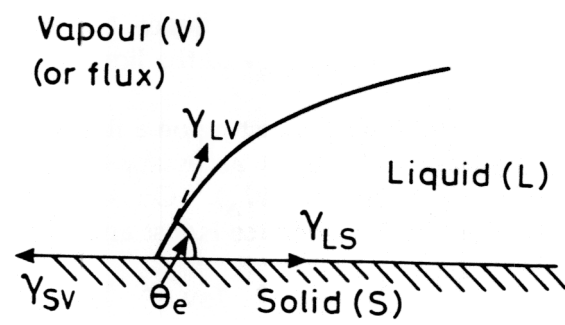


Figure 2 Schematic diagram showing the respective equilibrium surface tension forces acting at the point of three-phase contact between a liquid drop, and a solid substrate under a vapour.

whence (from (1)), $A = \gamma_{LV} \cos \theta_e$.

The greater the attraction between a solid and liquid, the smaller will be the value of (γ_{LS}) , and hence the greater the value of (A) . Obviously when $\theta = 0$, (A) is indeterminate and has a value $\geq (\gamma_{LV})$.

A relation for the bond strength between the two media in terms of the respective surface energies can be derived by considering a hypothetical vertical cylindrical column of a liquid, which has unit area of cross-section and is contained in a vacuum environment. Then, to completely separate the cylinder across a diametral plane would require the expenditure of work to create two new liquid/vacuum interfaces. The magnitude of the work required will be equal to twice the surface tension (γ_{LV}) and is termed the 'work of cohesion' (W_c) of the liquid ie

$$W_c = 2\gamma_{LV} \quad (2)$$

(Strictly speaking, to maintain dimensional equivalence, the right hand side of equation (2) should be expressed in terms of surface energy of the liquid.)

If the same hypothetical column of liquid is resting on a flat solid surface, then there will be unit area of liquid/solid interface. The work necessary to separate the two media at this interface is called the 'work of adhesion' (W_A) . On separation, two new surfaces are produced and the original solid/liquid interface is lost and thus,

$$W_A = \gamma_{LV} + \gamma_{SV} - \gamma_{SL} \quad (3)$$

From equations (1) and (3), the work of adhesion at equilibrium is:-

$$W_A = \gamma_{LV} (1 + \cos \theta_e) \quad (4)$$

Equation (4) implies that the maximum value for (W_A) would be $(2\gamma_{LV})$ which is, in general an unlikely limitation, and the equation is probably only valid for $180^\circ > \theta_e > 0^\circ$. (When $\theta = 0^\circ$, the system is unlikely to be strictly in equilibrium eg possibly due to chemical reaction.) Another factor which can affect the validity of equation (4) is, that in practice, the interfacial energy (γ_{SV}) is often reduced (to a value (γ_{SA})), due to adsorption at the surface of volatile species which either emanate from the liquid or are present in the surrounding atmosphere. The difference between the surface energies of the clean and the contaminated surfaces is termed 'the surface pressure' (π) ie

$$\pi = (\gamma_{SV} - \gamma_{SA}).$$

Thus equations (3) and (4) should strictly be expressed as:-

$$W_A = \gamma_{LV} + \gamma_{SA} - \gamma_{LS} + \pi \quad (5)$$

$$W_A = \gamma_{LV} (1 + \cos \theta'_e) + \pi \quad (6)$$

(where θ'_e is the equilibrium contact angle on the contaminated surface)

and it follows that equations (3) and (4) can only be applied to a situation in which the liquid has negligible vapour pressure. From equation (6), it can be seen that under these conditions, (W_A) can have values in excess of ($2\gamma_{LV}$).

To quantify the degree of spreading for any particular system, Harkins⁽⁷⁾ introduced the concept of the spreading coefficient (S), which is defined by the relation

$$S = \gamma_{SV} - \gamma_{LS} - \gamma_{LV} \quad (7)$$

(S) is a measure of the tendency for the liquid to spread on the solid, and the more positive the value of (S) the greater the extent of the wetting. It follows from (1) and (7) that (if adsorption on the solid is negligible):-

$$S = \gamma_{LV} (\cos \theta_e - 1) \quad (8)$$

and from (2), (3) and (7)

$$S = W_A - W_c \quad (9)$$

Equation (8) indicates, that the most positive value (S) can take is zero, and over the measurable range of θ ,

$$0 \geq S \geq -2\gamma_{LV}$$

This takes no account of the effect of surface pressure (π) on the spreading coefficient. Equation (7) however suggests that (S) could take values in excess of zero under the special circumstances given by $\gamma_{SV} > (\gamma_{LS} + \gamma_{LV})$.

The wetting of a solid metal surface by a liquid metal is sometimes inhibited by the presence of oxide layers which effectively give the solid surface a low surface energy. In soldering practice, this problem is overcome by the introduction of a suitable fluxing agent. The action of a flux in the promotion of wetting is a complex process, which in addition to removing oxide layers and preventing subsequent reoxidation of the solid, also appears (particularly for inorganic salt fluxes eg ZnCl_2) to entail some form of electrochemical action in which components of the liquid metal are transferred as ions through the flux and are ultimately deposited on the solid metal ahead of the moving line of three-phase contact. In circumstances where the metals are covered by liquid flux (F), the above relations are applicable provided the appropriate interfacial tensions (γ_{SF} ; γ_{LF}) are substituted for (γ_{SV}) and (γ_{LV}) respectively.

One important factor with respect to the integrity of a soldered joint, is whether the molten metal is able to infiltrate the grain boundaries of the substrate metal⁽⁸⁾. Such behaviour could lead to grain separation and produce embrittlement and consequent mechanical weakness at the interface. If the surface energy at the boundary between two grains of the same species is (γ_{GB}), then one necessary condition for wetting⁽⁸⁾ by liquid metal is:-

$$2\gamma_{LS} < \gamma_{GB}$$

Now, from equation (7), the criterion for spreading of the liquid across the solid under a gas (or vapour) is:-

$$(\gamma_{LS} + \gamma_{LV}) < \gamma_{SV}$$

Thus for wetting of a metal surface without penetration at the grain boundaries, the following conditions must be fulfilled:-

$$\gamma_{LS} < (\gamma_{SV} - \gamma_{LV})$$

$$\text{and} \left(\frac{\gamma_{GB}}{2} \right) < \gamma_{LS} \text{ i.e. } \frac{\gamma_{LS}}{\gamma_{GB}} = R < 0.5$$

With some metal systems for which (R) is known, the ratio is often not much greater than 0.5 at a given temperature and Bondi⁽⁸⁾ predicted that in such cases, a relatively small increase in temperature could lead to (R) being reduced below 0.5 and thus give rise to possible ingress of liquid along the grain boundaries. To illustrate, Bondi⁽⁸⁾ cites the molten Cu/solid Fe system for which $R = 0.51$ at 1100°C . Molten Ag on solid Cu is another metal system in which embrittlement due to penetration at the grain boundaries is known to occur.

From the definition of the spreading coefficient, Bondi notes that a necessary (though not exclusive) condition for liquid spreading is that $(\gamma_{SV}) > (\gamma_{LV})$. For many cases, this criterion is true, but some apparent exceptions exist. For example, Bailey and Watkins⁽⁹⁾ found that molten Pb ($\gamma_{LV} \approx 470 \text{ mNm}^{-1}$) would not wet Cu ($\gamma_{SV} > 1400 \text{ mJ.m}^{-2}$) at 400°C . Reference to equation (7) suggests that, since no spreading is observed, the value for (γ_{LS}) between the two metals must be high. Grigor'yev *et al*⁽¹⁰⁾ also found that Pb would not wet Cu (at 600°C) unless the environmental atmosphere were saturated with Pb vapour, which would result in adsorption of Pb at the Cu surface and reduction in (γ_{SV}) . Since $\cos \theta_e$ increases with improved wetting, it follows (from equation (1)) that under these circumstances (γ_{SL}) must be significantly reduced. It is difficult to obtain a totally oxide-free Cu surface, and thus for the above two cases, it is possible that failure to wet was simply due to the presence of a thin oxide layer which created a surface with low surface energy. Pb will readily wet Cu when in the presence of a suitable fluxing agent⁽¹¹⁾.

If, on initial contact between a liquid and a solid metal, the system were not in chemical equilibrium, then diffusion and interfacial adsorption of certain species would occur. There would be a progressive reduction in (γ_{LS}) until chemical equilibrium in the system was ultimately attained i.e. the chemical potentials in the respective phases were equal. The time to achieve equilibrium would be controlled by the diffusion rates and thus would depend upon the temperature of the system.

In a gaseous environment, the driving force (F) for spreading under these conditions has been defined⁽¹⁴⁾ as:-

$$F = \gamma_{LV} (\cos \theta_e - \cos \theta_t)$$

where θ_t = contact angle at time (t)

This relation applies to those systems in which surface-active species migrate to, but do not traverse, the solid/liquid interface i.e. there is no chemical interaction between the metals and γ_{LV} does not change.

When Pb is alloyed with Sn, the (γ_{LV}) of the molten metal will be increased, but the liquid will readily spread across the surface of clean copper. This is due to the substantial reduction in (γ_{SL}) resulting from the chemical action between Sn and Cu to produce an intermetallic compound at the solid/liquid interface. The formation of a compound layer at the interface is of prime importance in the production of high quality soldered joints, and it is essential that the particular compound produced is both solid and stable at the soldering temperature. It is important to ensure that temperature is kept below the decomposition temperature of the compound otherwise de-wetting of the solid may occur. For example, with the molten Pb + Sn/solid Cu system, the alloy readily wets the solid at low temperatures (less than 380 °C), due to the formation of a stable layer of Cu_6Sn_5 (η -phase) at the interface. However, at temperatures in excess of 380 °C this compound will dissociate and molten solder could de-wet from the copper surface⁽⁹⁾.

With some metal systems, the solid is highly soluble in the liquid and the reaction rate can be sufficiently fast that a stable compound interfacial layer is unable to form. Nowadays, the connectors for many high quality electronic components are plated with a thin layer of Au in order to provide both good contact properties and to prevent oxidation during storage. Attempts to solder Au-plated material using conventional Pb + Sn alloys are always fraught with problems and often result in unsatisfactory joints. The reaction between solder and Au is very fast and in the case of thin-layer plating could result locally in complete removal of Au and possible de-wetting from the substrate. In addition, the gold-tin system forms a number of intermetallic compounds eg $AuSn_2$; $AuSn_4$ which can lead to embrittlement at the joint. The reaction rate between Au and Sn alloys is strongly dependent upon the temperature and this is illustrated in Figure 3 which shows the relative levels of Au dissolution by various Sn-based alloys over a range of temperatures⁽¹²⁾. It can be seen that the dissolution rate for the Sn + Pb eutectic increases markedly when the temperature exceeds 230 °C. In practice, to solder Au-coated material it is necessary to use the lowest possible temperature together with special soldering alloys which react less strongly with Au eg Au + Sn + Si alloys have been suggested⁽¹³⁾ as suitable solders for use with Au-plated silicon substrates. 80 Au 20 Sn solders can be used for Au-plated metal substrates, wetting being very rapidly achieved. Soldering with these alloys is generally carried out under 'forming' gas or with a special rosin which will not carbonise at 350 °C. Reference to Figure 3 shows that the Sn + Pb + In + Zn alloy had the widest temperature range (~ 100 °C) over which the dissolution rate for Au was low. There have been numerous papers published on soft soldering of Au with In-based alloys.

In an attempt to analyse the situation in which chemical reactions occur between the two metals and a stable intermetallic compound is produced at the interface, Yost and Romig⁽¹⁵⁾ developed a simple model (Figure 4) based on the spread of a liquid drop (base radius = r) across the surface of a solid substrate under gas or vapour. During chemical reaction the values of both (γ_{LS}) and (γ_{LV}) will vary. It was proposed that in a reacting system the driving force for spreading $\frac{dE}{dr}$ would be made up from the sum of two separate terms viz

$$\frac{1}{2\pi r} \left(\frac{dE}{dr} \right) = \sigma + \Gamma(\theta)$$

where σ = contribution due to reaction energies.

$\Gamma(\theta)$ = contribution due to imbalance of interfacial energies.

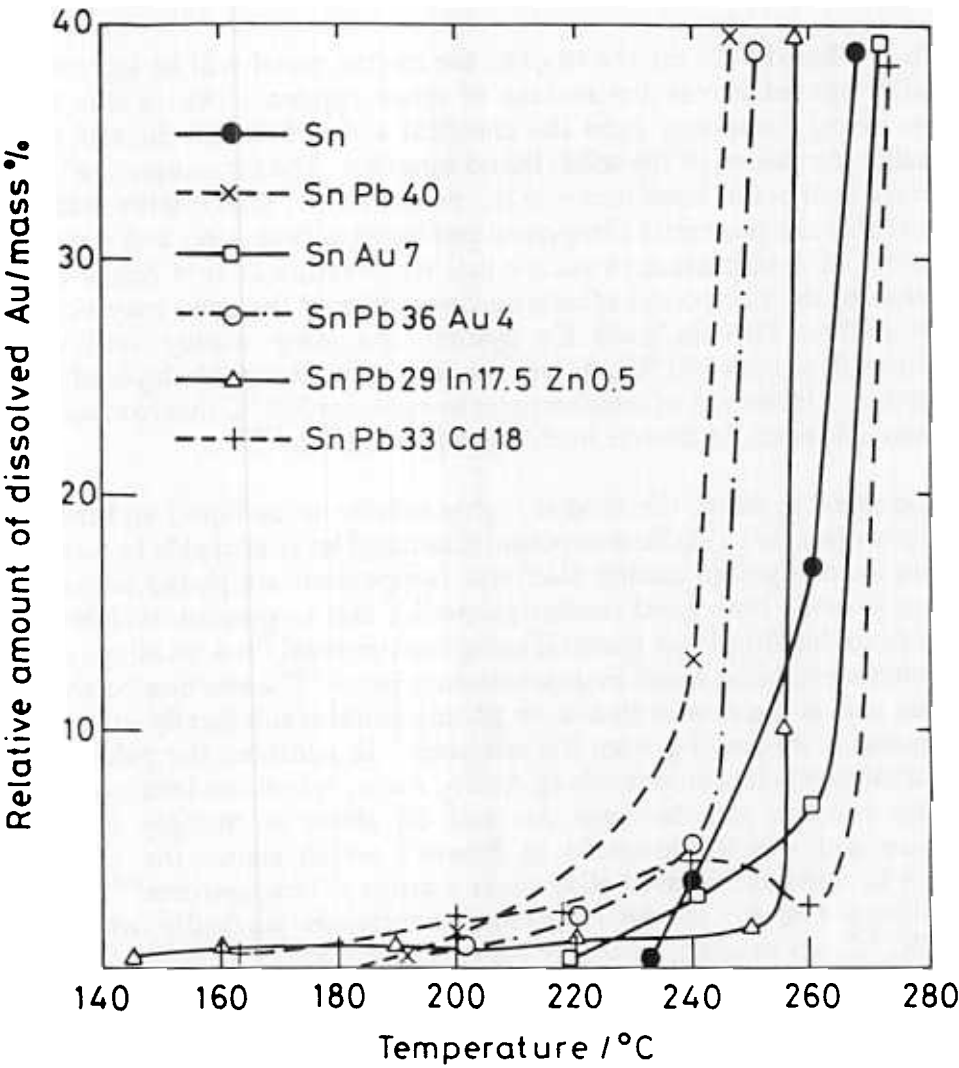


Figure 3 Curves showing the effect of temperature on the relative rate of dissolution of Au by various Sn-based solders (Ref 12).

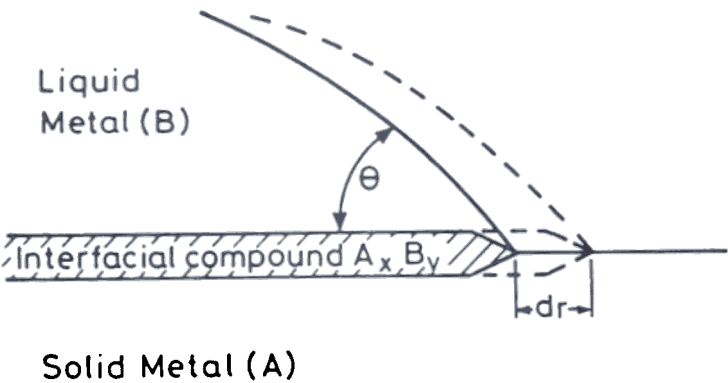


Figure 4 Diagram showing the situation when a liquid metal spreads across a solid metal substrate due to formation of an intermetallic compound at the solid/liquid interface (Ref 15).

The experimental aspect of the study was limited to wetting of pure Cu by three different pure metals (Sn, Sb and Cd). Values for the free energy of formation (ΔG) were calculated for the compounds Cu_6Sn_5 ; Cu_3Sn ; Cu_2Sb ; CuCd_3 and Cu_5Cd_8 . From these data, the respective values for (σ) were derived and it was found that in all cases, the magnitude of (σ) was substantially greater than that for $\Gamma(\theta)$. Yost and Romig acknowledged that with such a simple model it would be impossible to account for the effects of factors such as the presence of a fluxing agent and variations in alloy composition. Nevertheless it was considered that as a general rule, any chemical reaction between the metals would always be the dominant factor controlling the magnitude of the driving force for wetting. Based on the theory for the thermodynamics of irreversible processes and the Onsager equations of motion, Grigorev⁽¹⁶⁾ also developed a relation which expresses the wetting kinetics in terms of the sum of two factors due respectively, to the surface energy imbalance and chemical reaction energy. The validity of the relation was verified by experimental studies on the wetting of Cu by various Pb + Cu alloys.

The conclusions of Yost and Romig are in general agreement with the experimental observations of Bailey and Watkins⁽⁹⁾ who studied the wetting behaviour of a large number of metal/metal systems. Invariably it was found that good wetting was associated with metal combinations which would produce either a compound or a solid solution. By contrast, systems which exhibited no intermetallic reaction were characterised by either non-wetting or subsequent de-wetting between the two metals.

Viewed in simplistic terms, it may be considered that, for any metal/metal system in which strong chemical reaction occurs at the liquid/solid interface, the "effective" interfacial tension ($\bar{\gamma}_{SL}$) for the non-equilibrium state will, especially in the initial stages, always be very low and thus the driving force for spreading will be high. As the solute level in the liquid metal approaches saturation then ($\bar{\gamma}_{SL}$) will tend to the equilibrium interfacial tension (γ_{SL}) for the final liquid composition. In molten, slag/molten metal systems it has been observed⁽¹⁷⁾ that during periods of intense mass transfer across the liquid/liquid interface, the value of the non-equilibrium interfacial tension can fall to extremely low values which are very close to zero.

The success of most soldering techniques will be dependent to some extent on chemical reaction between the solid and liquid metals, and it follows from the above, that at least in the early stages of wetting, the interfacial properties will not play a major role in the spreading process. However, as noted by Thwaites⁽¹⁸⁾, one of the major problems encountered in modern soldering techniques is the phenomenon of subsequent de-wetting after soldering and this will have direct relevance to the surface properties of the system.

SURFACE TENSION AND STRUCTURE IN THE LIQUID STATE

For most binary metal systems, the surface tension isotherm shows a steady change with composition. However, as reference to Part 2 of this report reveals, for some systems, the isotherms exhibit anomalous behaviour in that points of inflexion or extrema are present. It has been found that these discontinuities often occur in the vicinity of compositions which equate either to the eutectic or to the formation of intermetallic components in the solid state.

Positive temperature coefficients $\left(\frac{d\gamma}{dT} \right)$ are sometimes observed at these compositions. It is possible that the anomalous behaviour reflects some retention of ordered structure in the

liquid, particularly for temperatures in the vicinity of the melting point. However, in some cases, the composition does not equate to any known compound or eutectic and it is thought that in these systems, the phenomenon could be due to the presence at the liquid surface of a significant number of associated atomic groups (clusters), the exact proportion of which will depend upon the particular composition eg for any binary system A+B, clusters of the form A_xB_y may be present at the surface.

Anomalous surface tension isotherms have been observed for a large number of binary metal alloys eg Sn+Ge⁽¹⁹⁾; Sn+Pb⁽²⁰⁾; Ga+Cd⁽²¹⁾; Ga+Hg⁽²¹⁾; Cu+Si⁽²²⁾; Ni+Si⁽²³⁾; Sn+Cu⁽²⁴⁾⁽²⁵⁾; Rh+Si⁽²⁶⁾; Pd+Al⁽²⁷⁾; Pd+Si⁽²⁷⁾; In+Hg⁽²⁸⁾; Ge+Co⁽²⁹⁾; Pt+B⁽³⁰⁾; Al+Co⁽³¹⁾; Al+Ni⁽³¹⁾; Tl+Hg⁽³²⁾; Tl+Pb⁽³³⁾; Mg+Pb⁽³⁴⁾; Ga+La⁽³⁵⁾; Pt+Si⁽³⁶⁾; Pt+Al⁽³⁶⁾; Ga+In⁽³⁷⁾.

Figure 5 presents the data obtained by Pelzel⁽³⁸⁾ for the Mg+Zn system, and shows the minimum in the γ ([Zn]) curve at a composition which approximates to that of the congruently melting intermetallic compound $MgZn_2$. Figure 5 also shows that positive

values for the temperature coefficient $\left(\frac{d\gamma}{dT}\right)$ were obtained in this compositional region, with the most positive value occurring at the stoichiometric composition for $MgZn_2$.

With some metal systems, there is disagreement between different authors as to the existence of irregularities in the surface tension isotherms. Without detailed knowledge of the respective experimental methods, it is difficult to account for these discrepancies, but two possible reasons for failing to observe this behaviour are:-

- (1) insufficient data obtained in the compositional range of interest
- (2) if during the initial stages of heating, the sample temperature is raised well in excess of the melting point, then any structure in the liquid may be lost and may not readily re-form on cooling to lower temperatures.

Trifinov and Alexsandrov⁽³⁹⁾ and Trifinov⁽⁴⁰⁾ proposed that the presence of compound structure in the liquid could be categorised by three different modes of surface-activity viz:-

- (i) compounds which are surface-active with respect to the melt and give rise to minima on the surface tension isotherm
- (ii) compounds which exhibit no surface-activity and will give rise to maxima on the surface tension isotherms
- (iii) compounds which are surface-active with respect to only one of the alloy constituents. These could produce points of inflexion on the isotherms.

Sergin et al⁽⁴¹⁾ developed a model relating the variation of structurally sensitive properties (eg viscosity, surface tension) with the composition of binary metal alloys. The model is based on the concept⁽⁴²⁾ that a metal melt consists of groups or clusters of the constituent atoms in various proportions and each system will be characterised by a preferred combination of clusters, the numbers of which will depend upon the particular alloy composition. In order to calculate certain equation parameters for the model, it is necessary to have experimental data for two compositions ($[x] \neq 1$ or 0) of the system. For each binary alloy system, it is possible to determine the index ratio of a cluster (n), (where for a cluster

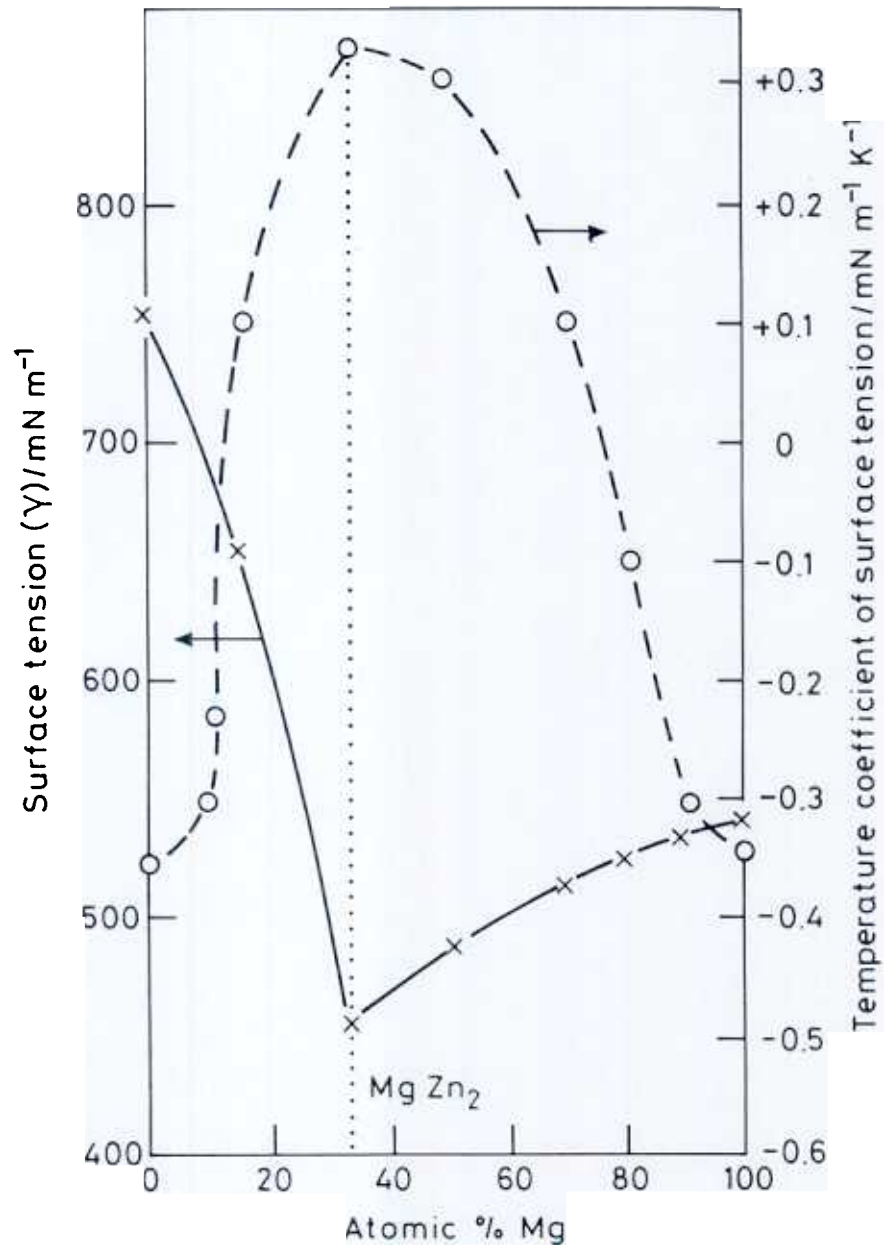


Figure 5 Effect of Mg concentration in Mg+Zn alloys on the surface tension at 700 °C and its temperature coefficient (Ref 38).

of form A_xB_y , $n = \frac{x}{y}$). Note the value for (n) only gives the ratio of [A]:[B] and for example, $n = 0.4$ could represent clusters of the form A_2B_5 , A_4B_{10}, etc. Use of model was illustrated using experimental data over the complete compositional range for various Pd-based alloys. Some of the alloys formed completely miscible systems (eg Pd+Co; Pd+Cu) whilst the others formed intermetallic compounds (eg Pd+Sb; Pd+Pb).

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PART 2

Literature Data for the Surface Tension of Tin and Tin-based Alloys

SURFACE TENSION DATA

This section collates, in graphical form, the literature data which relate to the influence of composition and of temperature on the surface tension of Sn alloys. In order to minimise errors introduced by transposition, curves have been traced (where possible) directly from diagrams given in the relevant references. Brief comments on the extant data are given for each system. For some systems the comments also include suggested $\gamma(t)$ relations for the particular metal which is alloyed with Sn. Comparison of the predicted value for (γ) of the alloying element, with that given by the reference may provide an indication of the relative quality of the metal used to manufacture the alloys (low values for (γ) of the metal implying the presence of surface-active impurities). For some of the Sn alloy systems, positive temperature coefficients of surface tension ($d\gamma/dt$) were observed, and this behaviour is usually associated with the retention of some structural form in the liquid state. This would be expected to apply particularly for compositions close to that of metallic compounds formed in the solid state. However, in some other liquid metal systems, the presence of low levels of surface-active elements, such as oxygen, can produce positive slopes for the $\gamma(t)$ curves, due to progressive desorption of the surfactant from the interface as temperature is increased. It has yet to be established, whether the presence of oxygen in Sn alloys would produce the same effect. If this were the case, then the impurity levels in the component metals (particularly the soluble oxygen content), together with any subsequent contamination introduced during the experiments, would not only reduce the value of (γ) but may also affect the slope of the $\gamma(t)$ curves.

Pure Sn

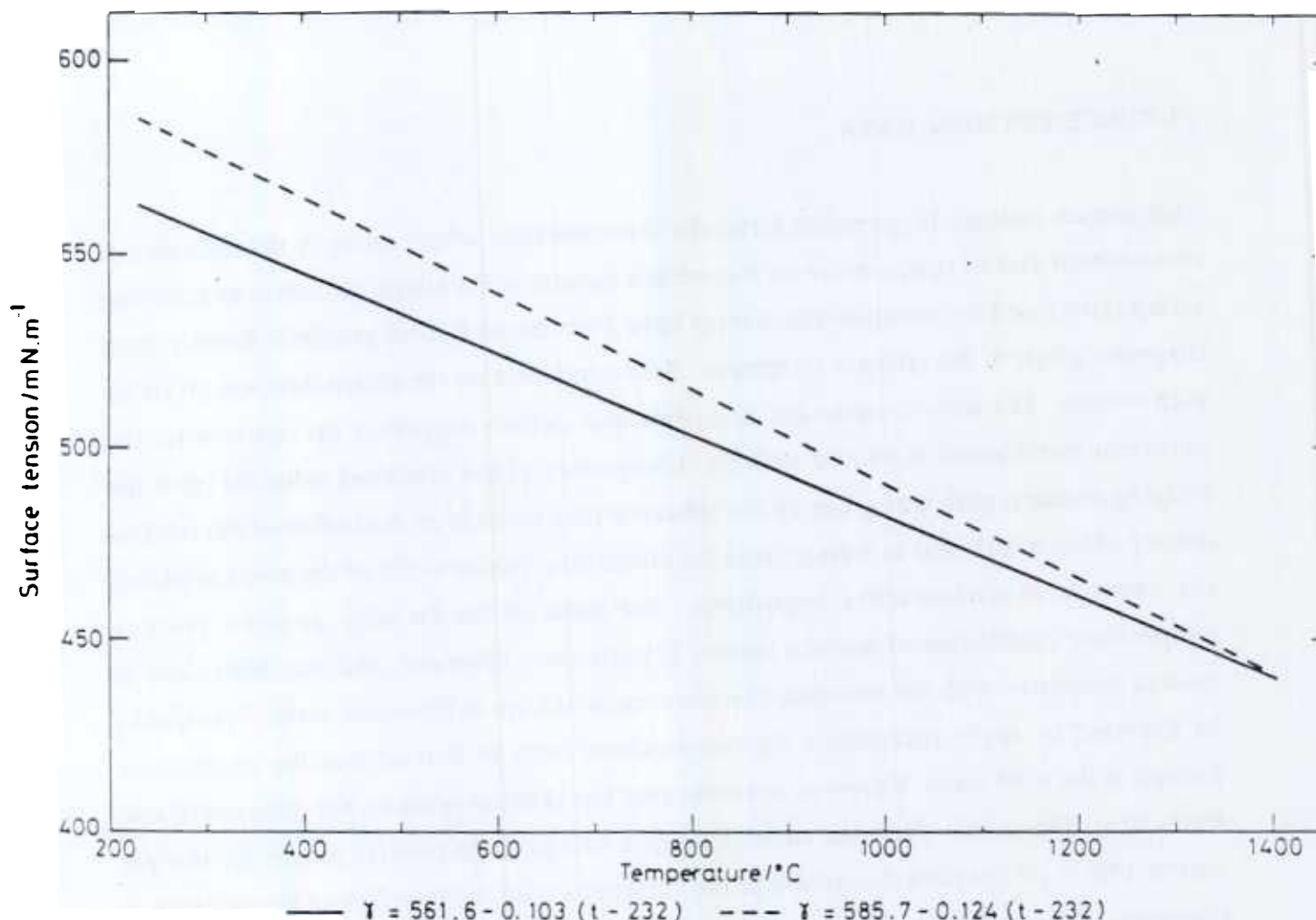


Figure 1 Variation of the surface tension of tin with temperature, showing the mean curves derived from data given in 36 different literature sources (Keene)⁽¹⁾.

— mean $\gamma(t)$ relation based on all the data.

--- mean $\gamma(t)$ relation based on the twelve sources which give the highest values for γ .

Comments

Figure 1 shows mean $\gamma(t)$ curves⁽¹⁾ for tin, which are based on data from thirty-six different literature sources. The two $\gamma(t)$ curves shown were derived by consideration of (a) data from all the literature sources and (b) data from the twelve sources which gave the highest values for γ . It was suggested that the higher values for γ probably pertain to material which contained low levels of surfactant impurities and as a consequence, the mean $\gamma(t)$ curve based on these values should more closely approach that for very pure tin.

Sn + Ag

Comments

Suggested⁽¹⁾ mean $\gamma(t)$ relations for (i) Ag and (ii) very pure Ag are:-

$$\left. \begin{array}{l} \text{(i)} \quad \gamma = 925 - 0.21 (t-960) \text{ mN.m}^{-1} \\ \text{(ii)} \quad \gamma = 955 - 0.31 (t-960) \text{ mN.m}^{-1} \end{array} \right\} \quad (t \text{ in } ^\circ\text{C})$$

Surface tension data⁽²⁾ for the Sn-Ag system are given in Figures 2 and 3. Over the temperature range 1000° - 1200 °C there is a monotonic decrease in (γ) with increase in [Sn]. The $\gamma(t)$ curves given in Figure 3 show that for the particular compositions studied, the temperature coefficients ($d\gamma/dt$) are negative. Of interest is the temperature buffering ($d\gamma/dt = 0$) at 75 at.% Ag, ie in the region of the composition Ag_3Sn . The limiting surface activity of Ag in Sn was found to be low (approximately 1 mN.m⁻¹ at.% Ag⁻¹).

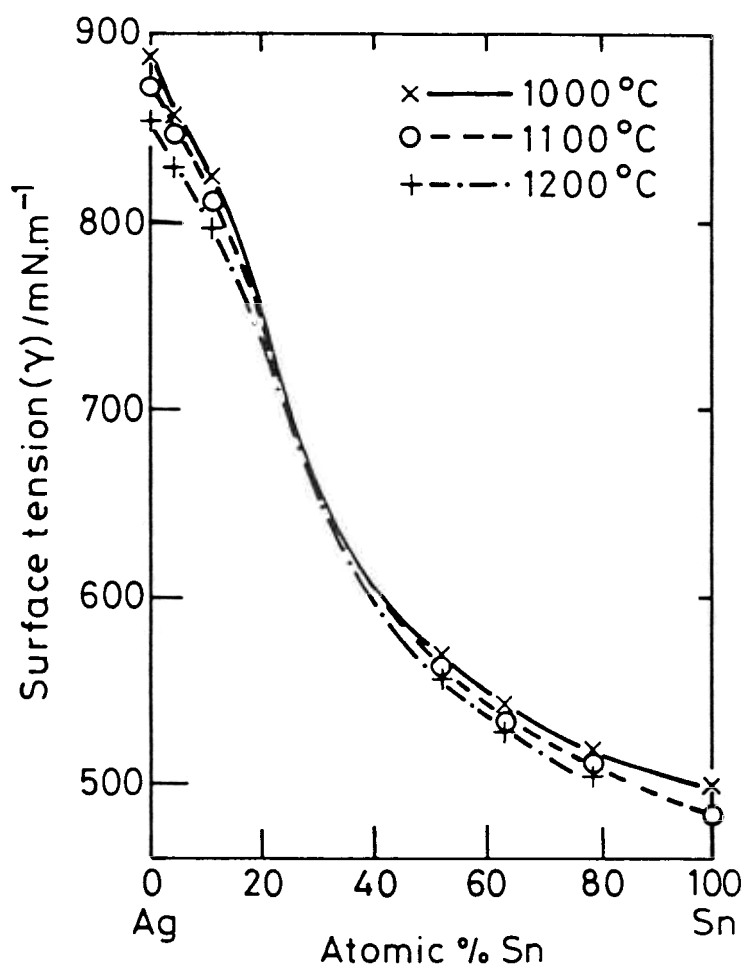


Figure 2 Effect of composition on the surface tension of Sn + Ag alloys at three different temperatures (Lauermann)⁽²⁾.

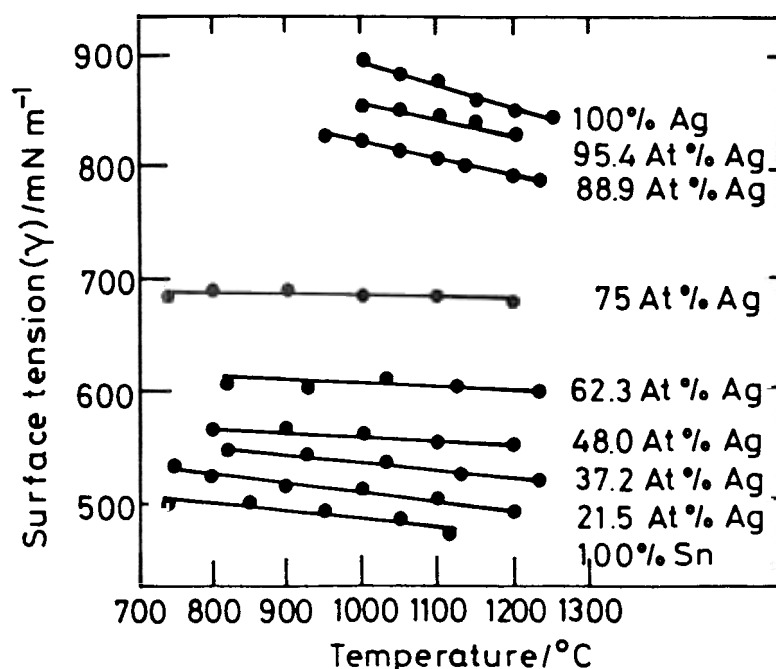


Figure 3 Effect of temperature on the surface tension of various Sn + Ag alloys (Lauermann)⁽²⁾.

Sn + As

Comments

Data⁽³⁾ for the effect of As (up to 5.9 at.%) on the (γ) of Sn are shown in Figure 4. Over the limited composition range studied, (γ) decreases linearly with increase in [As]. The temperature coefficients ($d\gamma/dt$) between 300° and 450 °C are negative and tend to decrease in magnitude with increase in [As]. The limiting surface activity of As in Sn at 350 °C is⁽³⁾ 3.7 mN.m⁻¹ at.% As⁻¹.

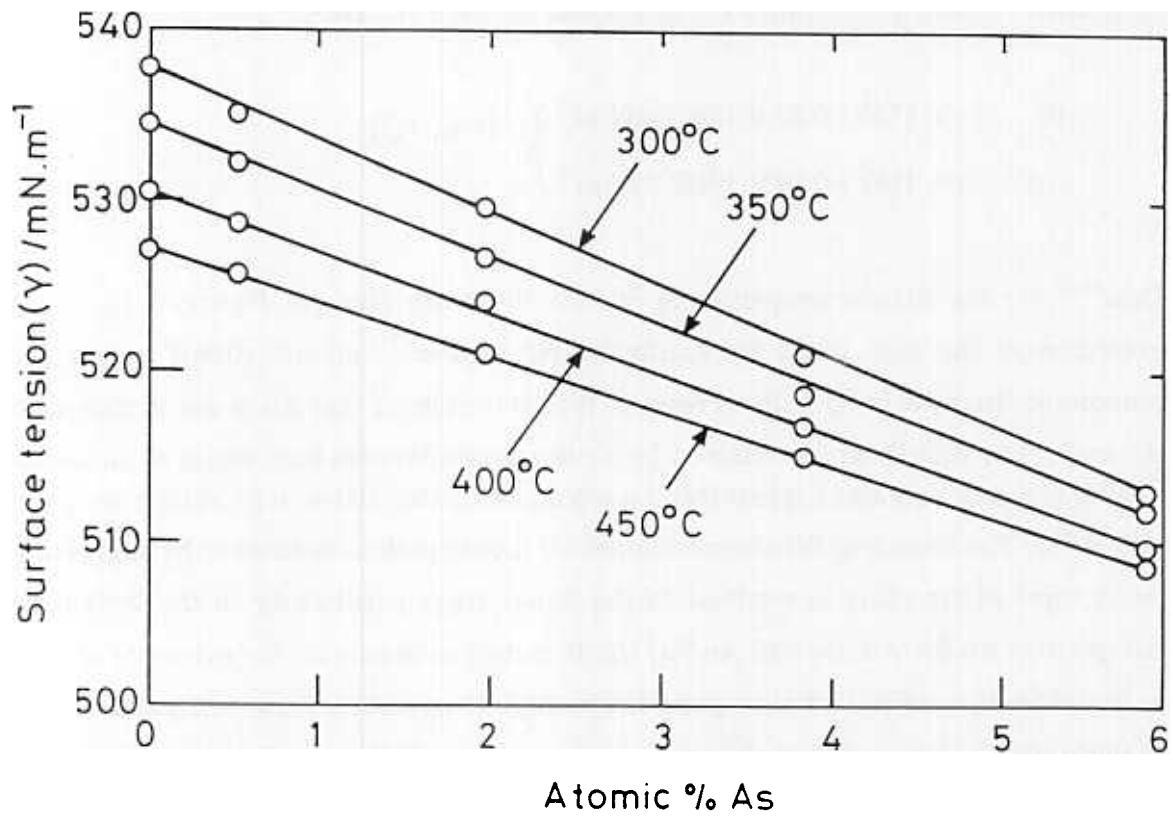


Figure 4 Effect of the addition of As to Sn on the surface tension at different temperatures (Pokrovskii)⁽³⁾.

Sn + Au

Comments

Suggested⁽¹⁾ mean $\gamma(t)$ relations for (i) Au and (ii) pure Au are:-

$$\left. \begin{array}{ll} \text{(i)} & \gamma = 1145 - 0.20 (t-1065) \text{ mN.m}^{-1} \\ \text{(ii)} & \gamma = 1162 - 0.18 (t-1065) \text{ mN.m}^{-1} \end{array} \right\} \quad (t \text{ in } ^\circ\text{C})$$

Data⁽⁴⁻⁷⁾ for the surface properties of Sn+Au alloys are given in Figures 5-10. With the exception of the data given by Kaufman and Whalen⁽⁷⁾, all the $\gamma(\text{Sn})$ curves show a monotonic decrease in (γ) with increase in [Sn] and indicate that Au is not surface-active in the melt. The $\gamma(\text{Sn})$ curves obtained by Kaufman and Whalen for a range of temperatures, exhibit extrema, and also suggest that Au would be surface-active in Sn at high temperatures ($\geq 950^\circ\text{C}$). Kaufman and Whalen accounted for the anomalous behaviour by suggesting that some form of structure is retained in the liquid state, particularly in the vicinity of the compounds Au Sn, Au Sn₂ and Au Sn₄ (confirmatory evidence for the existence of structure in liquid Sn+Au alloys had been provided by high-temperature X-ray analysis.) In contrast to these results, Pokrovskii et al⁽⁵⁾ (who conducted over 3000 separate measurements) failed to find any extrema in the $\gamma(\text{Sn})$ curves. It was suggested⁽⁵⁾ that possible reasons for this discrepancy could be differences in experimental procedures and/or the fact that Kaufman and Whalen studied a relatively small range of compositions. Pokrovskii et al noted that Au is weakly surface-active in Sn as witnessed by the fact that the $\gamma(t)$ curve for 0.35 at.% Au (Figure 9) lies below that for pure Sn.

Again there is a lack of agreement between the data of Kaufman and Whalen and of Pokrovskii et al in that with the former no positive temperature coefficients were found, whereas Pokrovskii et al (Figure 9) observed positive values for compositions between approximately 40 at.% Au and 65 at.% Au. Temperature buffering ($d\gamma/dt = 0$) occurred⁽⁵⁾ in the vicinity of the compositions 67 at.% Au (eutectic) and 33 at.% Au (AuSn₂). Verification of the existence of positive coefficients is given by the data of Khilya et al⁽⁶⁾ (Figure 10), although there is not total accord with Pokrovskii et al in that positive coefficients were found only for alloys up to about 40 at.% Sn. With compositions below 50 at.% Sn, the values of ($d\gamma/dt$) were temperature-dependent and become progressively more negative as the temperature increased. For compositions containing more than 50 at.% Sn, the temperature coefficients were always negative and did not show significant variation with temperature.

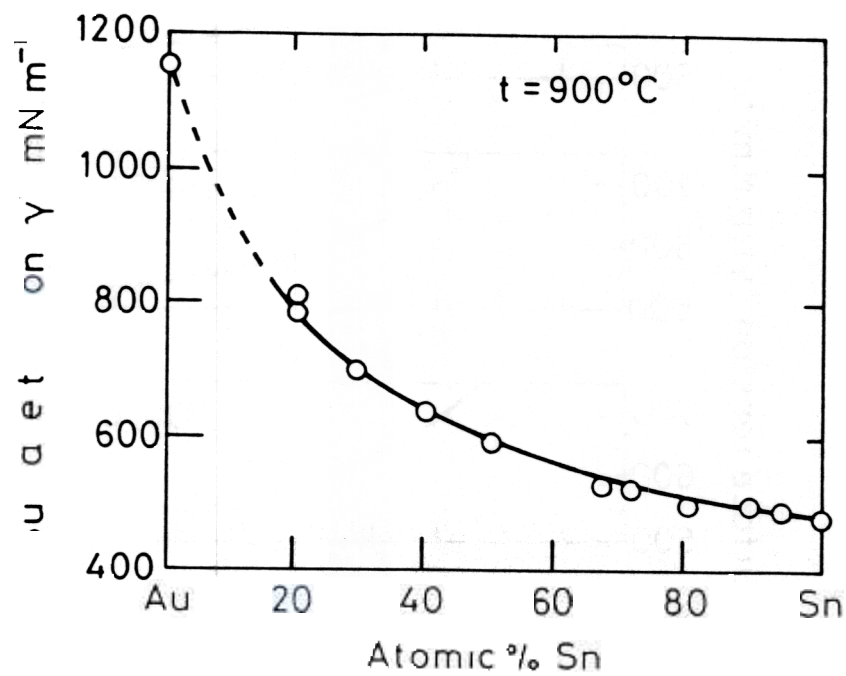


Figure Effect of composition on the surface tension of Sn-Au alloys 900°C
(Alchagirov)⁽⁴⁾

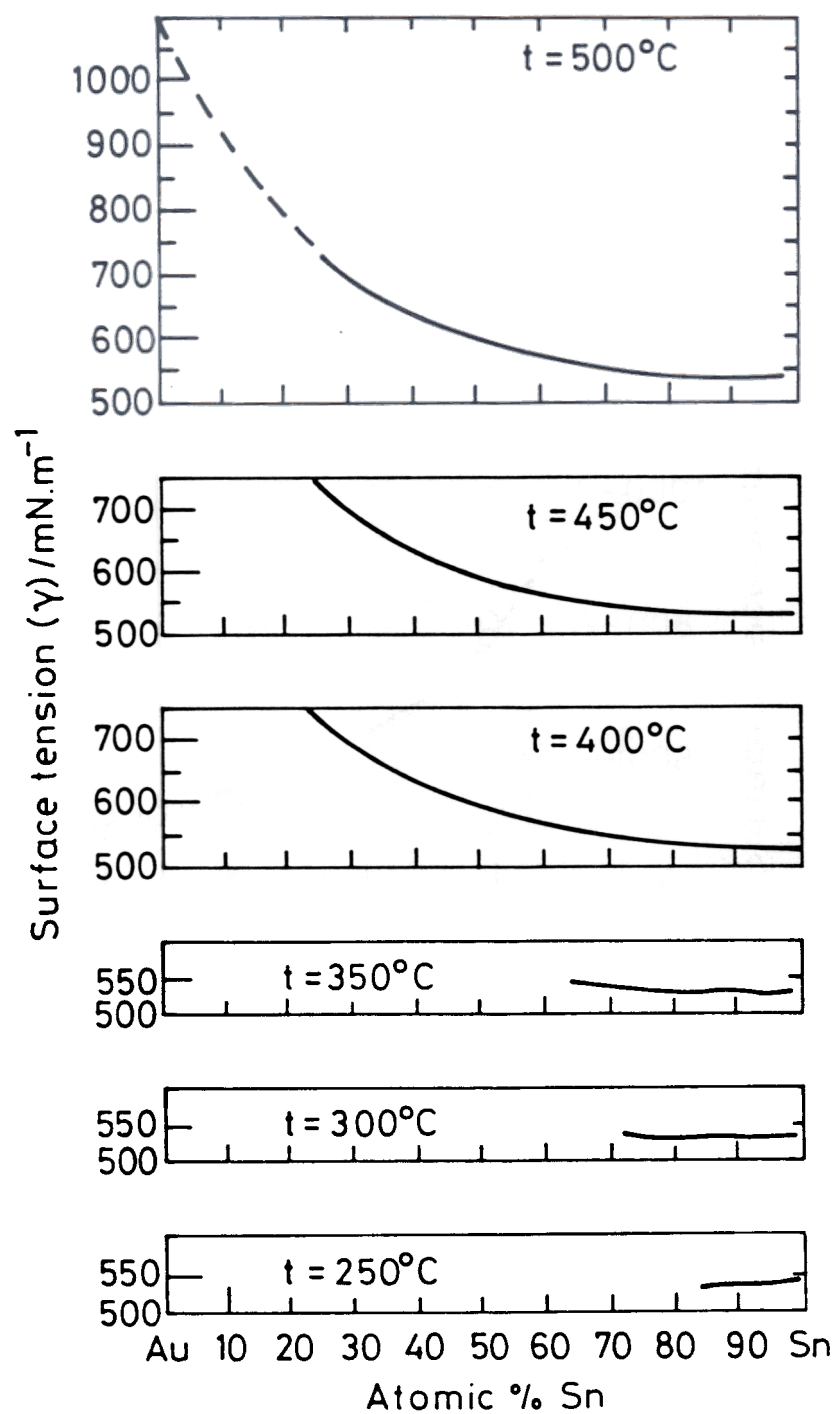


Figure 6

Effect of composition on the surface tension of Sn + Au alloys at various temperatures (Pokrovskii)⁽⁵⁾.

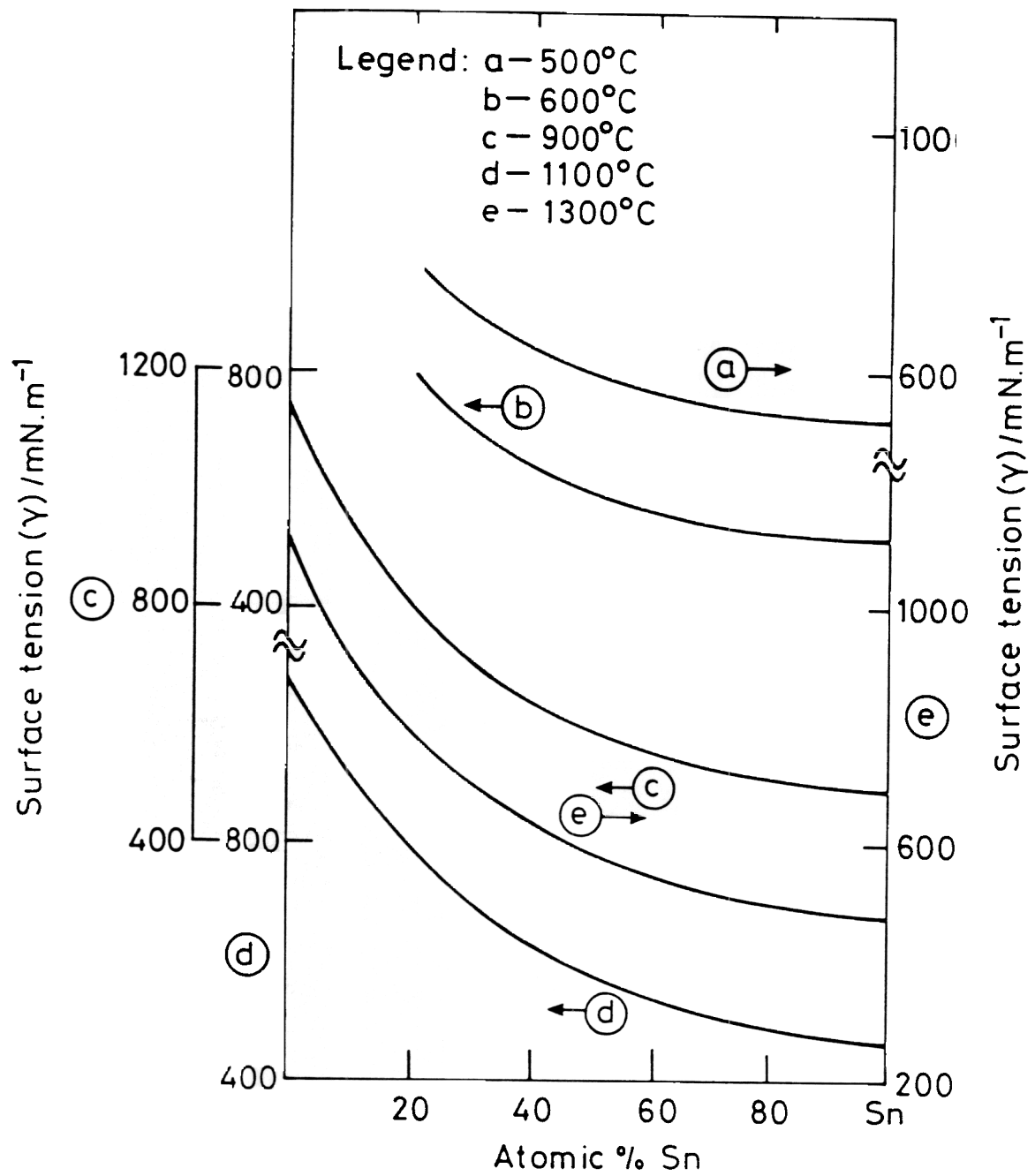


Figure 7 Effect of composition on the surface tension of Sn + Au alloys at various temperatures (Khilya)⁽⁶⁾.

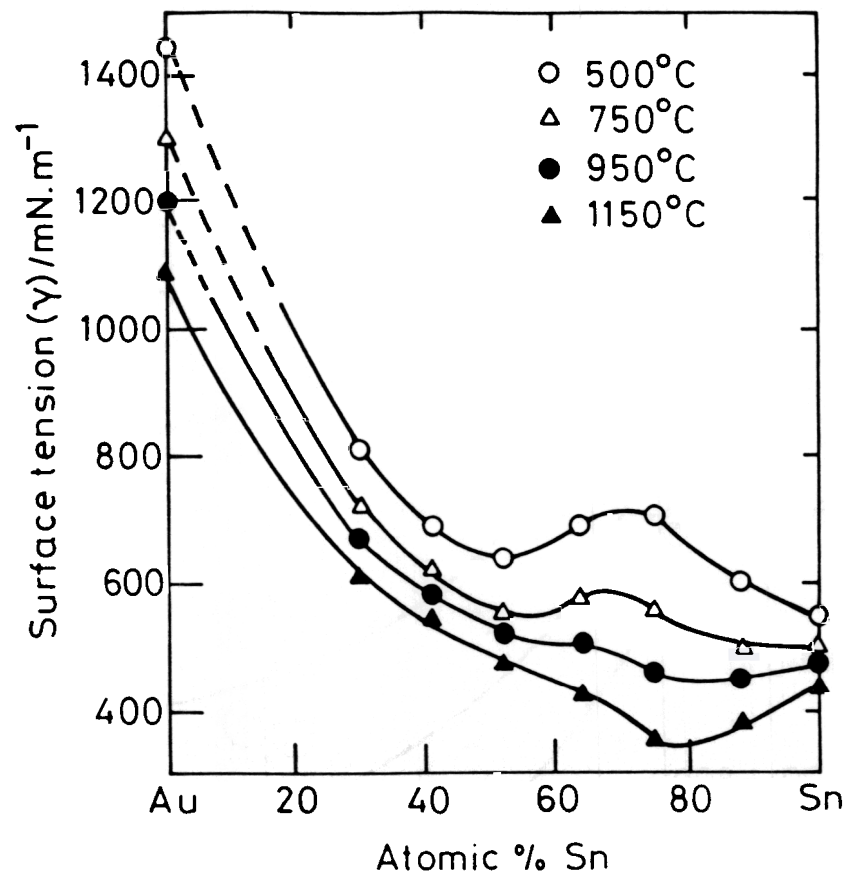


Figure 8 Effect of composition on the surface tension of Sn + Au alloys at different temperatures (Kaufman)⁽⁷⁾.

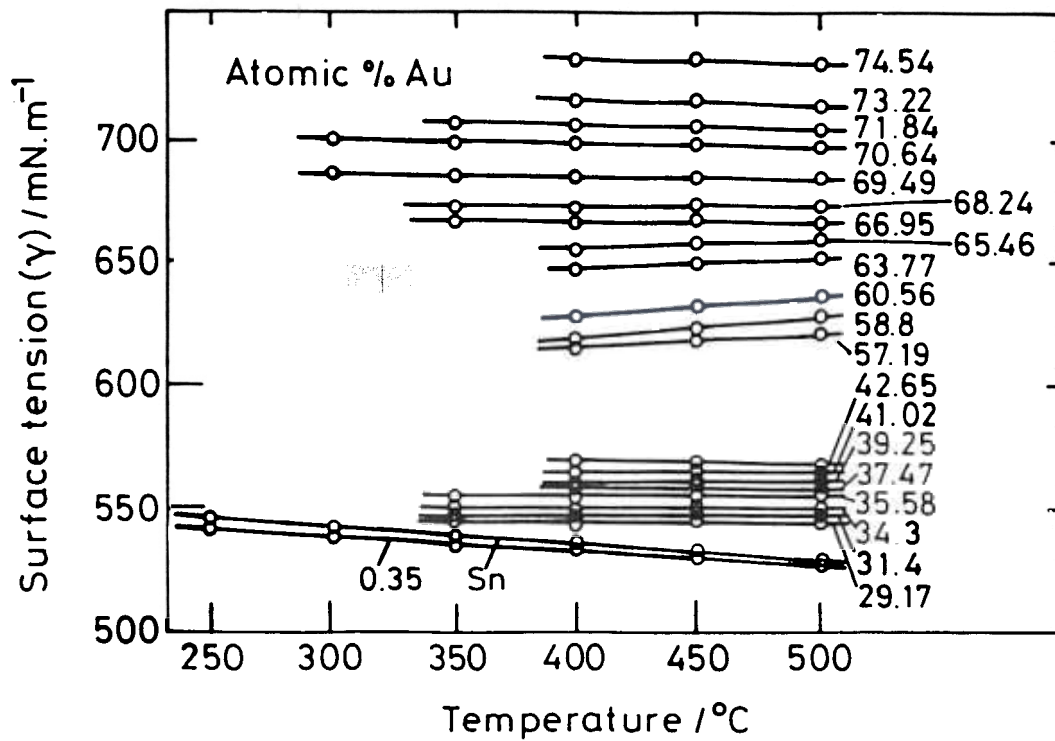


Figure 9 Variation of the surface tension of Sn + Au alloys with temperature (Pokrovskii)⁽⁵⁾.

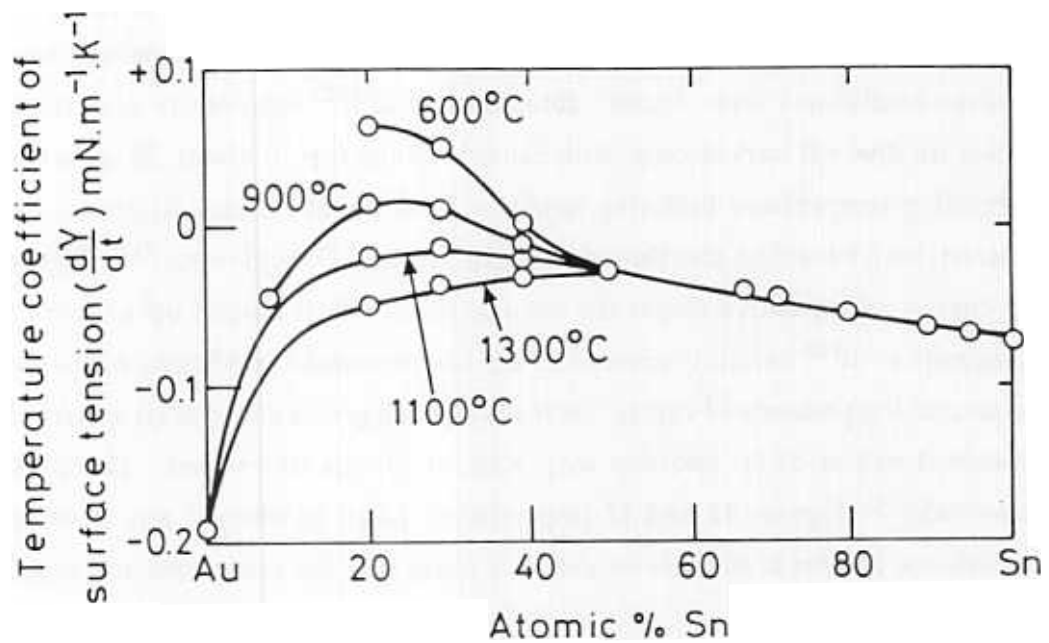


Figure 10 Effect of composition of Sn + Au alloys on the surface entropy at different temperatures (Khilya)⁽⁶⁾.

Sn + Bi

Comments

Suggested⁽¹⁾ mean $\gamma(t)$ relations for (i) Bi and (ii) pure Bi are:-

$$\left. \begin{array}{l} \text{(i)} \quad \gamma = 382 - 0.080 (t-270) \text{ mN.m}^{-1} \\ \text{(ii)} \quad \gamma = 389 - 0.097 (t-270) \text{ mN.m}^{-1} \end{array} \right\} \quad (t \text{ in } ^\circ\text{C})$$

Surface tension⁽⁸⁻¹⁴⁾ for the Sn+Bi system are shown in Figures 11-19. Most of the $\gamma(\text{Sn})$ curves⁽⁸⁻¹⁰⁾ show a monotonic decrease in (γ) with increase in $[\text{Bi}]$, but the results given by Klyachko and Kunin⁽¹¹⁾ (Figure 13) show a distinct minimum in the vicinity of the eutectic, the effect being most apparent at the lowest temperature (200 °C). However, data obtained by Ibragimov et al⁽¹²⁾ at 150 °C for this region (Figure 14) gives no indication of any minimum.

Positive values for $(d\gamma/dt)$ were observed in several studies^(8,11-13), being most evident at lower temperatures. There are however, differences in the composition ranges for which positive coefficients were found. Ibragimov et al^(8,12) (Figures 18 and 19) found positive slopes for the $\gamma(t)$ curves only with Sn-rich alloys (up to about 20 at.% Bi), their results suggesting temperature buffering ($d\gamma/dt = 0$) at about 2.5 at.% Bi and at 24.3 at.% Bi. In contrast, both Klyachko and Kunin⁽¹¹⁾ (Figure 16) and Dzhoglev et al⁽¹³⁾ (Figure 15) observed $\gamma(t)$ curves with positive slopes for compositions, which ranged up to about 50-55 at.% Bi. Ibragimov et al⁽¹²⁾ carefully controlled the environmental conditions of the experiment and noted that the presence of vapour such as stopcock grease could exert a marked effect on the measured values of (γ) and this may account for the differences. Reshchetnikov⁽¹⁰⁾ and Sauerwald⁽¹⁴⁾ (Figures 12 and 17 respectively), failed to observe any positive temperature coefficients, but for both these studies it is likely that the experimental temperatures would have been too high.

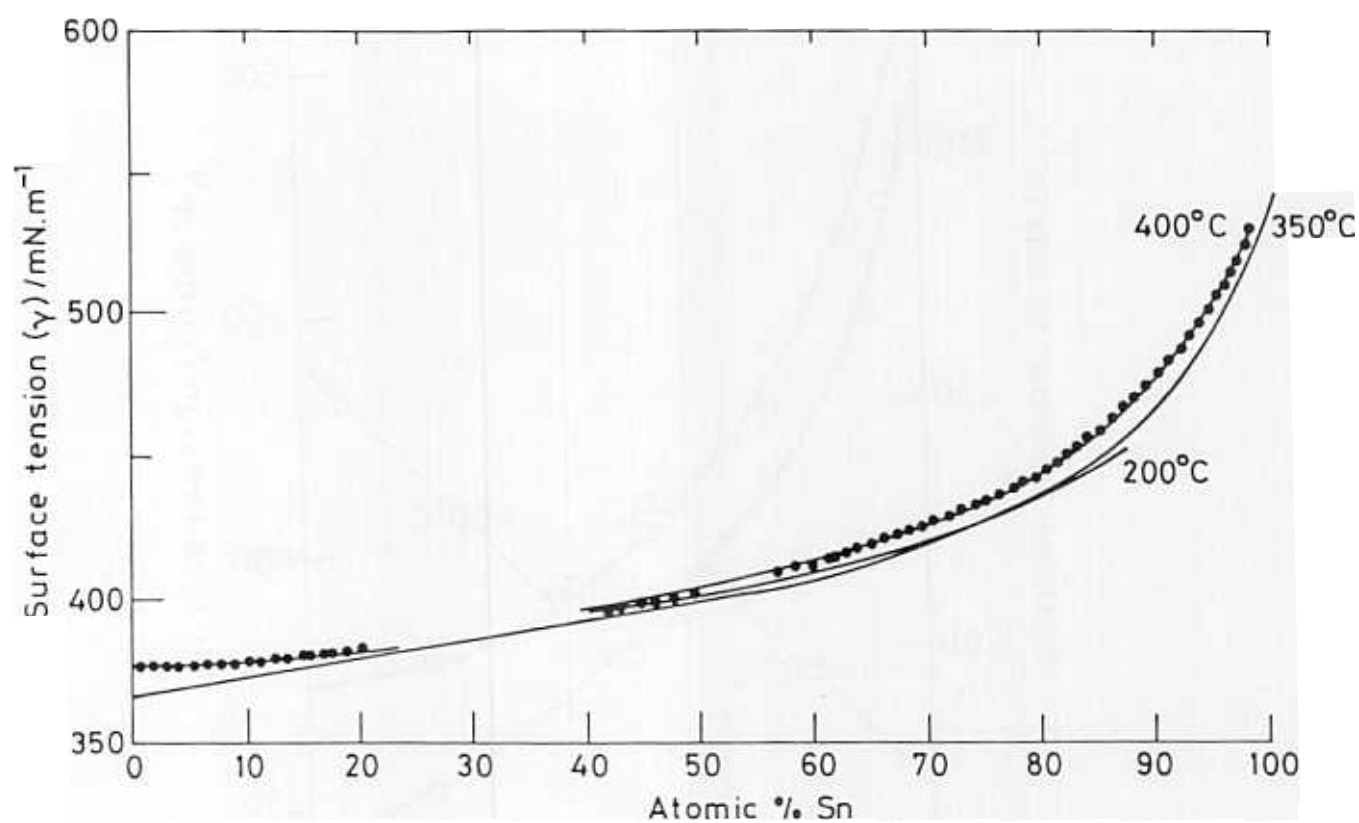


Figure 11 Effect of composition on the surface tension of Sn + Bi alloys at 200 °C and 350 °C (Ibragimov)⁽⁸⁾ and at 400 °C (Smirnova)⁽⁹⁾.

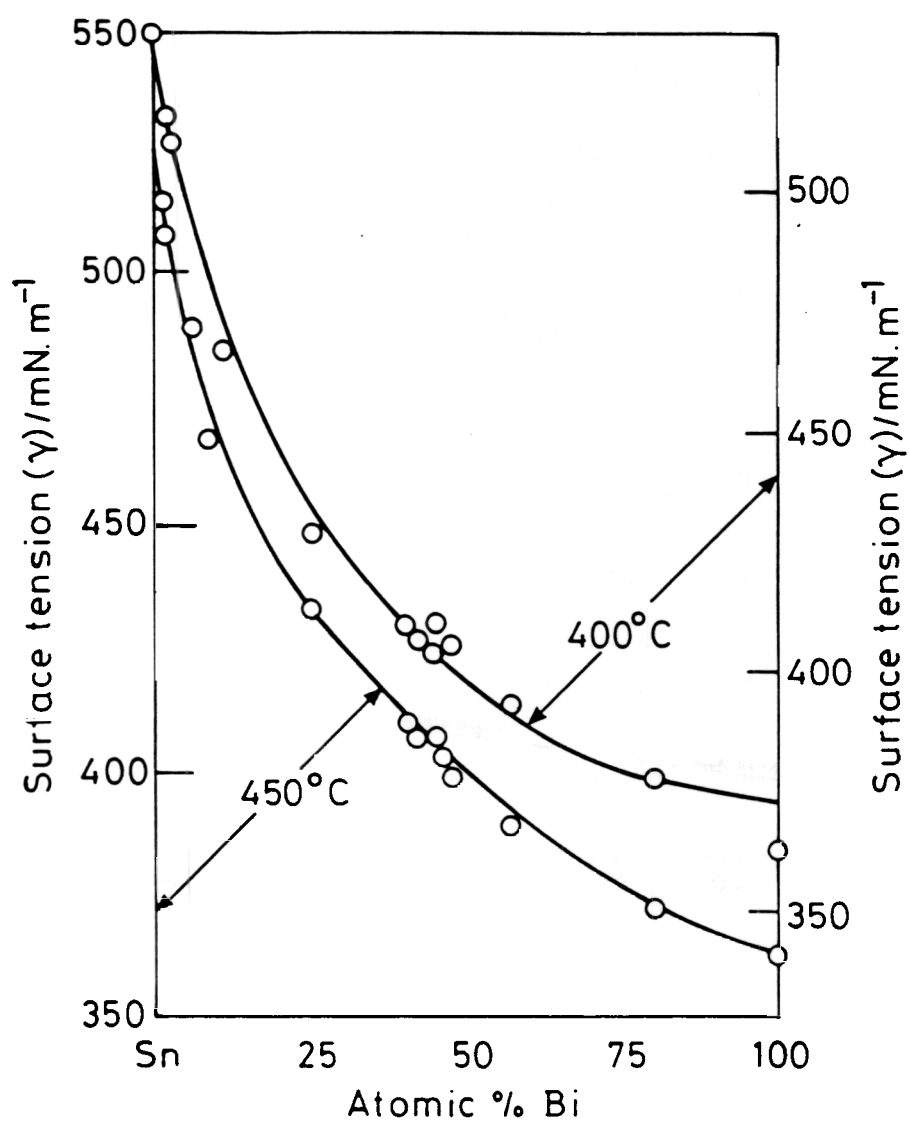


Figure 12 Effect of composition of Sn + Bi alloys on the surface tension at 400 °C and 450 °C (Reshchetnikov)⁽¹⁰⁾.

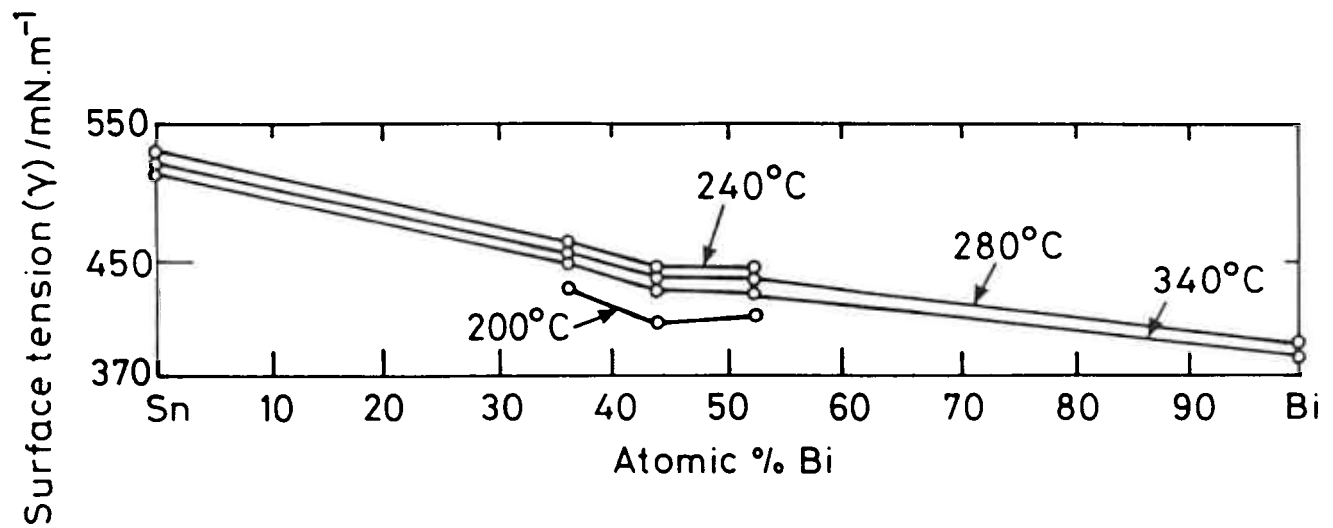


Figure 13 Effect of composition of Sn + Bi alloys on the surface tension at different temperatures (Klyachko)⁽¹¹⁾.

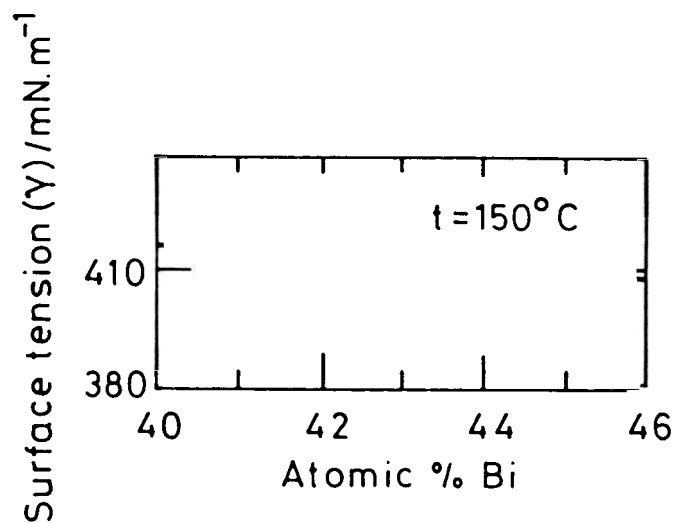


Figure 14 Effect of composition on the surface tension of Sn + Bi melts in the vicinity of the eutectic (Ibragimov)⁽¹²⁾.

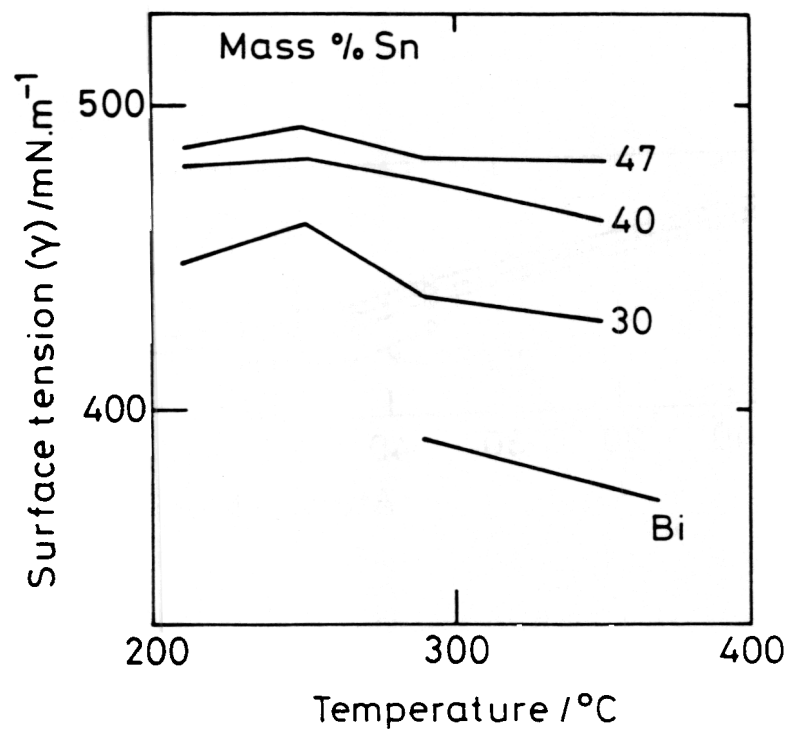


Figure 15 Effect of temperature on the surface tension of Bi and various Sn + Bi alloys (Dzhoglev)⁽¹³⁾.

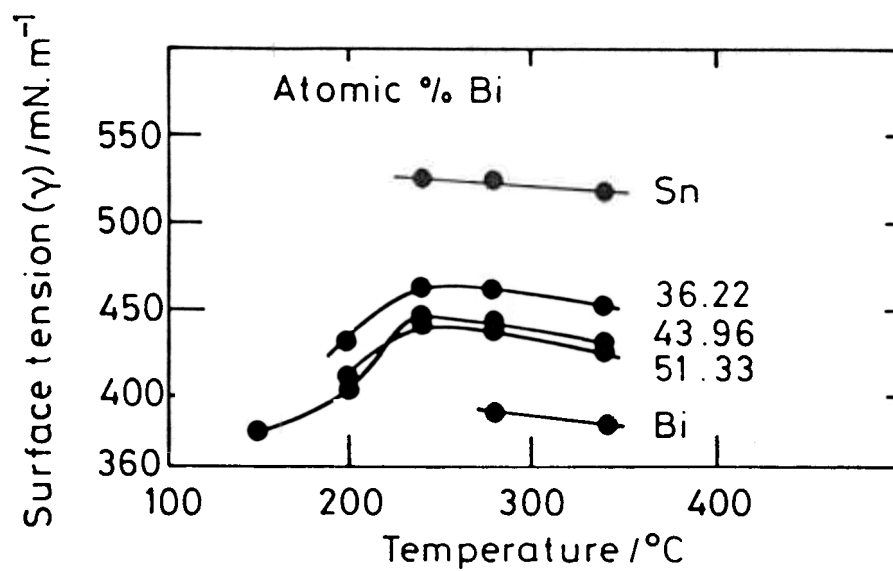


Figure 16 Effect of temperature on the surface tension of Bi, Sn and three of their alloys (Klyachko)⁽¹¹⁾.

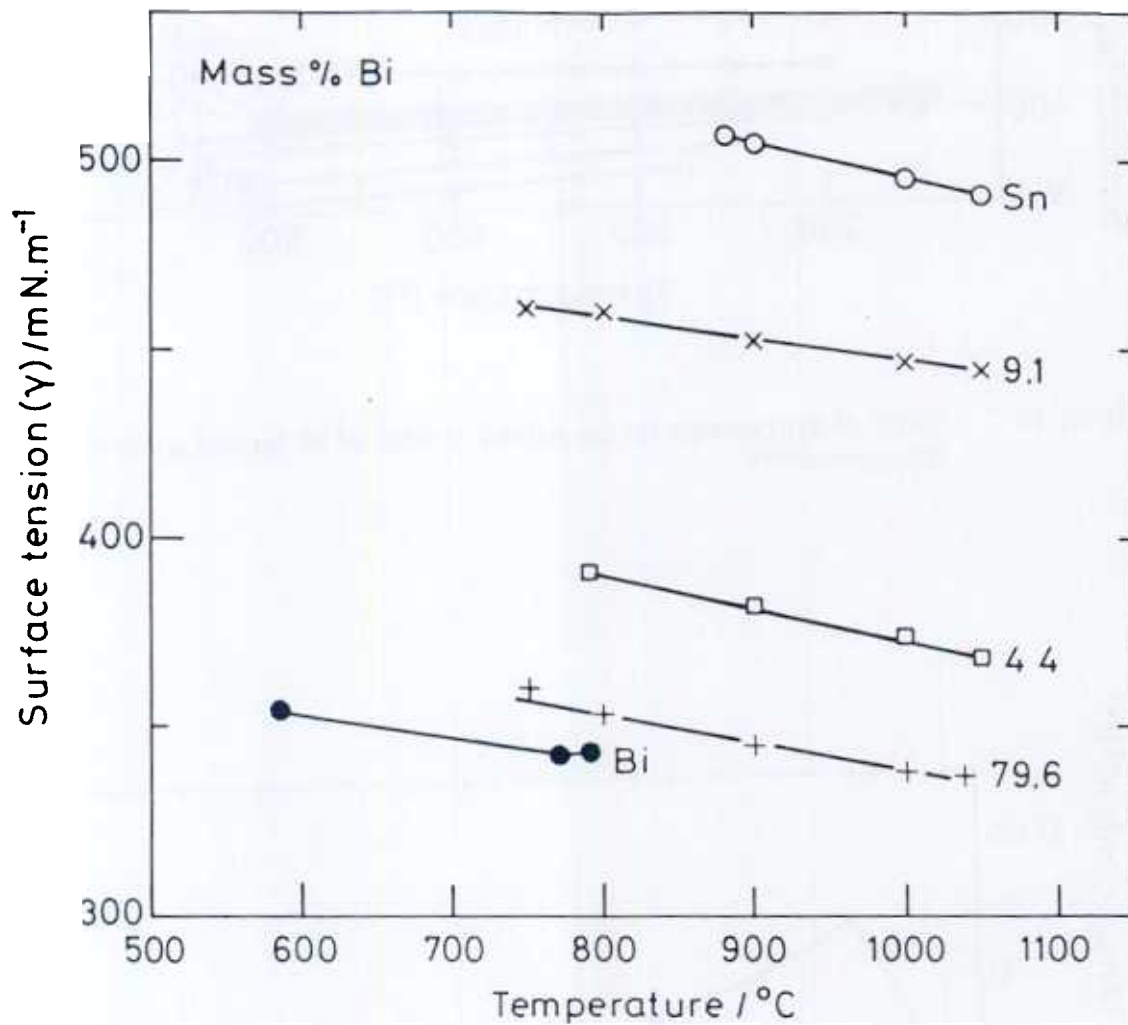


Figure 17 Effect of temperature on the surface tension of Bi, Sn and three of their alloys (Sauerwald)⁽¹⁴⁾.

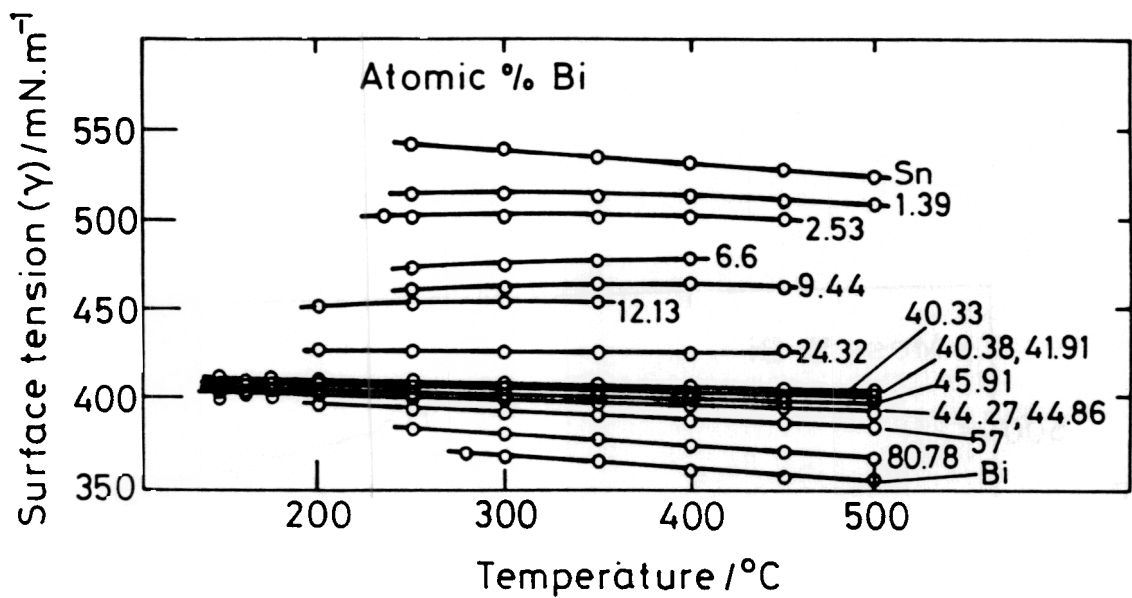


Figure 18 Effect of temperature on the surface tension of Bi, Sn and some of their alloys (Ibragimov)⁽¹²⁾.

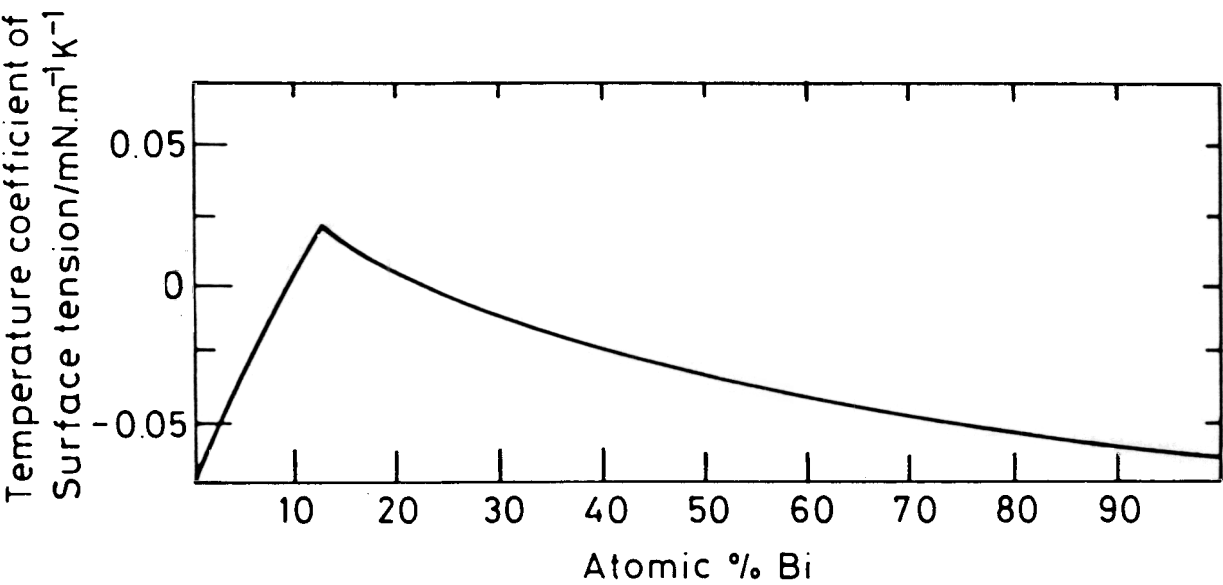


Figure 19 Effect of composition of Sn + Bi alloys on the surface entropy (Ibragimov)⁽⁸⁾.

Sn + Cd

Comments

Suggested⁽¹⁾ mean $\gamma(t)$ relation for Cd is:-

$$\gamma = 637 - 0.15 (t-321) \text{ mN.m}^{-1} \quad (t \text{ in } ^\circ\text{C})$$

Surface tension data^(10,15) for the Sn+Cd system are shown in Figures 20-21. The $\gamma(\text{[Sn]})$ curves given by the work of Reshchetnikov⁽¹⁰⁾ (Figure 21) reveals that at 450 °C, (γ) of the alloys decreases almost linearly with increase in [Sn]. The results given by Pokrovskii and Saidov⁽¹⁵⁾ (Figure 21), pertain to Sn-rich alloys (up to 20 at.% Cd) only, and show similar trends (the small minimum in the curve at approximately 4 at.% Cd is only about 1-2 mN.m⁻¹ and is probably not statistically significant).

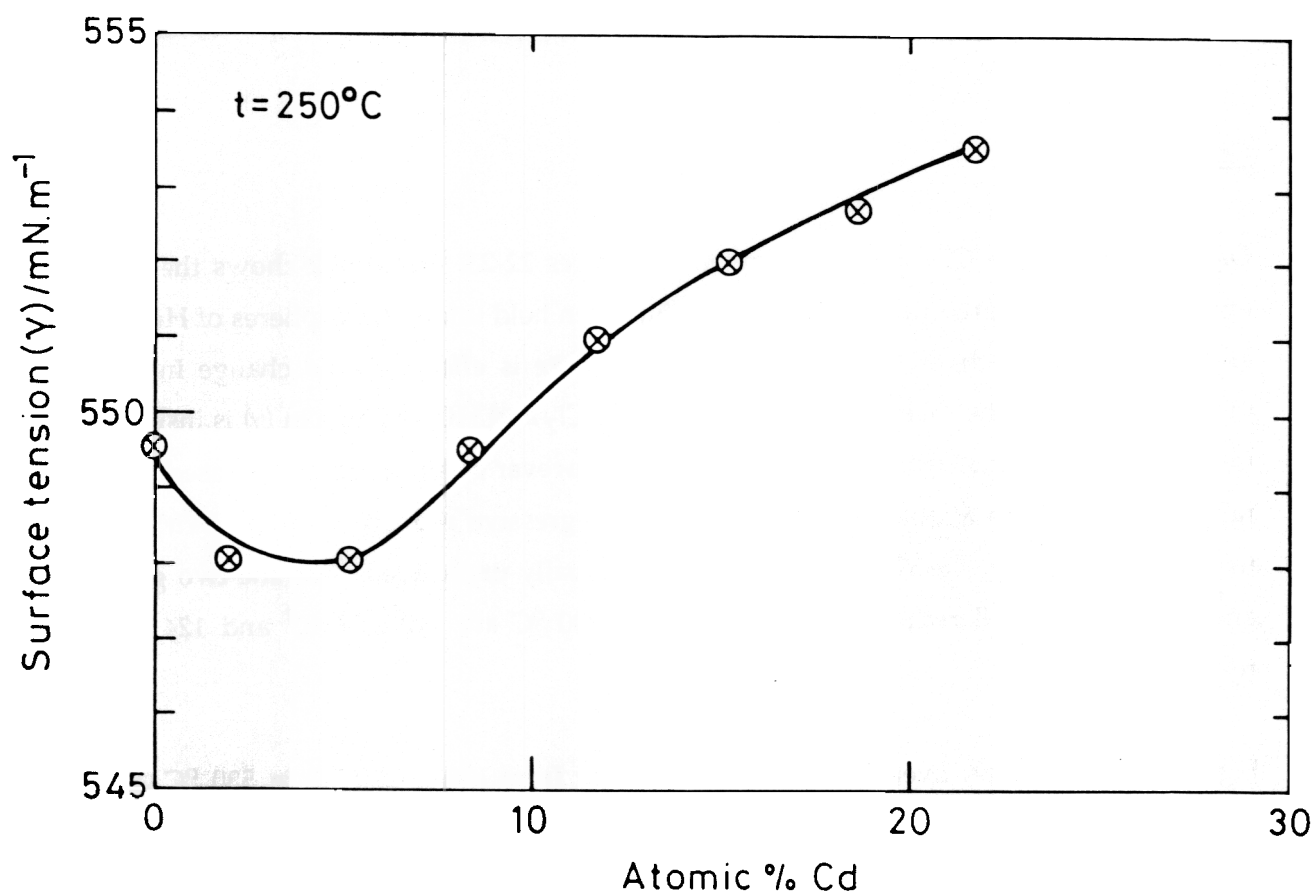


Figure 20 Effect of composition on the surface tension of Sn + Cd alloys at 250 °C (Pokrovskii)⁽¹⁵⁾.

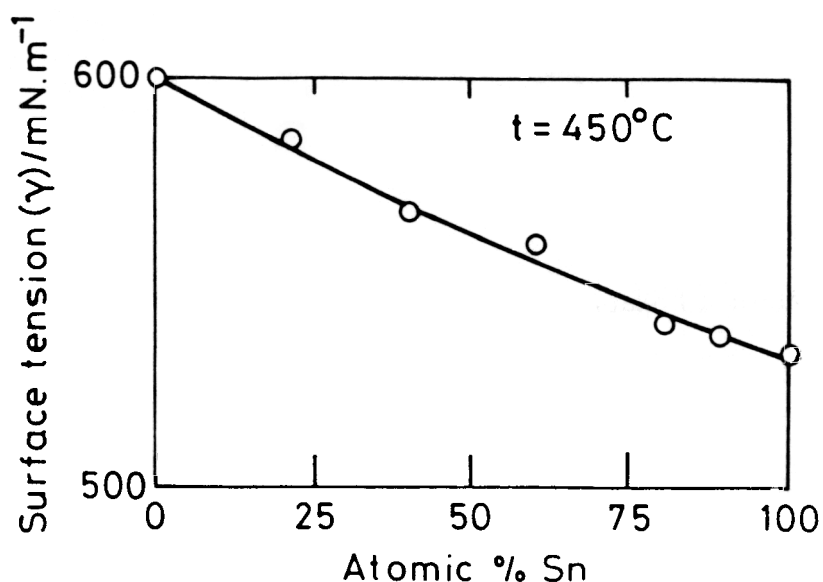


Figure 21 Effect of composition on the surface tension of Sn + Cd alloys at 450 °C (Reshchetnikov)⁽¹⁰⁾.

Sn + "Cl"

Comments

Data⁽¹⁶⁾ for the Sn+"Cl" system are given in Figures 22-23. Figure 22 shows the effect of environmental gas pressure (P) on the (γ) of Sn when held under atmospheres of He, dry Cl₂ and dry HCl respectively. With the inert gas, there is effectively no change in (γ) with increase in (P). In the case of the two active gases Cl₂ and HCl, change in (γ) is insignificant for pressures less than about 1.33×10^{-2} g.Pa. However as pressure is increased over the range 1.33×10^{-2} to about 200 g.Pa there is a progressive reduction in (γ). With further increase in pressure, the value for (γ) remains virtually unchanged. For the two gases Cl₂ and HCl, the overall reductions in (γ) of Sn at 400 °C are 140 mN.m⁻¹ and 124 mN.m⁻¹ respectively.

Figure 23 shows that, over the temperature range from about 270 °C to 530 °C, the γ(t) curves for Sn under He, HCl and Cl₂ have a small negative slope. The Figure also shows γ(t) data obtained by measurements under HCl or Cl₂ plasma.

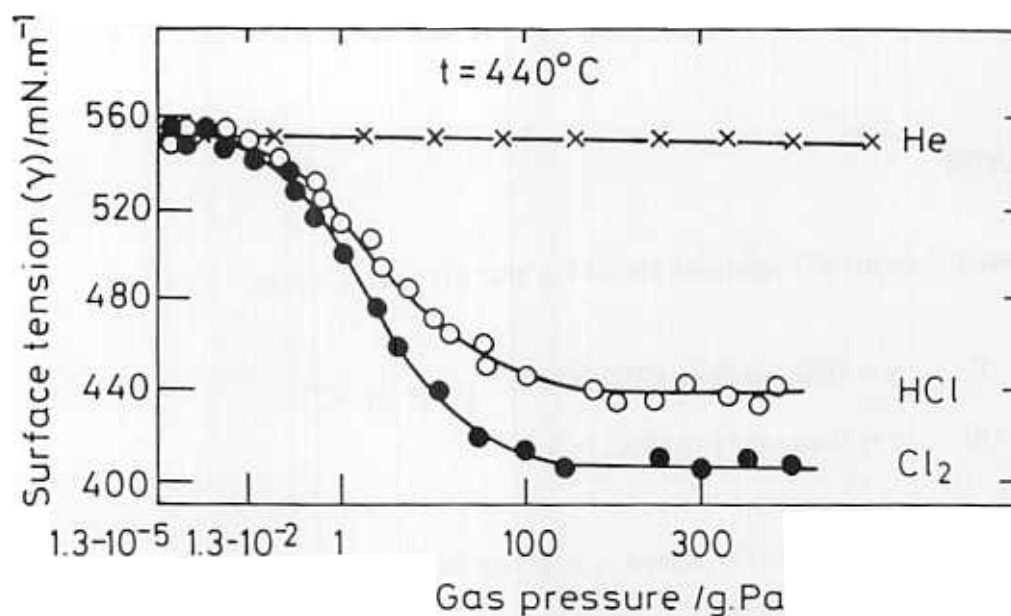


Figure 22 Variation of the surface tension of Sn at 440°C with the environmental gas pressure for dry He, HCl and Cl_2 (Makhova)⁽¹⁶⁾.

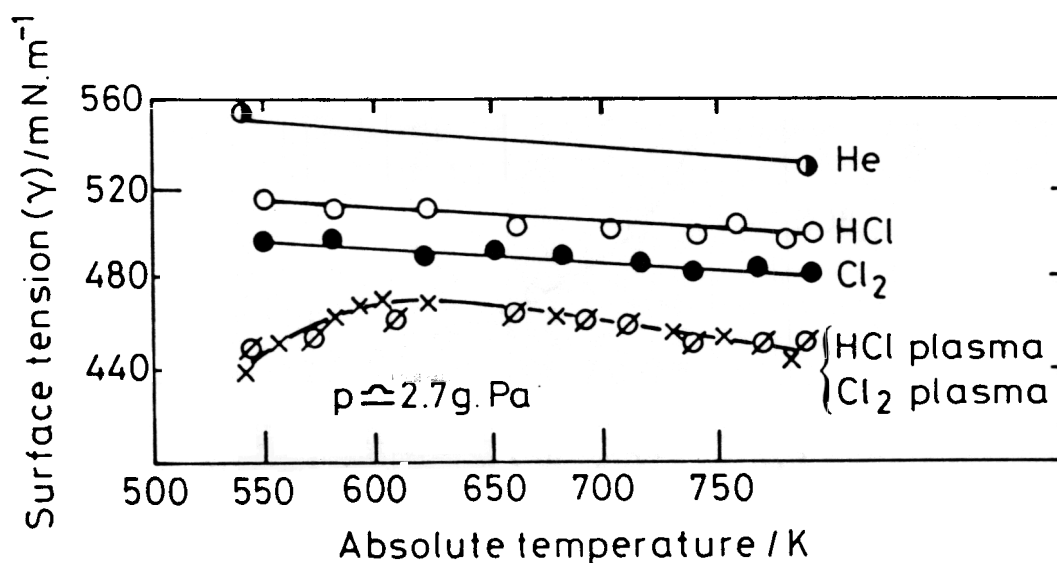


Figure 23 Variation with temperature of the surface tension of Sn under dry He, HCl, Cl_2 and HCl and Cl_2 plasma (Makhova)⁽¹⁶⁾.

Sn + Co

Comments

Suggested⁽¹⁾ mean $\gamma(t)$ relations for (i) Co and (ii) pure Co are:

$$\left. \begin{array}{l} \text{(i)} \quad \gamma = 1881 - 0.34 (t-1500) \text{ mN.m}^{-1} \\ \text{(ii)} \quad \gamma = 1928 - 0.44 (t-1500) \text{ mN.m}^{-1} \end{array} \right\} \quad (t \text{ in } ^\circ\text{C})$$

Data^(10,17) for (γ) of Sn+Co alloys are given in Figures 24-25, both curves showing a monotonic decrease in (γ) with increase in [Sn].

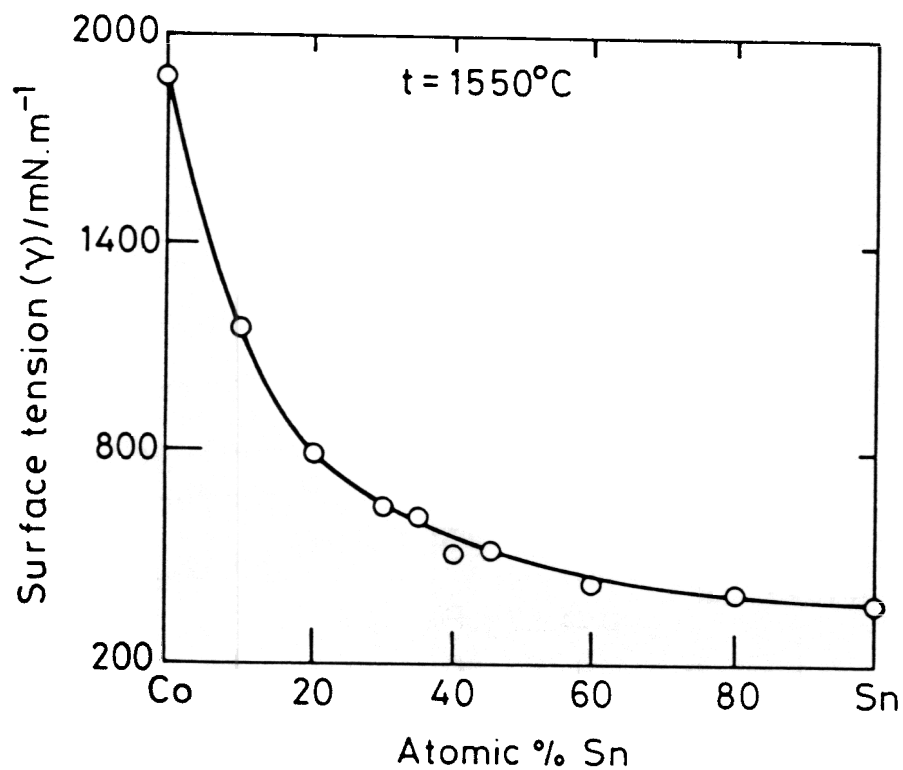


Figure 24 Effect of composition on the surface tension of Sn + Co alloys (Eremenko)⁽¹⁷⁾.

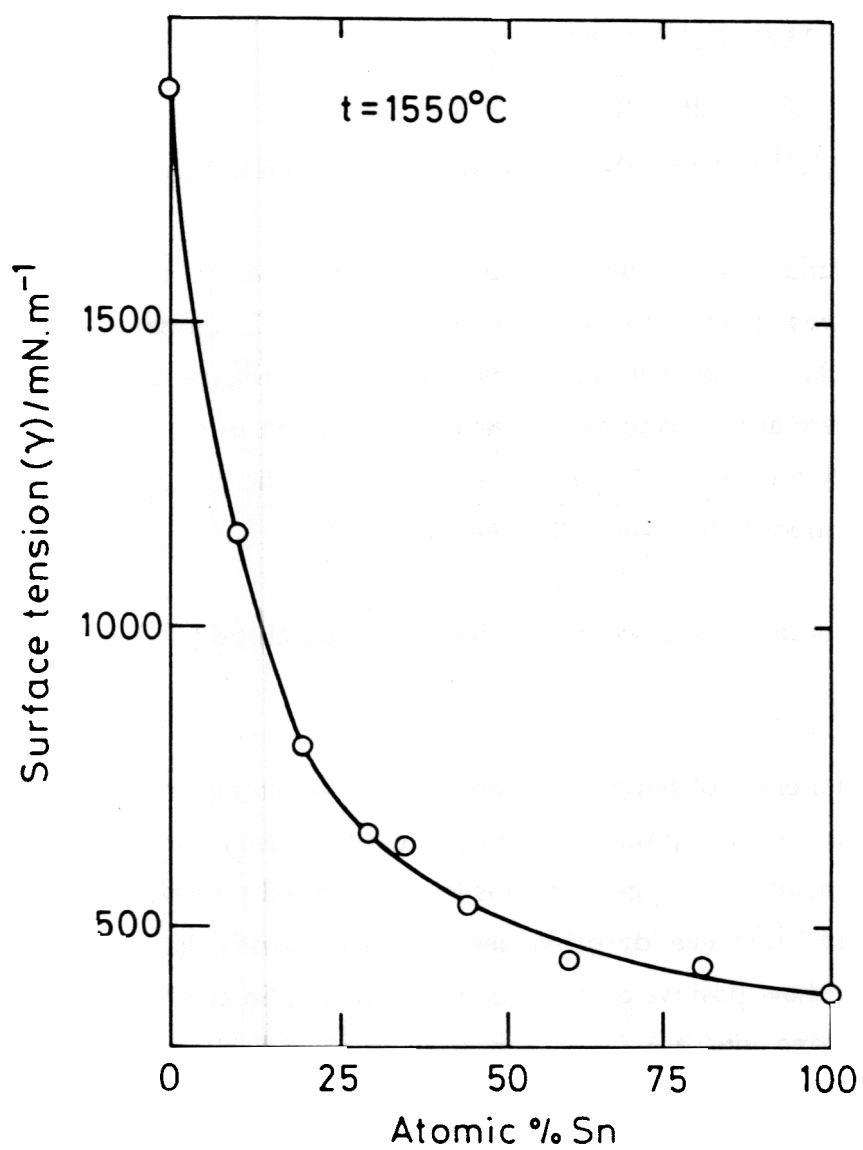


Figure 25 Effect of composition on the surface tension of Sn + Co alloys (Reshchetnikov)⁽¹⁰⁾.

Sn + Cu

Comments

Suggested⁽¹⁾ mean $\gamma(t)$ relations for (i) Cu and (ii) pure Cu are:-

$$\left. \begin{array}{l} \text{(i)} \quad \gamma = 1330 - 0.23 (t-1085) \\ \text{(ii)} \quad \gamma = 1374 - 0.26 (t-1085) \end{array} \right\} \quad (t \text{ in } ^\circ\text{C})$$

Surface tension data^(14,18-23) for the Sn+Cu system are given in Figures 26-32.

Kawai et al⁽¹⁸⁾ found a monotonic decrease in (γ) of Sn+Cu alloys at 1200 °C with increase in [Sn] and showed good agreement with the results of Lauermann and Sauerwald⁽¹⁹⁾ (Figure 26). Similar results were found by Raue et al⁽²⁰⁾ (Figure 27) and by Yu et al⁽²¹⁾ (Figure 28a). There are indications of a small perturbation in the γ ([Sn]) curves⁽¹⁸⁻²⁰⁾ at around 30 mass % Sn (18.7 at % Sn). (Yu et al gave insufficient experimental data in the vicinity of this composition to verify the phenomenon.)

Kawai et al also observed a discontinuity in the density curve for this system at around 20 at.% Sn.

With regard to the effect of temperature on (γ), both the studies of Sauerwald⁽¹⁴⁾ and of Zagonkin⁽²²⁾ show strong positive temperature coefficients for Cu, which suggests contamination, probably by oxygen which is known to yield positive coefficients with this metal. (Sauerwald found +ve ($d\gamma/dt$) values for all the Cu-rich alloys studied.) The data given by Yu et al show positive coefficients for 37 mass % Sn and for 50 mass % Sn, with temperature buffering ($d\gamma/dt = 0$) at compositions around 70 mass % Sn and between 37 mass % Sn and 10 mass % Sn. This is in general agreement with the data of Kawai et al who obtained $\gamma(t)$ curves with positive slope for compositions between approximately 30 mass % Sn and 60 mass % Sn; the most positive value for ($d\gamma/dt$) being found for 32 mass % Sn. It was suggested^(18,21) that the positive temperature coefficients could be due to progressive dissociation at the surface of atomic clusters associated with the γ -phase of the system.

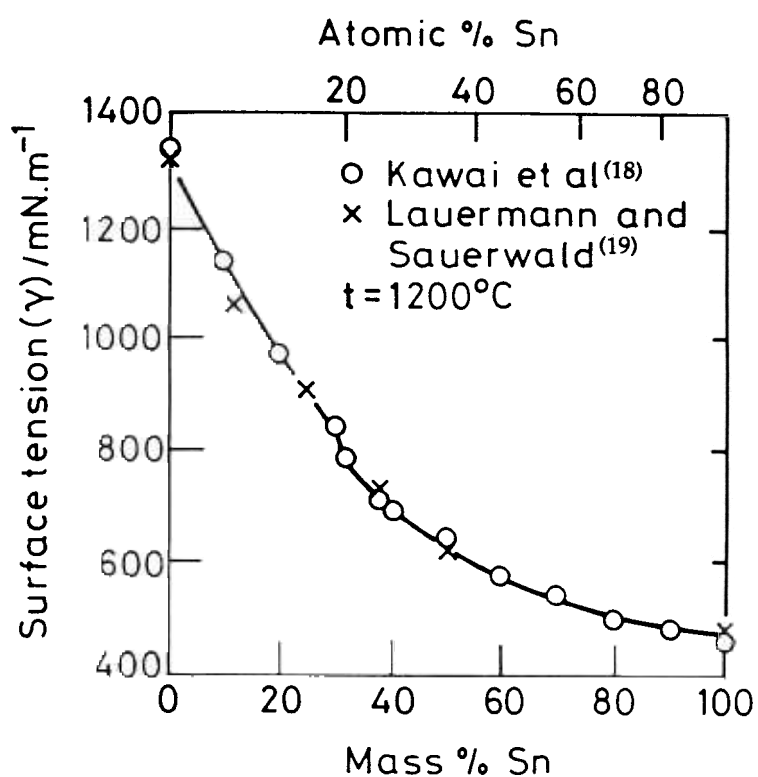


Figure 26 Curve showing the agreement between the data obtained by (Kawai)⁽¹⁸⁾ and by (Lauermaun) for the variation of surface tension with the composition of Sn + Cu alloys.

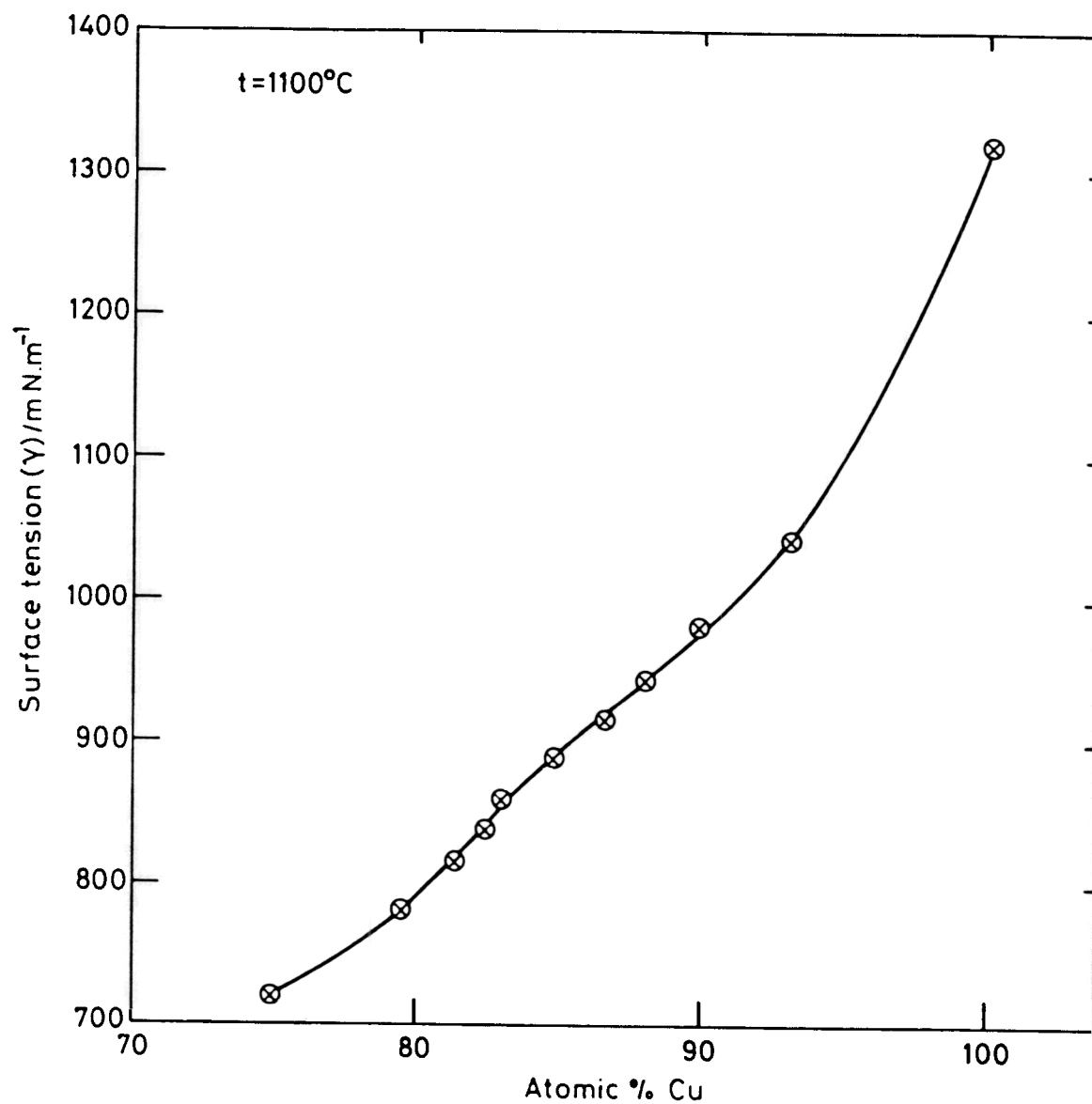


Figure 27 Relation between the surface tension and composition of Sn + Cu alloys (Raue)⁽²⁰⁾.

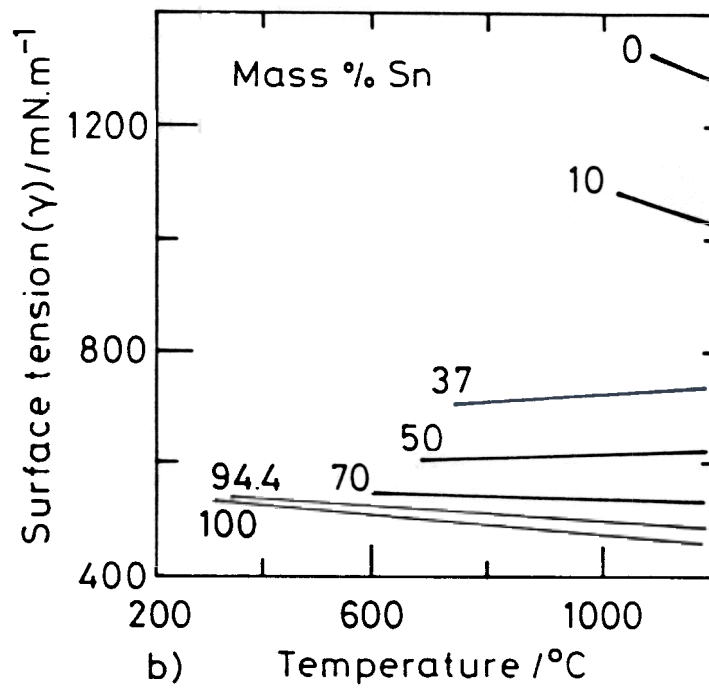
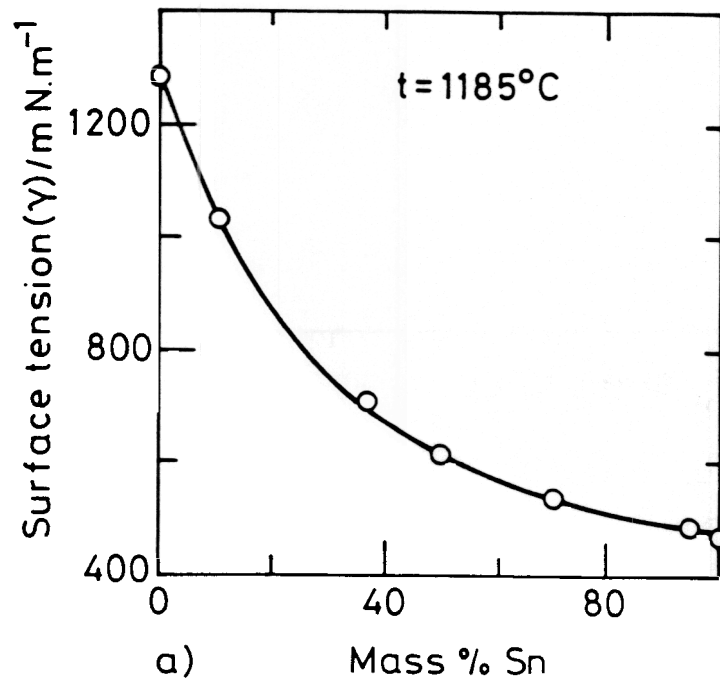


Figure 28(a) Effect of composition on the surface tension of Sn + Cu alloys at 1185 $^\circ\text{C}$.

(b) Effect of temperature on the surface tension of Sn, Cu and Sn + Cu alloys (note curves indicating positive $\frac{d\gamma}{dT}$) (Yu)⁽²¹⁾.

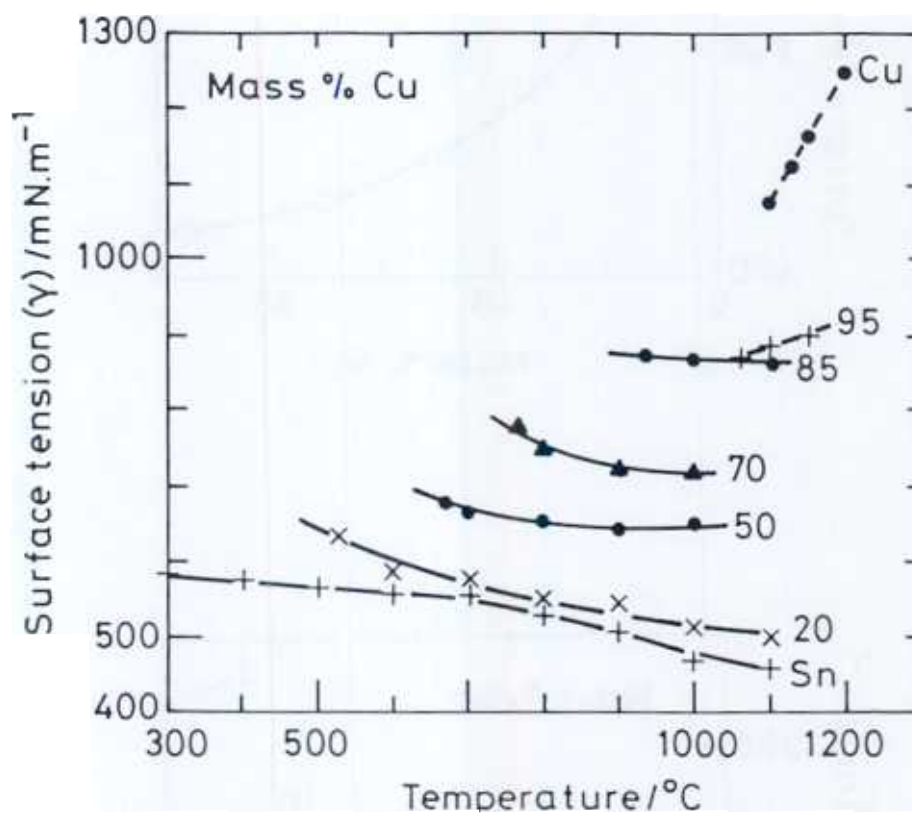


Figure 29 Effect of temperature on the surface tension of Sn, Cu and some of their alloys (Zagonkin)⁽²²⁾. [Note positive $\frac{d\gamma}{dT}$ for pure Cu suggests that the metal was contaminated with a surfactant (probably oxygen)].

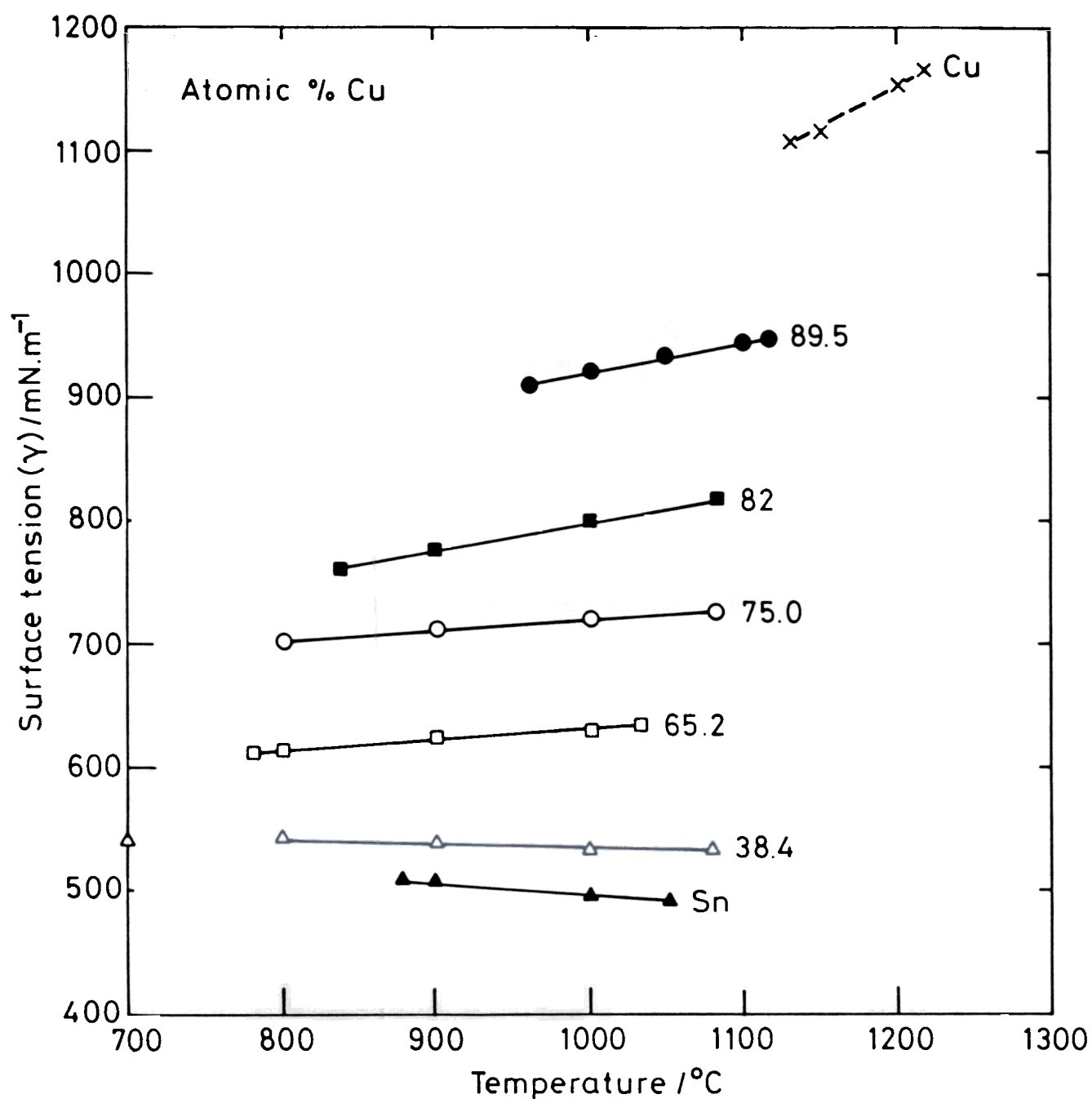


Figure 30 Effect of temperature on the surface tension of Sn, Cu and some of their alloys (Sauerwald)⁽¹⁴⁾. [Note the positive value of $\frac{d\gamma}{dT}$ for pure Cu suggests that the metal was probably contaminated with oxygen].

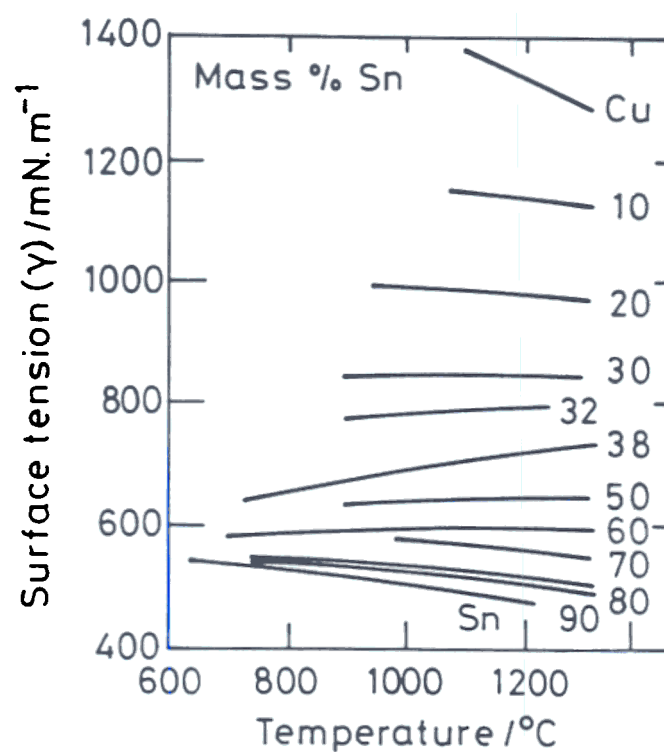


Figure 31 Effect of temperature on the surface tension of Sn, Cu and some of their alloys (Kawai)⁽¹⁸⁾.

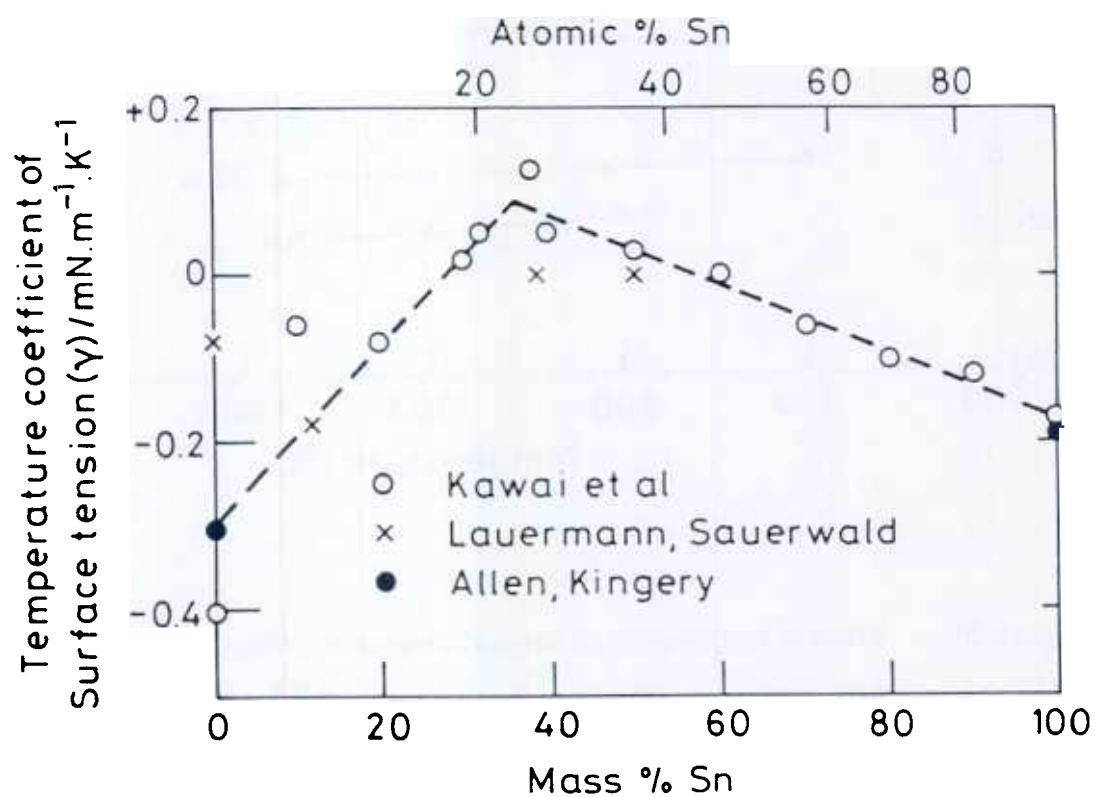


Figure 32 Comparison of the values obtained for surface entropy of Sn + Cu alloys by (Kawai)⁽¹⁸⁾, (Lauermann)⁽¹⁹⁾ and (Allen)⁽²³⁾.

Sn + Fe

Comments

Suggested⁽¹⁾ mean $\gamma(t)$ relations for (i) Fe and (ii) pure Fe are:-

$$\left. \begin{array}{ll} \text{(i)} & \gamma = 1862 - 0.39 (t-1530) \\ \text{(ii)} & \gamma = 1909 - 0.52 (t-1530) \end{array} \right\} (t \text{ in } ^\circ\text{C})$$

Surface tension data for the Sn+Fe system are given in Figures 33-34. The $\gamma(\text{[Sn]})$ data given in Figure 33 show good agreement between Kozakevitch and Urbain⁽²⁵⁾, Nizhenko and Floka⁽²⁶⁾ and Dyson⁽²⁷⁾. The study of Nizhenko and Floka covered the whole composition range and shows a monotonic decrease in (γ) with increase in $[\text{Sn}]$ at 1550 °C. Similar results were obtained by Zhukov and Maslova⁽²⁸⁾ (Figure 34a) for a higher temperature (1640 °C). These authors found positive temperature coefficients of surface tension (Figure 34b) for the Fe-rich compositions, with temperature buffering ($d\gamma/dt = 0$) at approximately 2 at.% Sn and at 54 at.% Sn. The positive coefficients were thought to be due to desorption of Sn from the surface layer as temperature increased. (Note:- low levels of oxygen in pure iron are known⁽²⁴⁾ to give rise to positive temperature coefficients, but it is uncertain whether this behaviour also applies to Fe+Sn alloys.

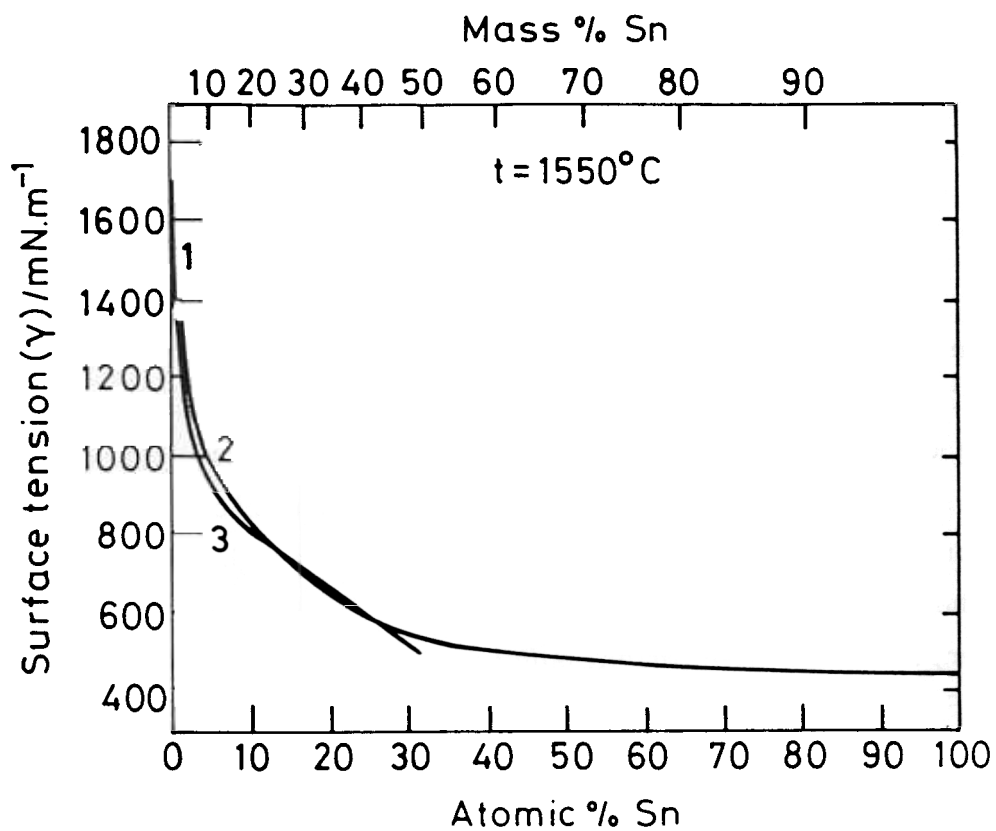


Figure 33 Relations between surface tension and composition of Sn + Fe alloys at 1550 °C (Keene)⁽²⁴⁾.

Curve 1 - (Kozakevitch)⁽²⁵⁾

Curve 2 - (Nizhenko)⁽²⁶⁾

Curve 3 - (Dyson)⁽²⁷⁾

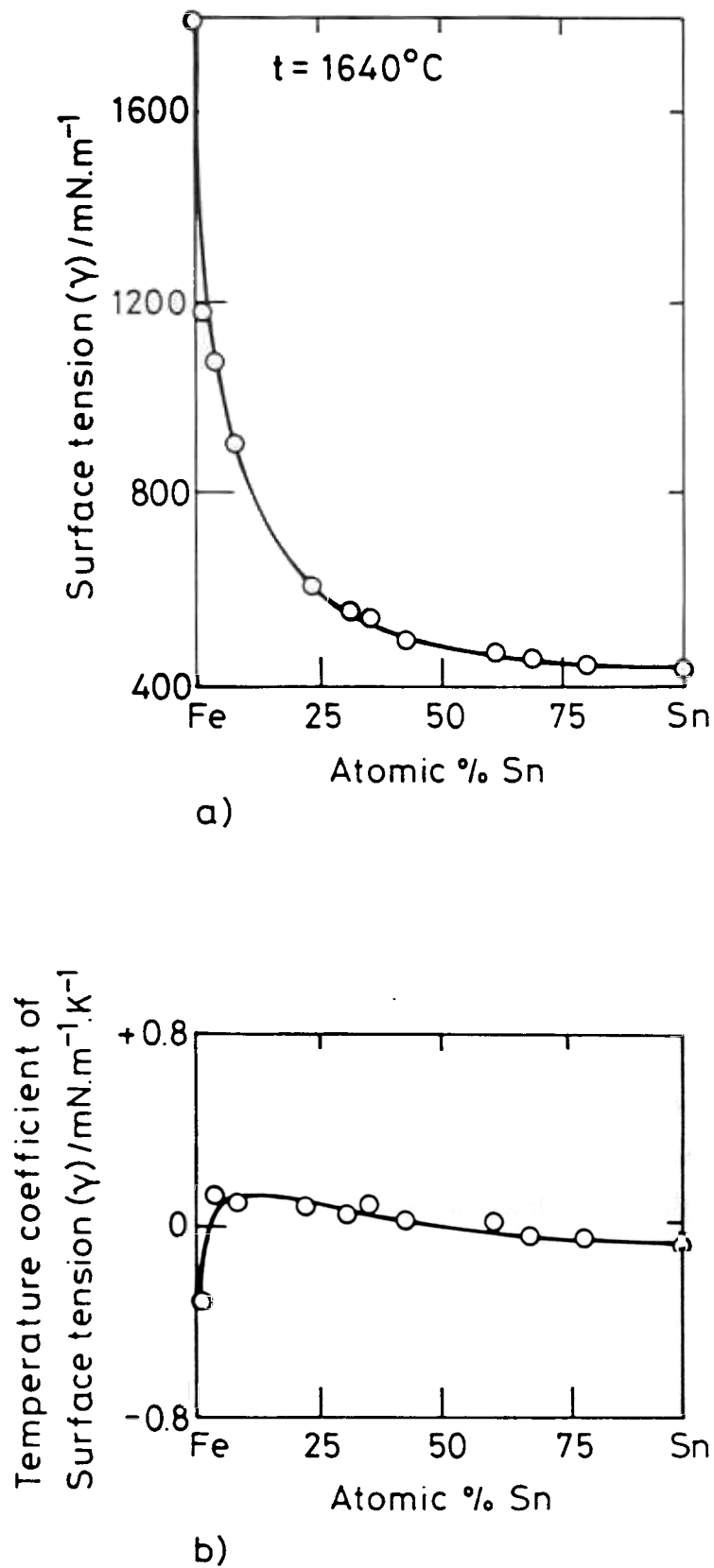


Figure 34 Effect of composition of Sn + Fe alloys on the surface tension (curve a) and the surface entropy (curve b) (Zhukov)⁽²⁸⁾.

Sn + Ga

Comments

Suggested⁽¹⁾ mean $\gamma(t)$ relations for (i) Ga and (ii) pure Ga are:-

$$\left. \begin{array}{ll} \text{(i)} & \gamma = 711 - 0.070 (t-30) \\ \text{(ii)} & \gamma = 724 - 0.072 (t-30) \end{array} \right\} \quad (t \text{ in } ^\circ\text{C})$$

Surface tension data⁽²⁹⁻³²⁾ for the Sn+Ga system are given in Figures 35-40. With one possible exception⁽³⁰⁾, all the $\gamma(\text{[Sn]})$ data are in accord (Figures 35-38) in that, for the temperatures studied, a steady decrease in (γ) with increase in $[\text{Sn}]$ is observed. Data due to Ibragimov and Nal'giev⁽³⁰⁾ (Figure 36) indicate a small perturbation in the $\gamma(\text{[Sn]})$ curve at around 60 at.% Sn but there are no compounds or eutectic in this vicinity.

For the specific compositions studied, Ofitserov et al⁽³¹⁾ (Figure 39), found positive temperature coefficients only for 10 at.% Sn, with temperature buffering ($d\gamma/dt = 0$) at around 30 at.% Sn. This is in general agreement with the results of Ibragimov and Nal'giev⁽³⁰⁾ (Figure 40) who obtained $\gamma(t)$ curves for a larger number of compositions and found positive slopes for Sn contents between 2 at.% and 26 at.%. The slopes of the $\gamma(t)$ curves are most positive at the lower temperatures.

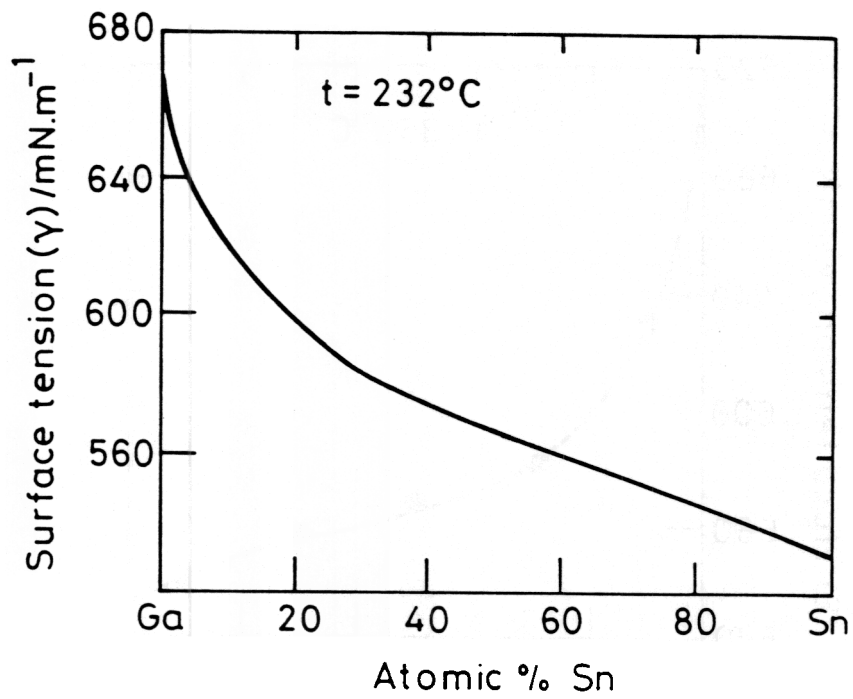


Figure 35 Variation of surface tension with composition of Sn + Ga alloys at 232°C (Kononenko)⁽²⁹⁾.

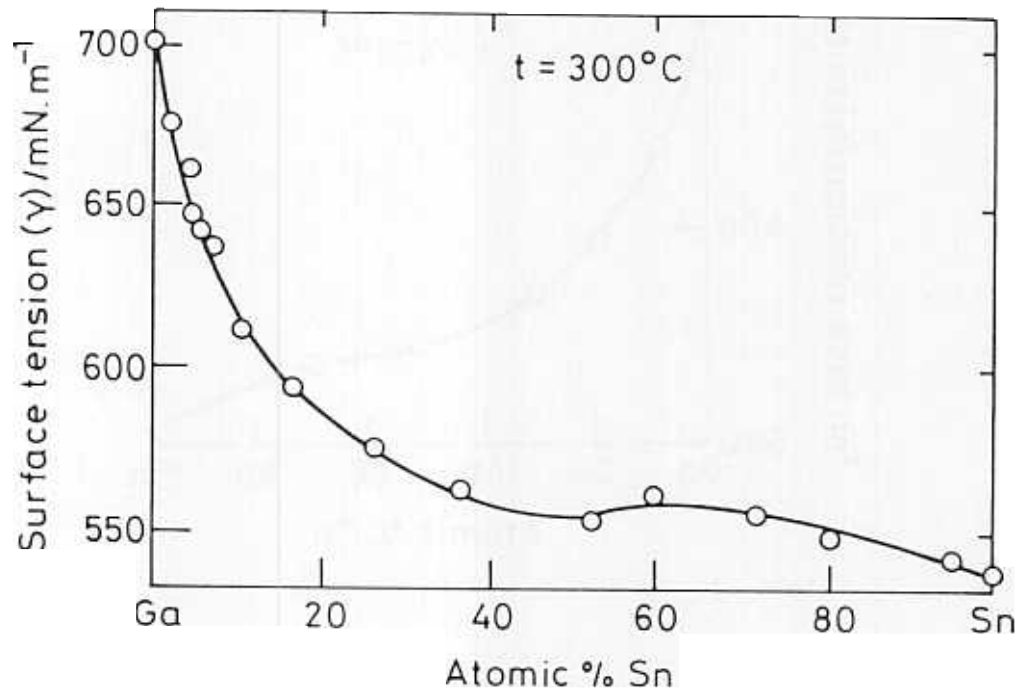


Figure 36 Variation of surface tension with composition of Sn + Ga alloys at 300°C (Ibragimov)⁽³⁰⁾.

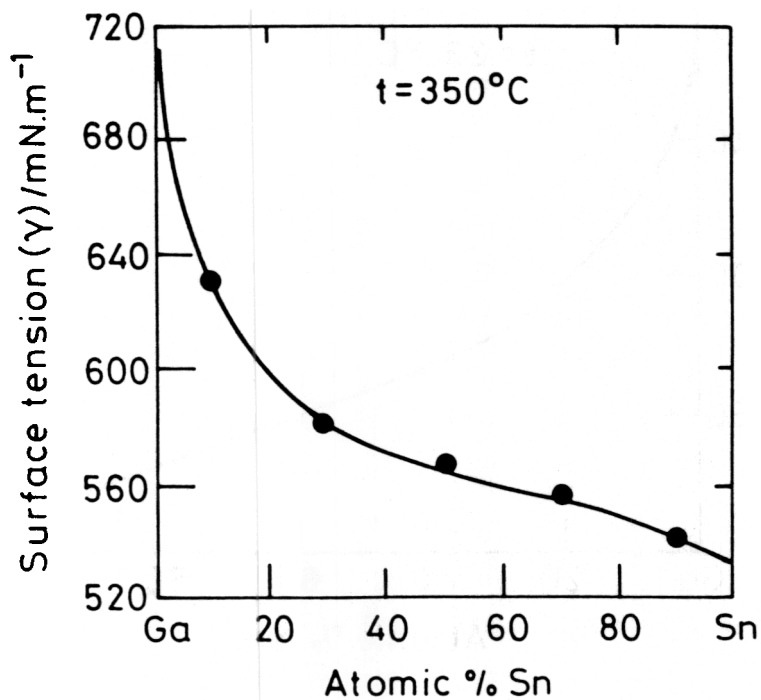


Figure 37 Variation of surface tension with composition of Sn + Ga alloys at 350°C (Ofitserov)⁽³¹⁾.

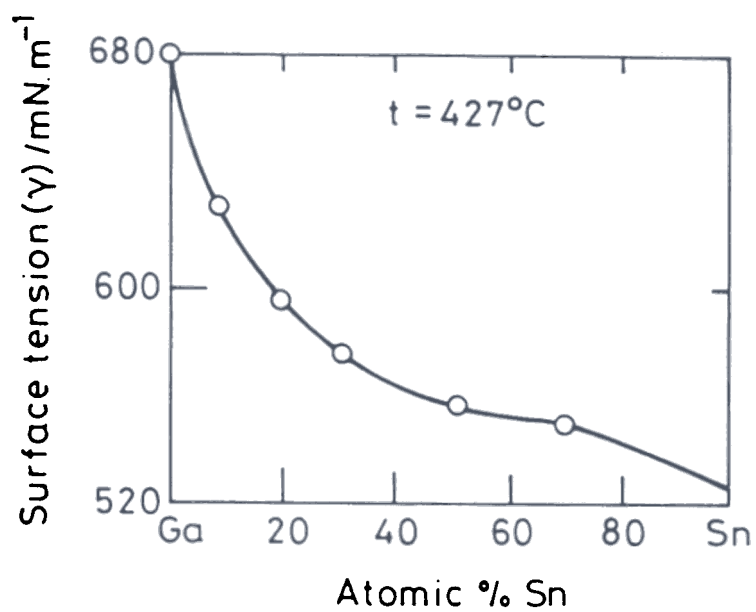


Figure 38 Variation of surface tension with composition of Sn + Ga alloys at 427°C (Sukhman)⁽³²⁾.

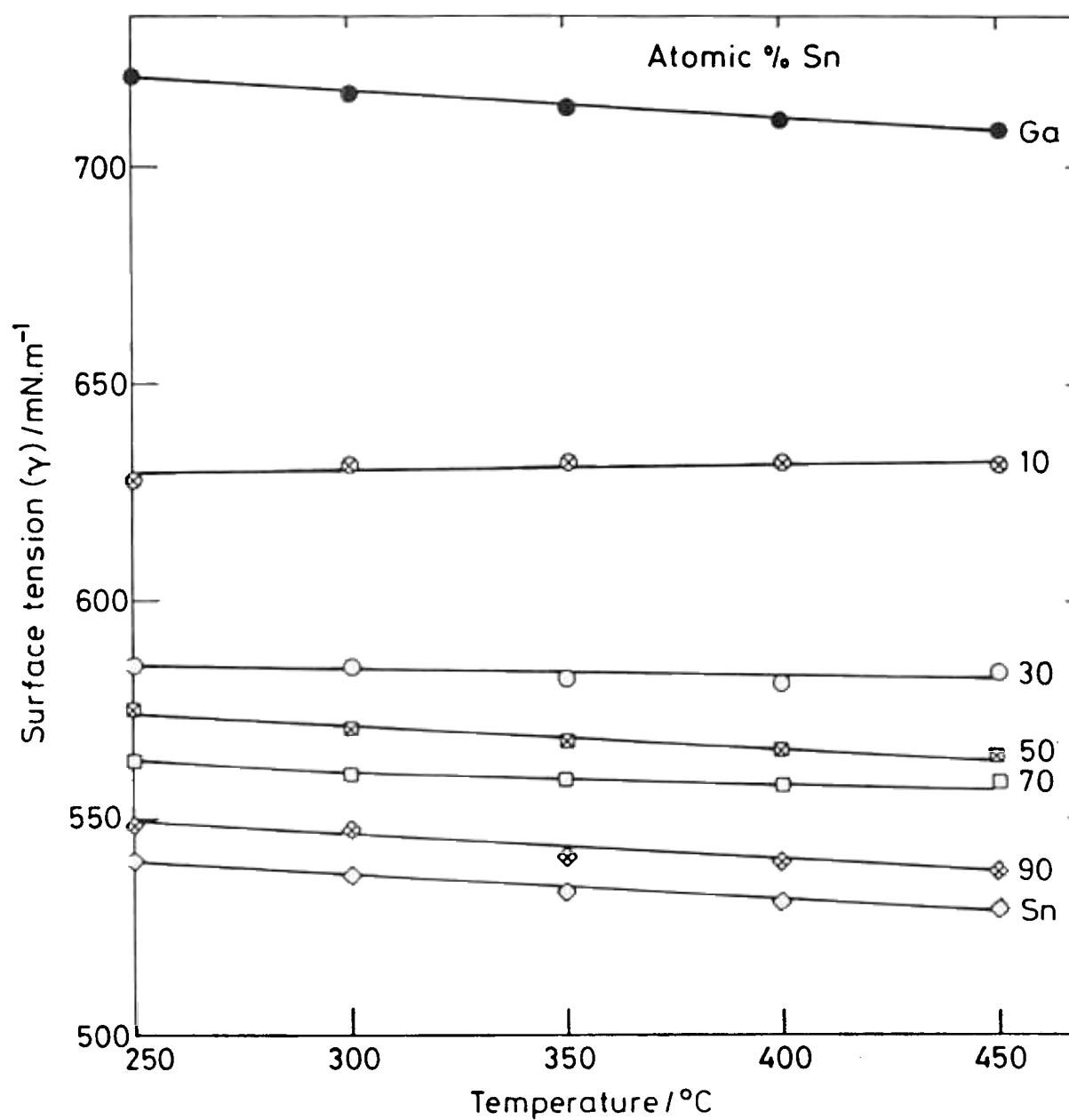


Figure 39 Effect of temperature on the surface tension of Sn, Ga and some of their alloys (Ofitserov)⁽³¹⁾.

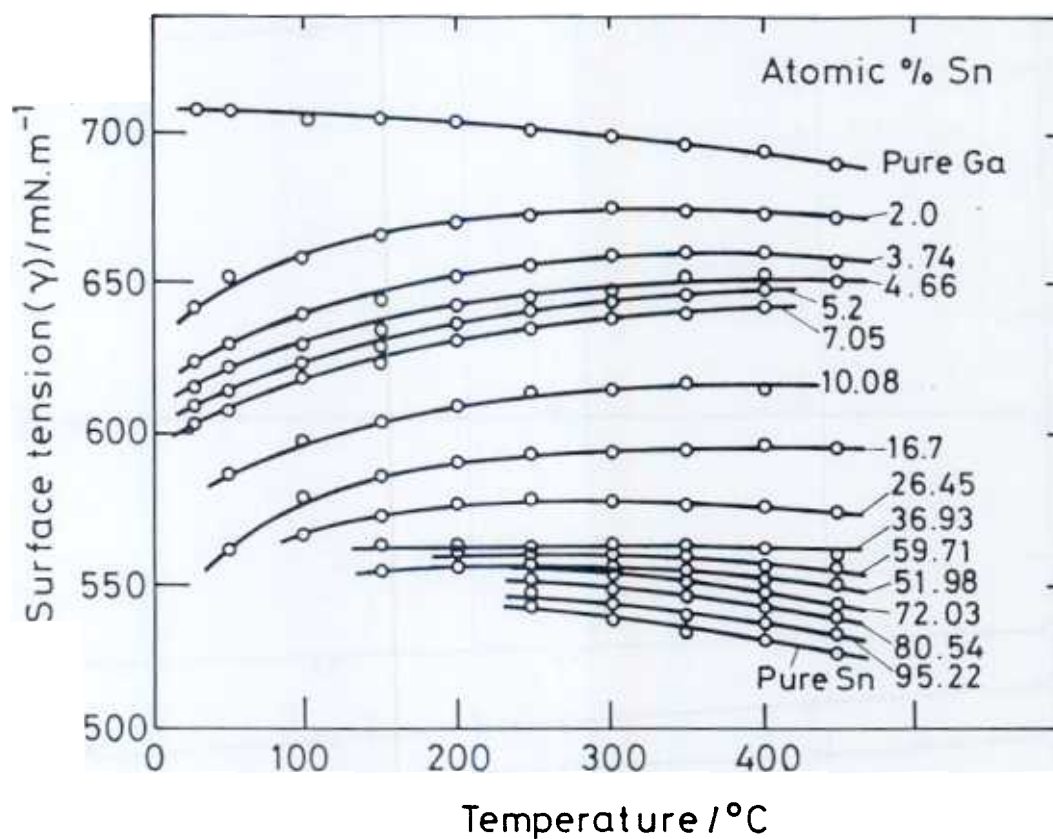


Figure 40 Effect of temperature on the surface tension of Sn, Ga and some of their alloys (Ibragimov)⁽³⁰⁾.

Sn + Ge

Comments

Suggested⁽¹⁾ mean $\gamma(t)$ relations for (i) Ge and (ii) pure Ge are:-

$$\left. \begin{array}{ll} \text{(i)} & \gamma = 607 - 0.12 (t-960) \\ \text{(ii)} & \gamma = 631 - 0.12 (t-960) \end{array} \right\} \quad (t \text{ in } ^\circ\text{C})$$

Surface tension data^(10,33-35) for the Sn+Ge system are given in Figures 41-45. Figure 41⁽³³⁾ shows that Ge is not surface-active in Sn, since up to 2 at.% addition has no significant effect on (γ) . The results of Tsuladze et al⁽³⁴⁾ and of Reshchetnikov⁽¹⁰⁾ are in good agreement (Figures 42 and 43) and show that, at 1000 °C, (γ) decreases monotonically with increase in [Sn]. Data given by Naidich and Perevertailo⁽³⁵⁾ (Figure 44) for 1000 °C, also concur with these findings, but for lower temperatures, anomalous behaviour was observed, in that a minimum was apparent in the $\gamma([\text{Ge}])$ curves, in the vicinity of 17.5 at.% Ge. The magnitude of the minimum was found to progressively decrease with increase in temperature ie in this region the temperature coefficients were positive (Figures 44 and 45). It is difficult to account for this behaviour, since the Sn+Ge phase-diagram fails to show the formation of any compound or eutectic. The $\gamma(t)$ curves shown in Figure 44 suggest that temperature buffering ($d\gamma/dt = 0$) would occur at around 10 at.% Ge and 42 at.% Ge.

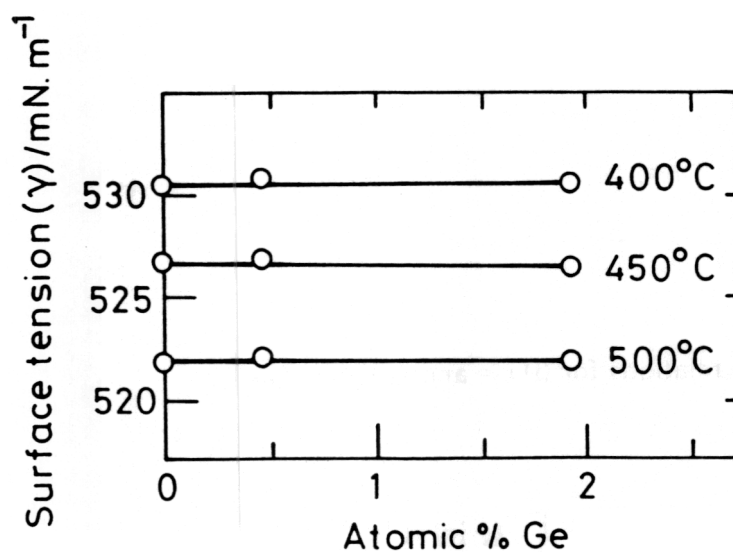


Figure 41 Effect of small additions of Ge on the surface tension of Sn at three different temperatures (Pokrovskii)⁽³³⁾.

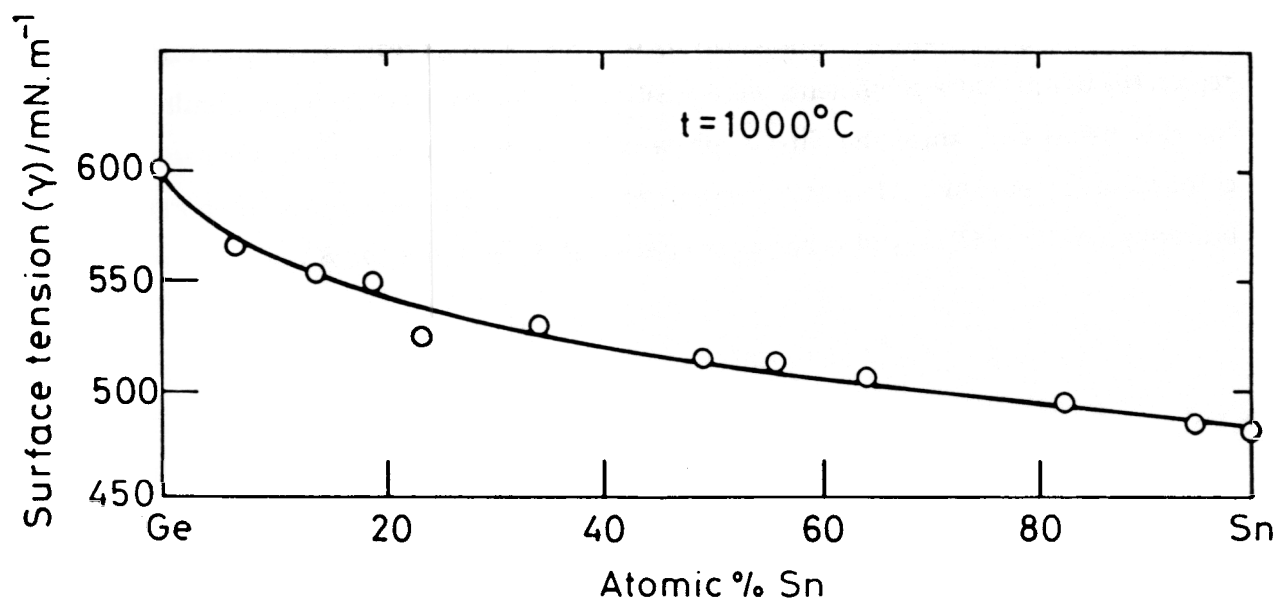


Figure 42 Variation of surface tension with composition of Sn + Ge alloys at 1000 °C (Tsuladze)⁽³⁴⁾.

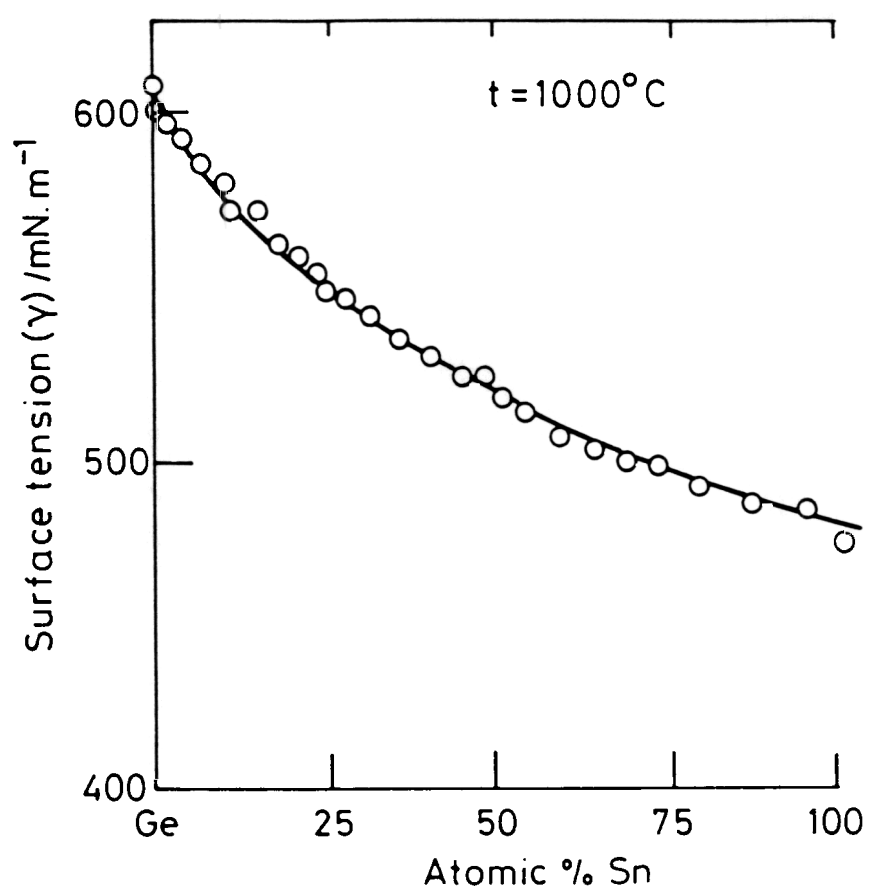


Figure 43 Variation of surface tension with composition of Sn + Ge alloys at 1000 °C
(Reshetnikov)⁽¹⁰⁾

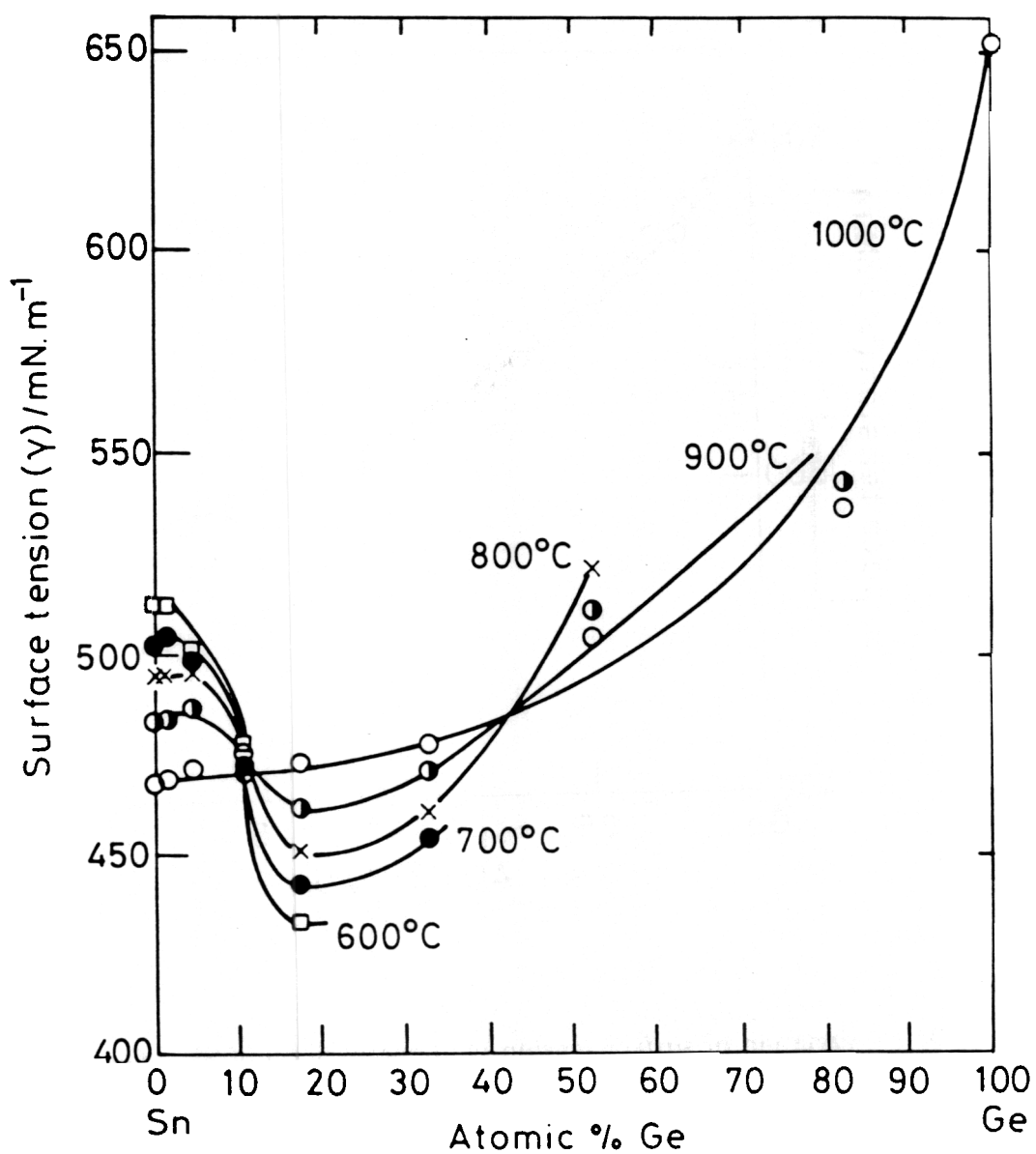


Figure 44 Effect of composition and temperature on the surface tension of Sn + Ge alloys (Naidich)⁽³⁵⁾.

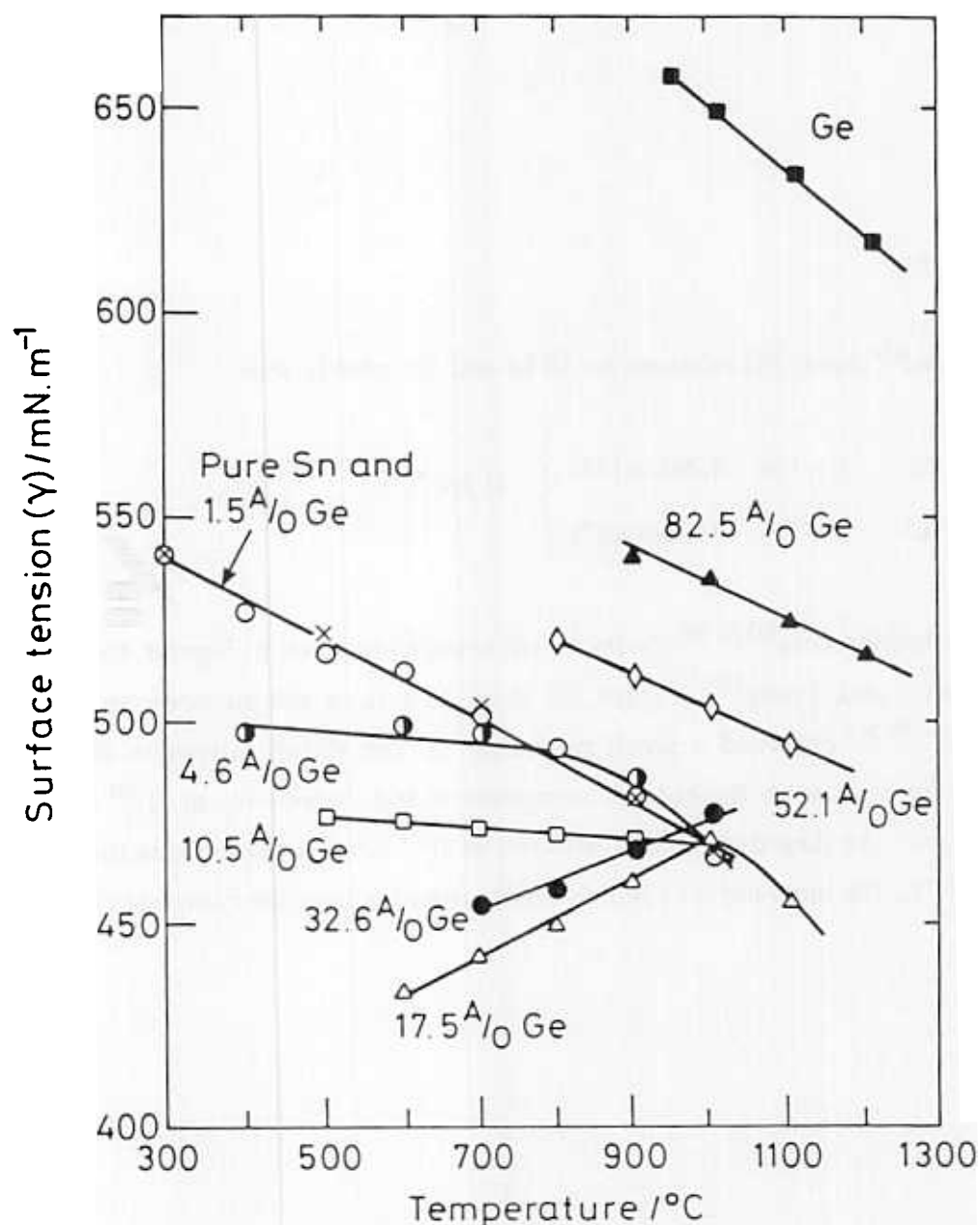


Figure 45 Effect of temperature on the surface tension of Sn, Ge and some of their alloys (Naidich)⁹⁵.

Sn + In

Comments

Suggested⁽¹⁾ mean $\gamma(t)$ relations for (i) In and (ii) pure In are:-

$$\left. \begin{array}{l} \text{(i)} \quad \gamma = 556 - 0.090 (t-157) \\ \text{(ii)} \quad \gamma = 561 - 0.095 (t-157) \end{array} \right\} \quad (t \text{ in } ^\circ\text{C})$$

Surface tension data^(33,36-39) for the Sn+In system are given in Figures 46-50. The results of Pokrovskii and Tissen⁽³³⁾ (Figure 50) show that In is not surface-active in Sn. Several studies^(36,37,39) observed a small minimum on the $\gamma(\text{[Sn]})$ curves in the vicinity of 50-60 at.% Sn ie close to the eutectic composition, but Kononenko et al⁽³⁸⁾ failed to find any minimum. The data derived by Dadashev et al⁽³⁹⁾ (Figure 49) indicate that between 250 °C and 500 °C, the temperature coefficients are negative over the complete composition range.

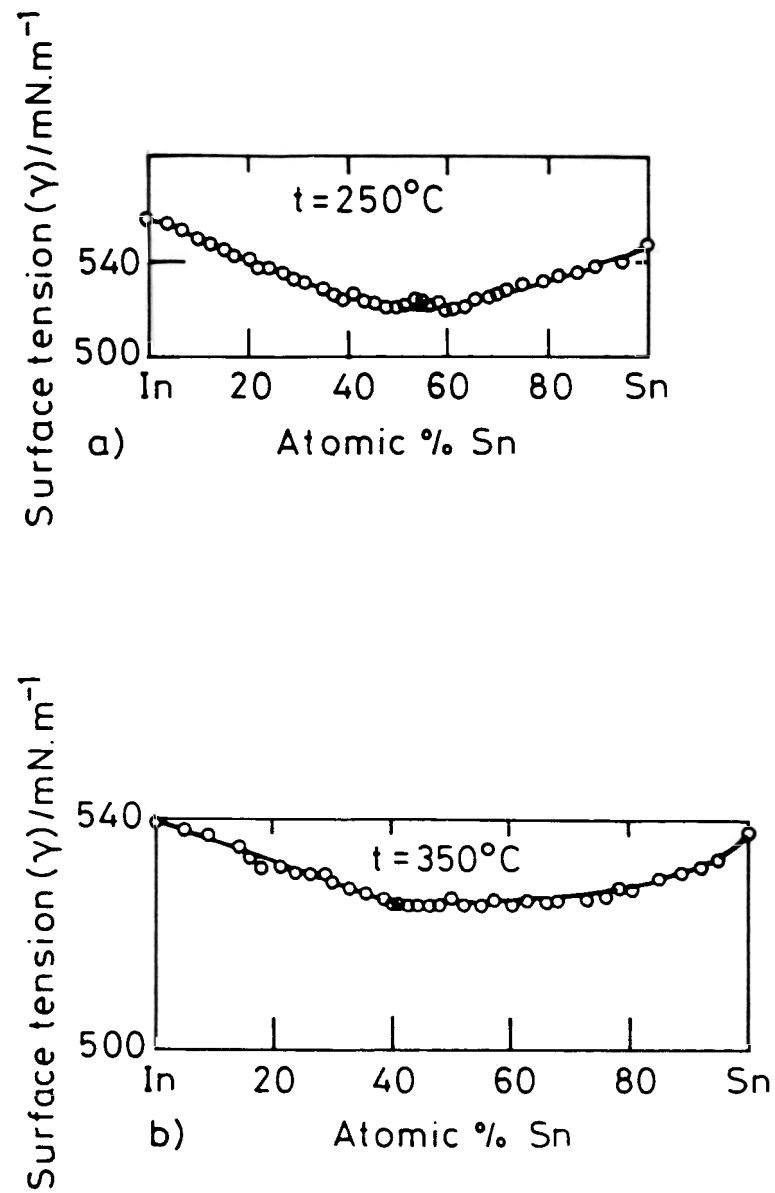


Figure 46 Effect of composition on the surface tension of Sn + In alloys at 250 °C (Figure (a)) and at 350 °C (Figure (b)) (Koval'chuk)⁽³⁶⁾.

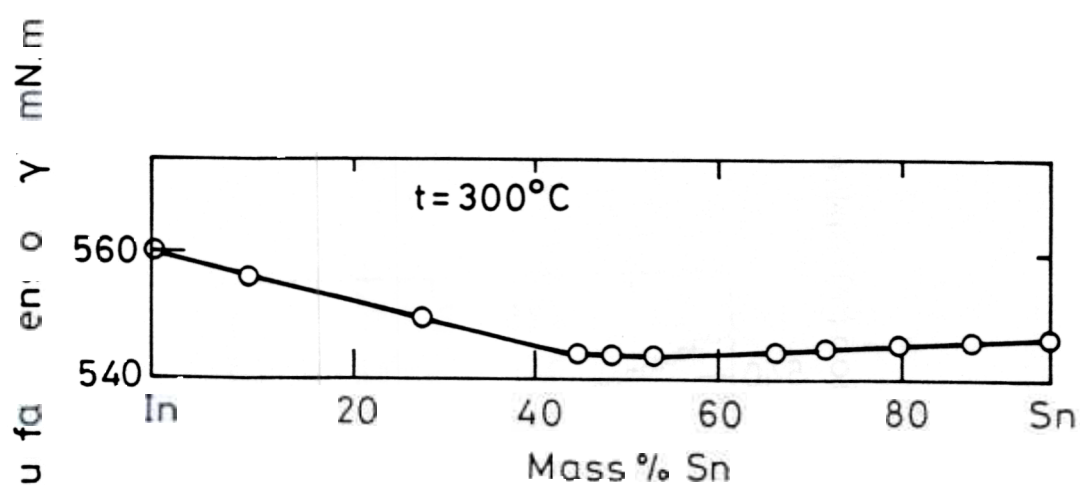


Figure 47 Effect of composition on the surface tension of Sn-In alloys at 300 °C (Ozniev)⁽³⁷⁾

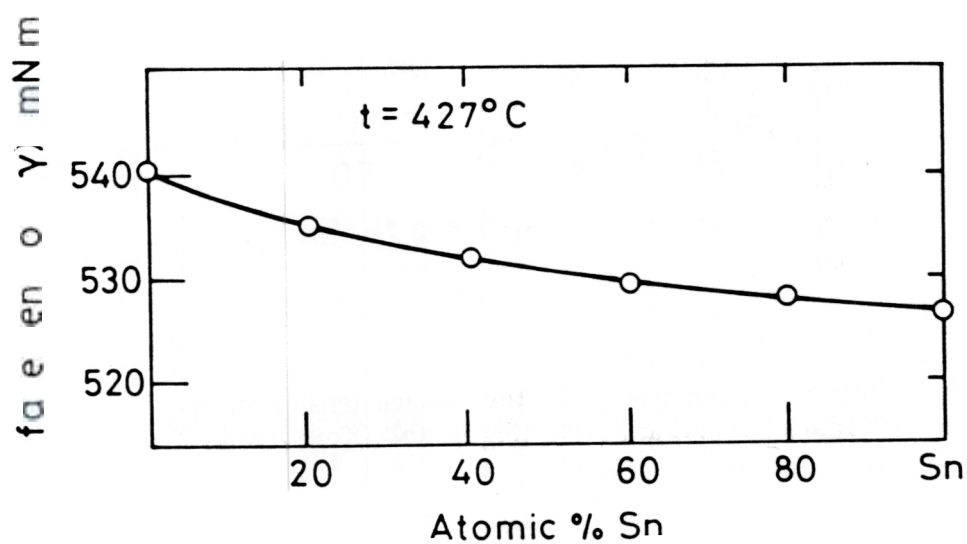


Figure Effect of composition on the surface tension of Sn-In alloys at 427 °C (Kononenko)⁽³⁸⁾

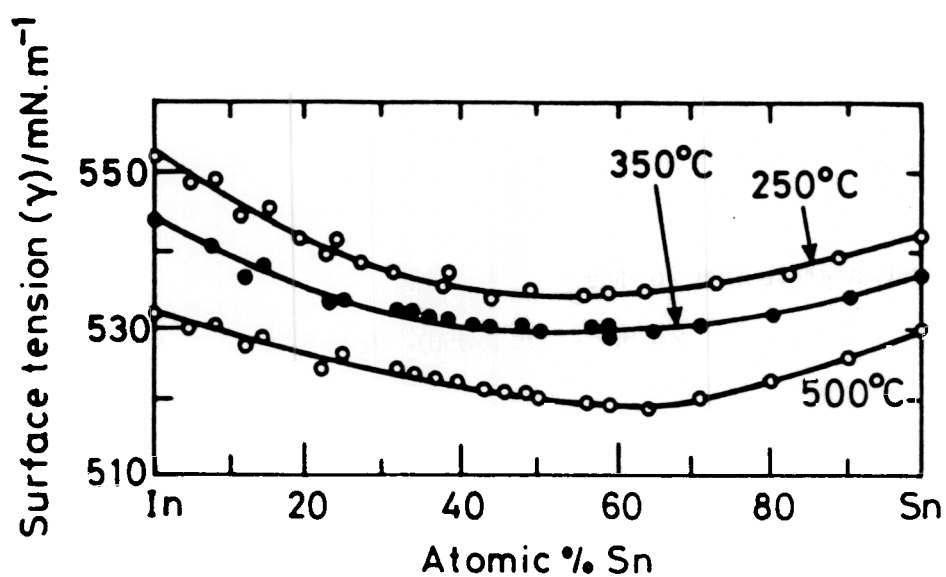


Figure 49 Variation of surface tension of Sn + In alloys at three different temperatures (Dadashev)⁽³⁹⁾.

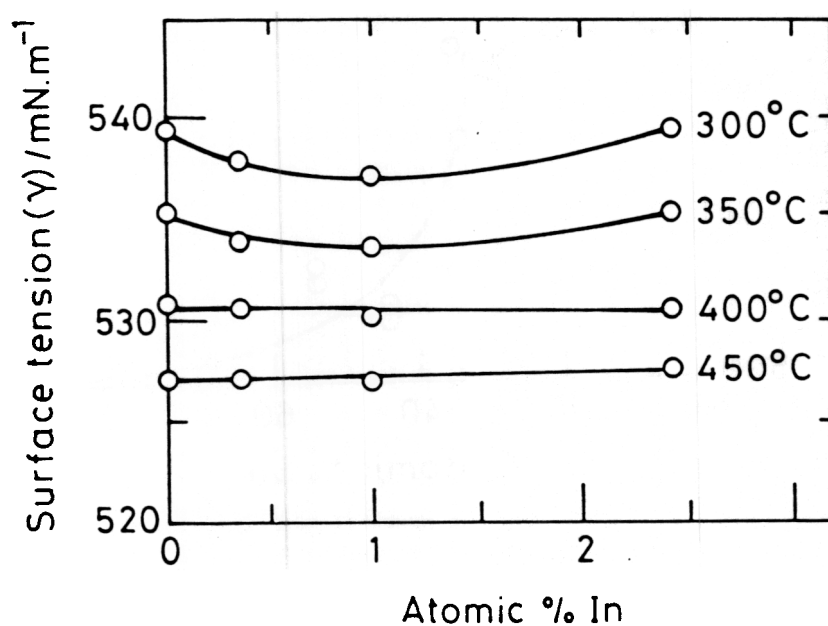


Figure 50 Effect of small additions of In on the surface tension of Sn at four different temperatures (Pokrovskii)⁽³³⁾.

Sn + Mg

Comments

Suggested⁽¹⁾ mean $\gamma(t)$ relation for Mg is:-

$$\gamma = 577 - 0.26 (t-650) \quad (t \text{ in } ^\circ\text{C})$$

Surface tension data⁽⁴⁰⁾ for the Sn+Mg system are given in Figure 51. The $\gamma(\text{Sn})$ curve for 800 °C shows that as the Sn content is progressively increased there is little change in the surface tension until the vicinity of 33 at.% Sn (Mg_2Sn), at which point there is an abrupt decrease in (γ) .

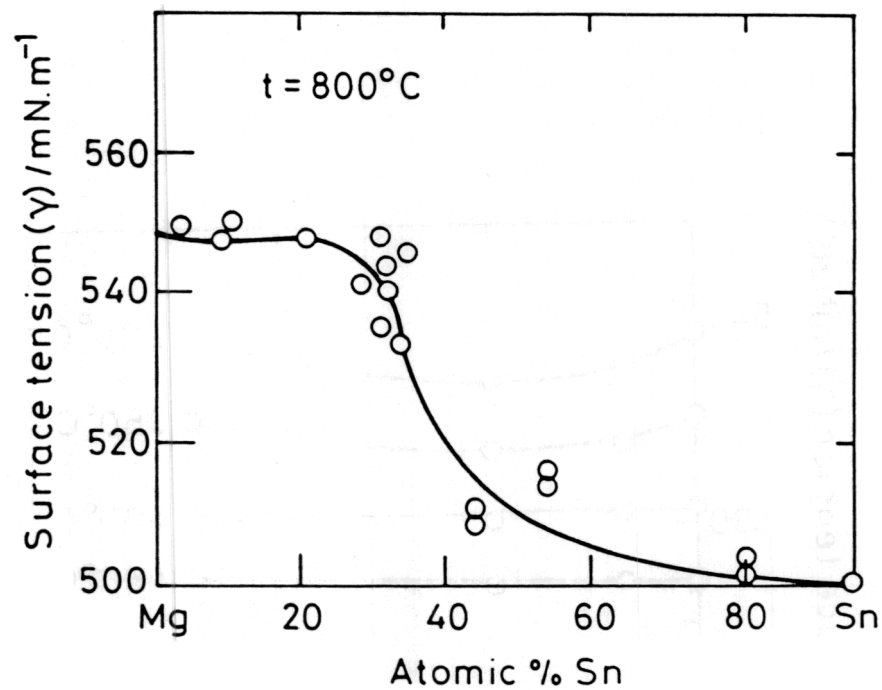


Figure 51 Variation of surface tension with composition of Sn + Mg alloys at 800 °C (Eremenko)⁽⁴⁰⁾.

Sn + Mn

Comments

Suggested⁽¹⁾ mean $\gamma(t)$ relation for Mn is:-

$$\gamma = 1152 - 0.35 (t - 1245) \quad (t \text{ in } ^\circ\text{C})$$

Surface tension data⁽¹⁵⁾ for the Sn+Mn system are given in Figure 52. Only a small range of compositions (up to about 4.5 at.% Mn) have been studied. The $\gamma(\text{[Mn]})$ curves show that there is only a slight increase in (γ) for manganese additions up to 4.5 at. %. Figure 52 also shows that, for the compositions studied, over the temperature range 400° - 500 °C, all temperature coefficients are negative.

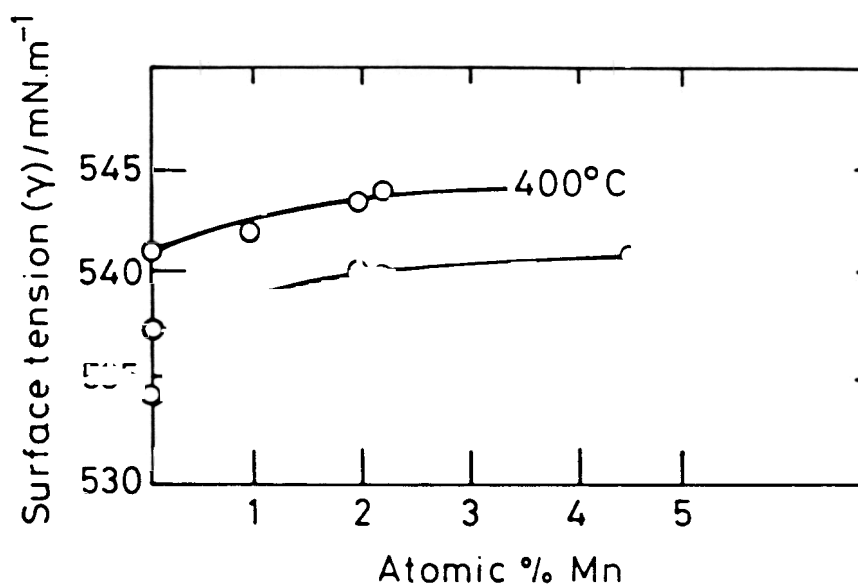


Figure 52 Effect of small additions of Mn on the surface tension of Sn at three different temperatures (Pokrovskii)⁽¹⁵⁾.

Sn + Ni

Comments

Suggested⁽¹⁾ mean $\gamma(t)$ relations for (i) Ni and (ii) pure Ni are:

$$\left. \begin{array}{ll} \text{(i)} & \gamma = 1796 - 0.35 (t-1455) \\ \text{(ii)} & \gamma = 1834 - 0.376 (t-1455) \end{array} \right\} (t \text{ in } ^\circ\text{C})$$

Surface tension data⁽⁴¹⁾ for the Sn+Ni system are given in Figure 53, which shows a monotonic decrease in (γ) with increase in [Sn] over the whole composition range at 1500 °C.

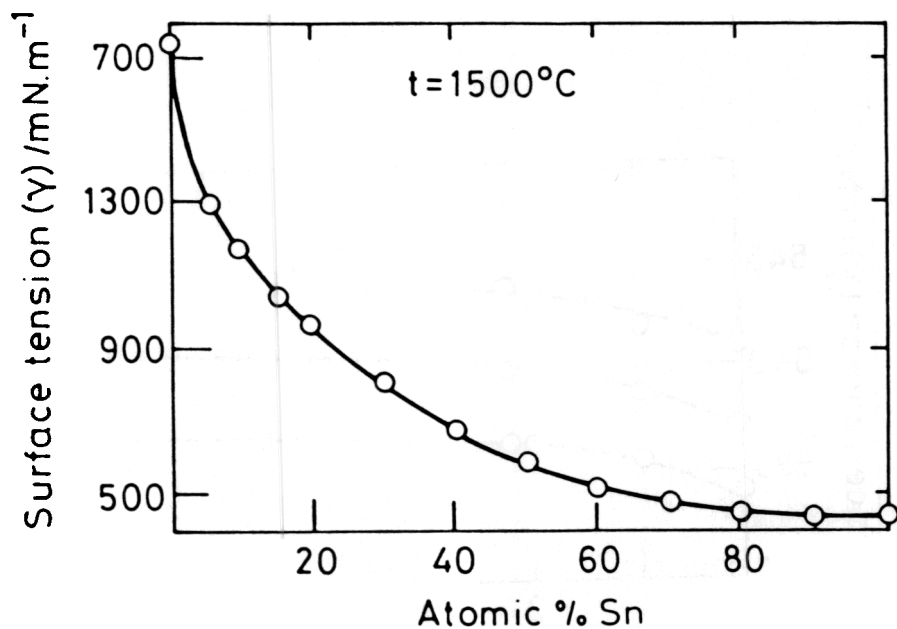


Figure 53 Variation of surface tension with composition of Sn + Ni alloys at 1500 °C (Nizhenko)⁽⁴¹⁾.

Sn + O

Comments

Data^(42,43) for the effect of oxygen on the surface tension of tin are given in Figures 54-55. Passerone et al⁽⁴²⁾ note that the molar fraction of oxygen at bulk saturation in Sn is very low (1.8×10^{-8} at 300 °C). Since the bulk content corresponding to maximum oxygen adsorption at the surface is significantly less than this, it follows that even under carefully controlled environmental conditions, it is easily possible to have sufficient residual oxygen to produce surface saturation. The results of Passerone et al show that oxygen is strongly surface-active in tin, most notably in the vicinity of the melting point, where a difference $\sim 110 \text{ mN.m}^{-1}$ was found between the value of (γ) for Sn in equilibrium with a $P_{\text{O}_2} < 10^{-20}$ bar and that for oxidised Sn. This is in general agreement with the work of Bradhurst and Buchanan*. No actual values for (γ) of the Sn+O system were quoted in this source, but the authors found that at 800 °C the maximum observed reduction in (γ) (at oxygen saturation) was 20.4% ie if, based on the data in ref (1), (γ) of Sn at 800 °C is taken to be about 515 mN.m^{-1} , the (γ) of oxygen-saturated material would be about 100 mN.m^{-1} lower.

The individual data points by Sangiorgi et al⁽⁴³⁾ (Figure 54) were obtained from measurements on sessile drops contained in the chamber of an Auger spectrometer. With this system it was possible to establish a range of equilibrium oxygen levels in the tin by ion-etching of the sample and subsequent exposure to controlled atmospheres. Measurements were made on the variation of (γ) with the Auger peak height ratio (R) (Figure 55) (where $R = \frac{\text{height of oxygen Auger peak}}{\text{height of tin Auger peak}}$). For (R) values up to ~ 0.2 (ie the

lowest oxygen levels), the (γ) of Sn at 287 °C remained virtually constant (598 mN.m^{-1}). At this point there was an abrupt decrease in (γ) (to $\sim 535 \text{ mN.m}^{-1}$). Further increase in (R) produced little change in (γ) . To supplement the Auger spectrometry results, Sangiorgi et al also carried out LEELS experiments on low (R) systems. A model based upon their overall data suggested that, over the region up to $R = 0.2$, "islands" of SnO were floating on the metal, and that the abrupt change in (γ) at $R = 0.2$ was due to the formation of a continuous oxide layer at the surface. At higher (R) values, a chemical shift in the Sn Auger peak was observed which would be consistent with the $\text{SnO} \rightarrow \text{SnO}_2$ transition. The fact that there was no change in (γ) associated with the observed chemical shift verified the existence of a continuous oxide layer at the surface.

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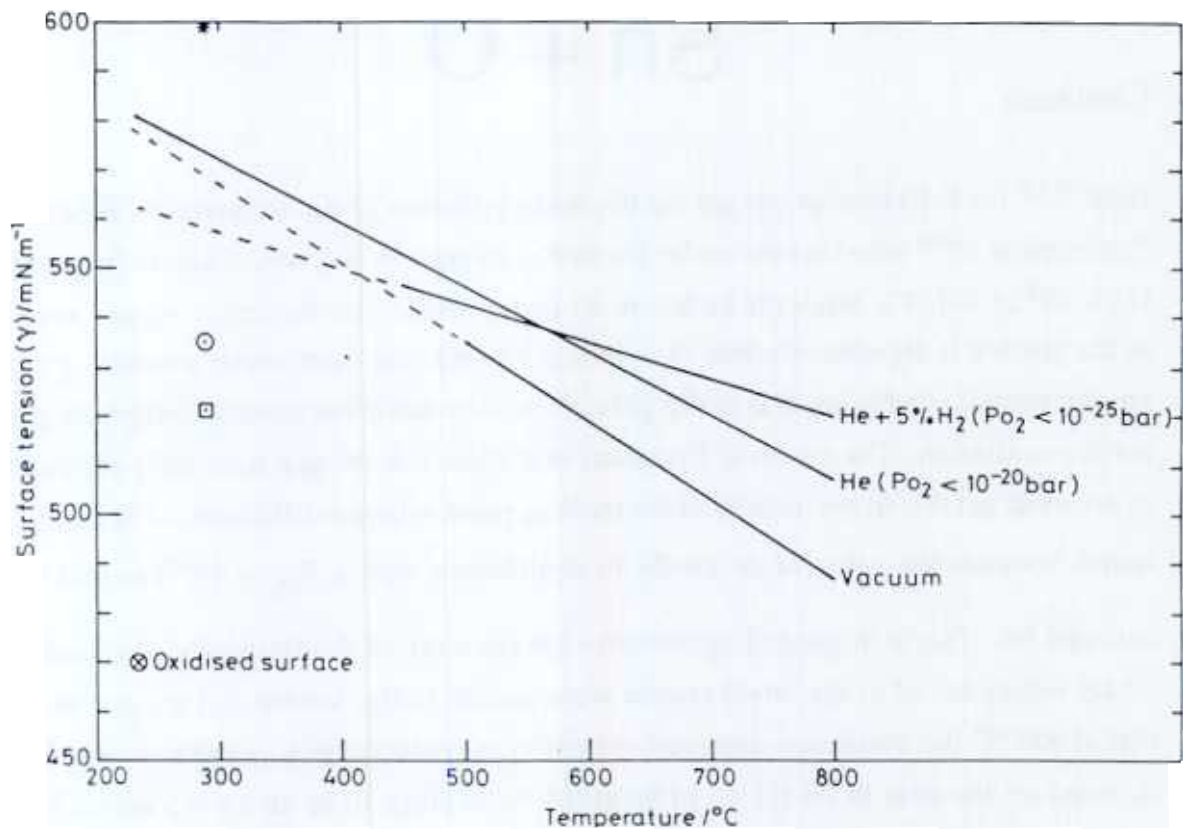


Figure 54 Variation of the surface tension of Sn with temperature under different oxidation conditions.

⊗ and curves - (Passerone)⁽⁴²⁾.

- - As-received Sn melted in vacuum (4×10^{-5} Pa)
- - As-received Sn after holding under 10^{-6} Pa for 16 hr at 287 °C) (Sangiorgi)⁽⁴³⁾
- Sn under very low partial pressure of oxygen)

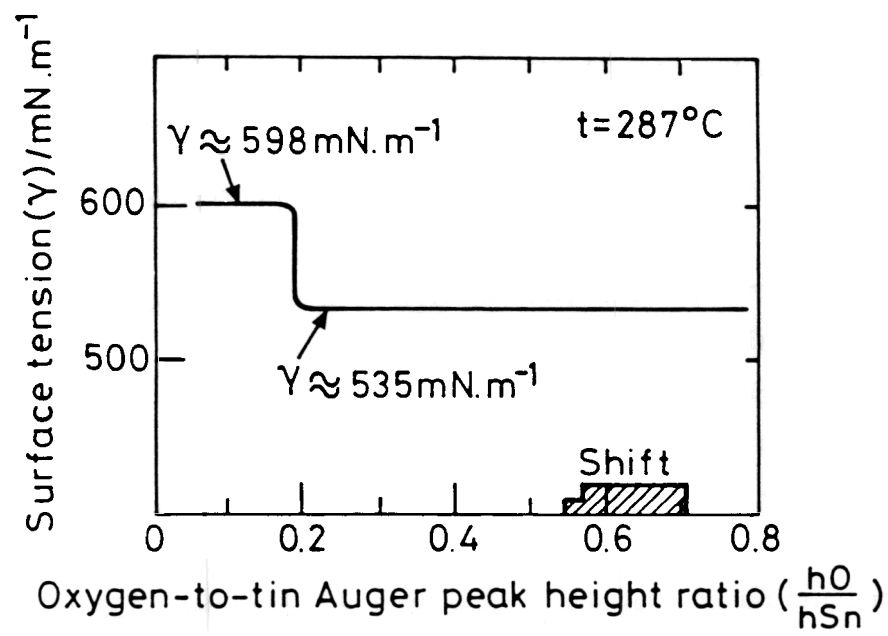


Figure 55 Change in surface tension of Sn at 287 °C with the oxygen-to-tin peak height ratio observed by Auger Electron Spectroscopy (Sangiorgi)⁽⁴³⁾.

Sn + Pb

Comments

Suggested⁽¹⁾ mean $\gamma(t)$ relations for (i) Pb and (ii) pure Pb are:-

$$\left. \begin{array}{l} \text{(i)} \quad \gamma = 457 - 0.11 (t-327) \\ \text{(ii)} \quad \gamma = 471 - 0.156 (t-327) \end{array} \right\} (t \text{ in } ^\circ\text{C})$$

Surface tension data^(8,10,44-56) for the Sn+Pb system are presented in Figures 56-73.

Figure 56 shows mean surface tension values obtained by Deighan⁽⁴⁴⁾ for industrial solder (60 Sn 40 Pb) at the melting point ($\sim 190^\circ\text{C}$) under different atmospheres. As would be expected, the highest values were found for samples which had been pre-cleaned and subsequently melted in the presence of H_2 . Samples melted in air which had been (i) neither pre-cleaned nor fluxed (ii) pre-cleaned but not fluxed and (iii) fluxed but not pre-cleaned, all had similar and the lowest values for (γ) . It was only for samples which had been both pre-cleaned and fluxed, that any increase in (γ) was observed ($\sim 53 \text{ mN.m}^{-1}$). Even in the presence of hydrogen, the values of (γ) obtained for industrial solders were generally lower than those obtained for alloys made from pure components.

Whilst several studies^(10,45-48,54) found that (γ) showed a steady decrease with increase in [Pb], there are strong indications from other data^{(8,45-53)*}, of anomalous behaviour in the vicinity of the eutectic composition (73.9 at.% Sn). This phenomenon generally manifests itself^(8,49,52,53) as a minimum in the $\gamma([\text{Sn}])$ curve, which decreases in magnitude as the temperature is increased; however the results given by Adachi et al⁽⁵⁰⁾ (Figure 62) are at variance with this in that a maximum is observed in the $\gamma([\text{Sn}])$ curves, which becomes more apparent as temperature is increased (these authors account for their results by suggesting that 'clusters' of the same species are produced in the vicinity of the eutectic and that the cluster size increases with temperature up to $200^\circ - 800^\circ\text{C}$). The curves given by Demeri et al⁽⁵¹⁾ (Figure 63) should be treated with caution since, if the notation on the diagrams is correct, the data imply that $(d\gamma/dt)$ for the Sn+Pb system would be positive over a wide range of compositions and temperatures, which is completely at variance with the works of other authors.

The bulk of the studies^(8,10,46,48,50,52-56) found only negative values for the temperature coefficients. White⁽⁵⁶⁾ observed some small positive coefficients, particularly in the vicinity of the liquidus temperatures. The γ ([Sn]) curves given by Ambrok et al⁽⁴⁹⁾ (Figure 61), which cover three discrete temperatures (400 °C, 500 °C, 627 °C), suggest that over a limited composition range in the vicinity of the eutectic, positive values for $(d\gamma/dt)$ would exist, particularly at lower temperatures. Date^(18,48,50,52) given in Figures 70-73 indicate that values for $(d\gamma/dt)$ of the Sn+Pb system are least negative for compositions close to that of the eutectic. Adachi et al⁽⁵⁰⁾ also observed a similar pattern of behaviour for the variation of the temperature coefficient of density (dp/dt) with composition.

Data given by Pandey and Pandey⁽⁵³⁾ were taken from three Russian sources viz:

V B LAZAREV - Teor. i Ebsp. Khim. 3 (4) 1967.

Kh I IBRAGIMOV - Poverkh. Yav. Rasp. Voz. Tverd. Faz. 1965, p 269.

V L SHEINFEILD - Ibid. p 61.

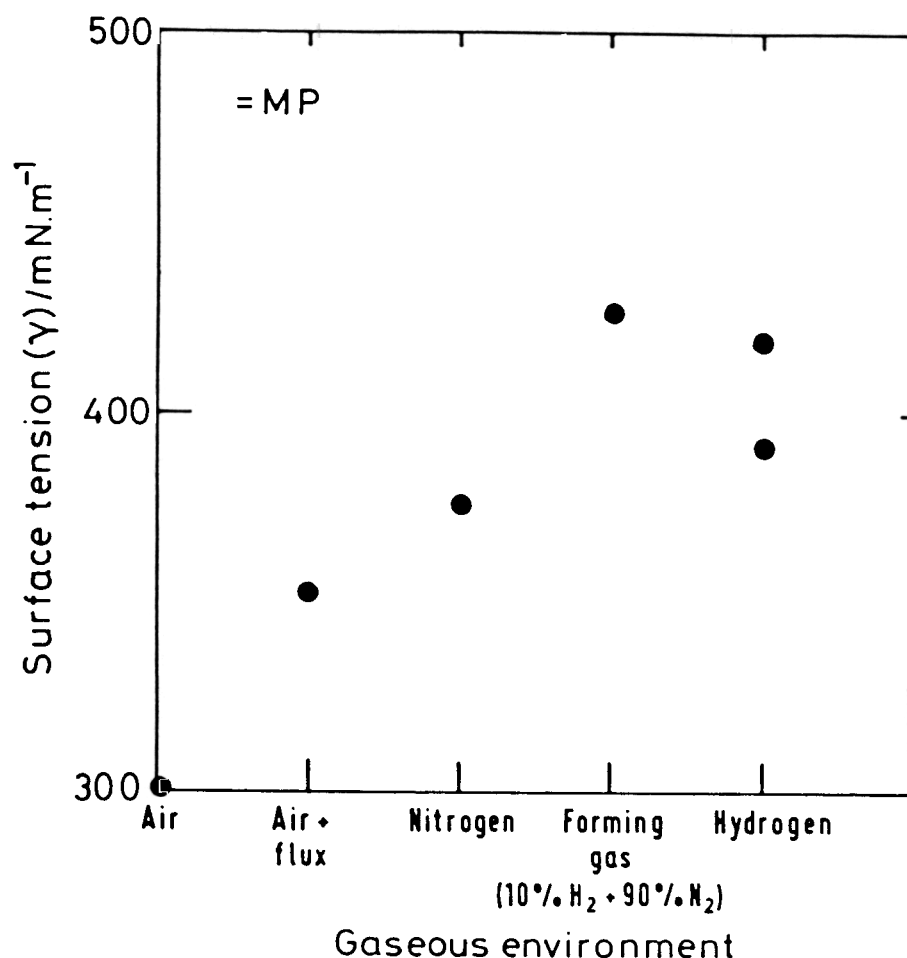


Figure 56 Effect of various gaseous environments on the surface tension of industrial solder (nominal mass % composition 60 Sn 40 Pb) in the vicinity of the melting point (Deighan)⁽⁴⁴⁾.

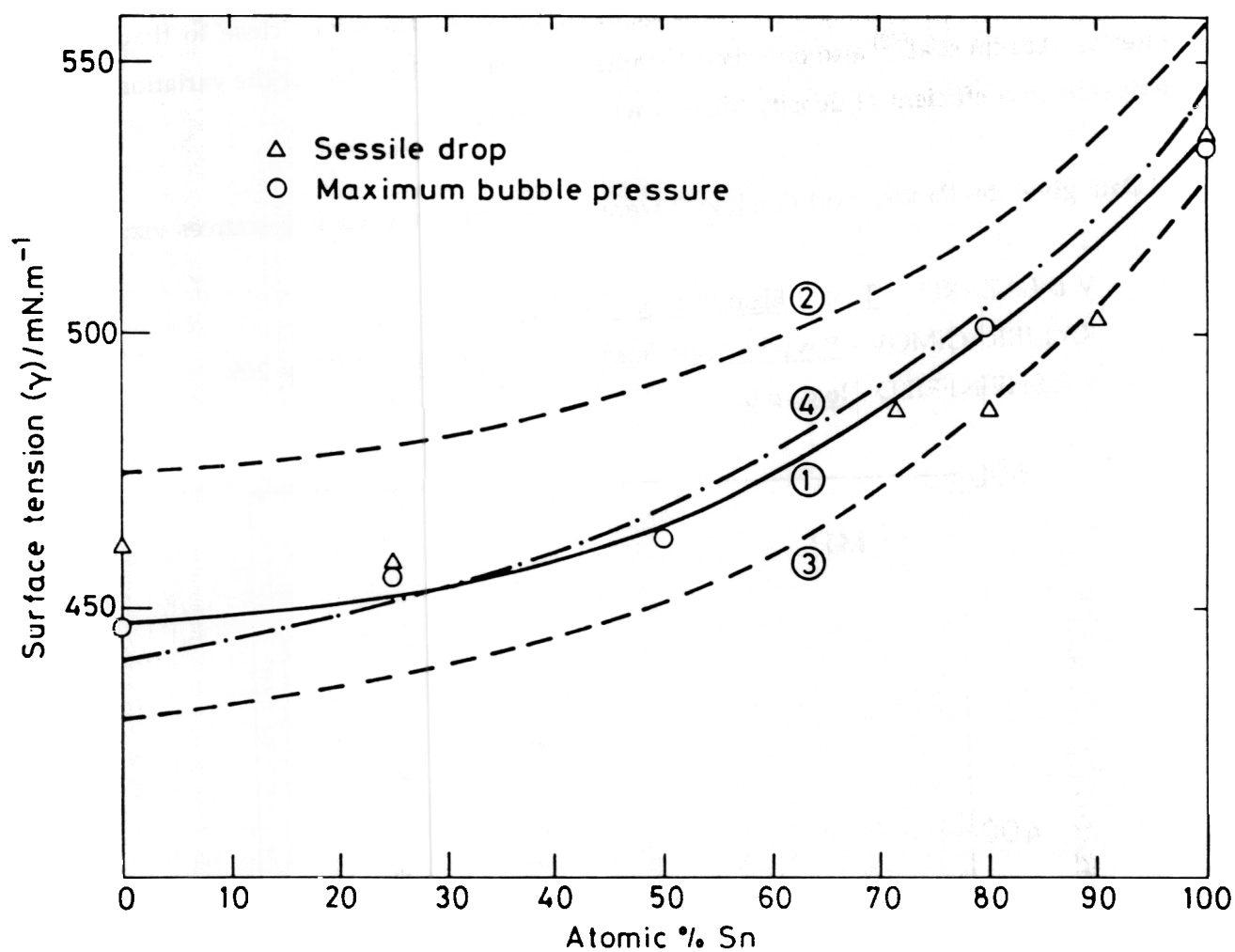


Figure 57 Variation of surface tension with composition of Sn + Pb alloys at 400 °C obtained by (Howie)⁽⁴⁵⁾ (curve 1) in comparison with the data given by (Hoar)⁽⁴⁶⁾ at 350 °C (curve 2) and at 550 °C (curve 3) together with the data given by (Schwaneke)⁽⁴⁷⁾ at 400 °C.

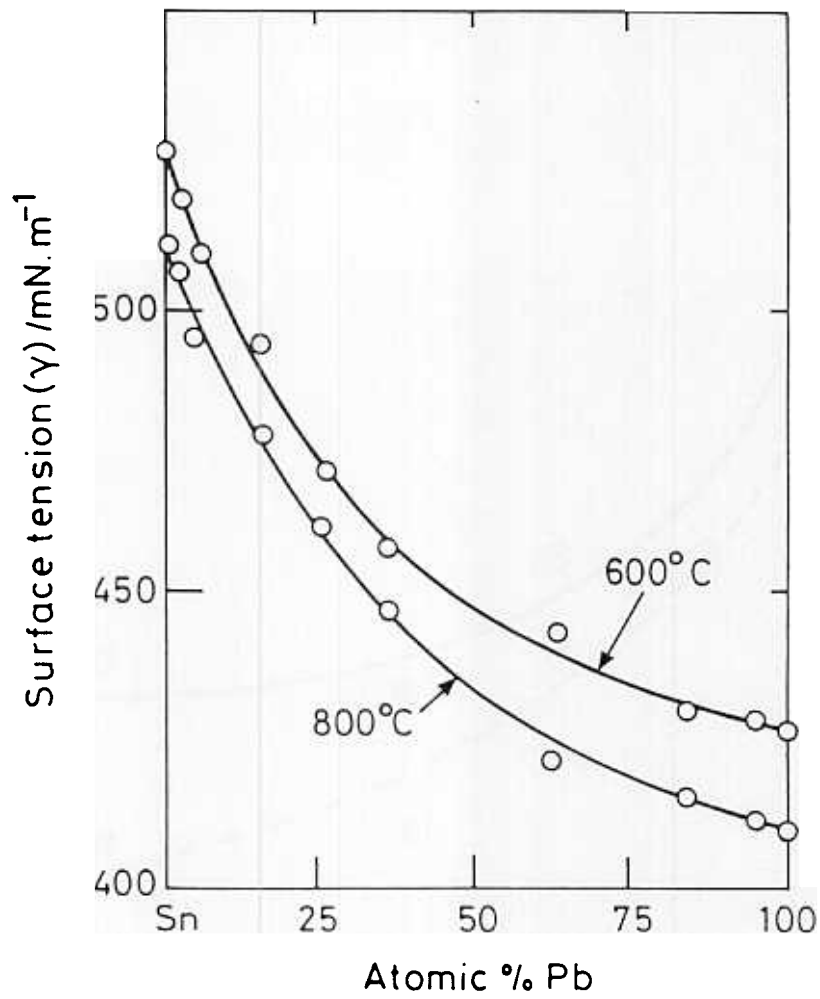


Figure 58 Variation of surface tension with composition of Sn + Pb alloys at 600 °C and 800 °C (Reshchetnikov)⁽¹⁰⁾.

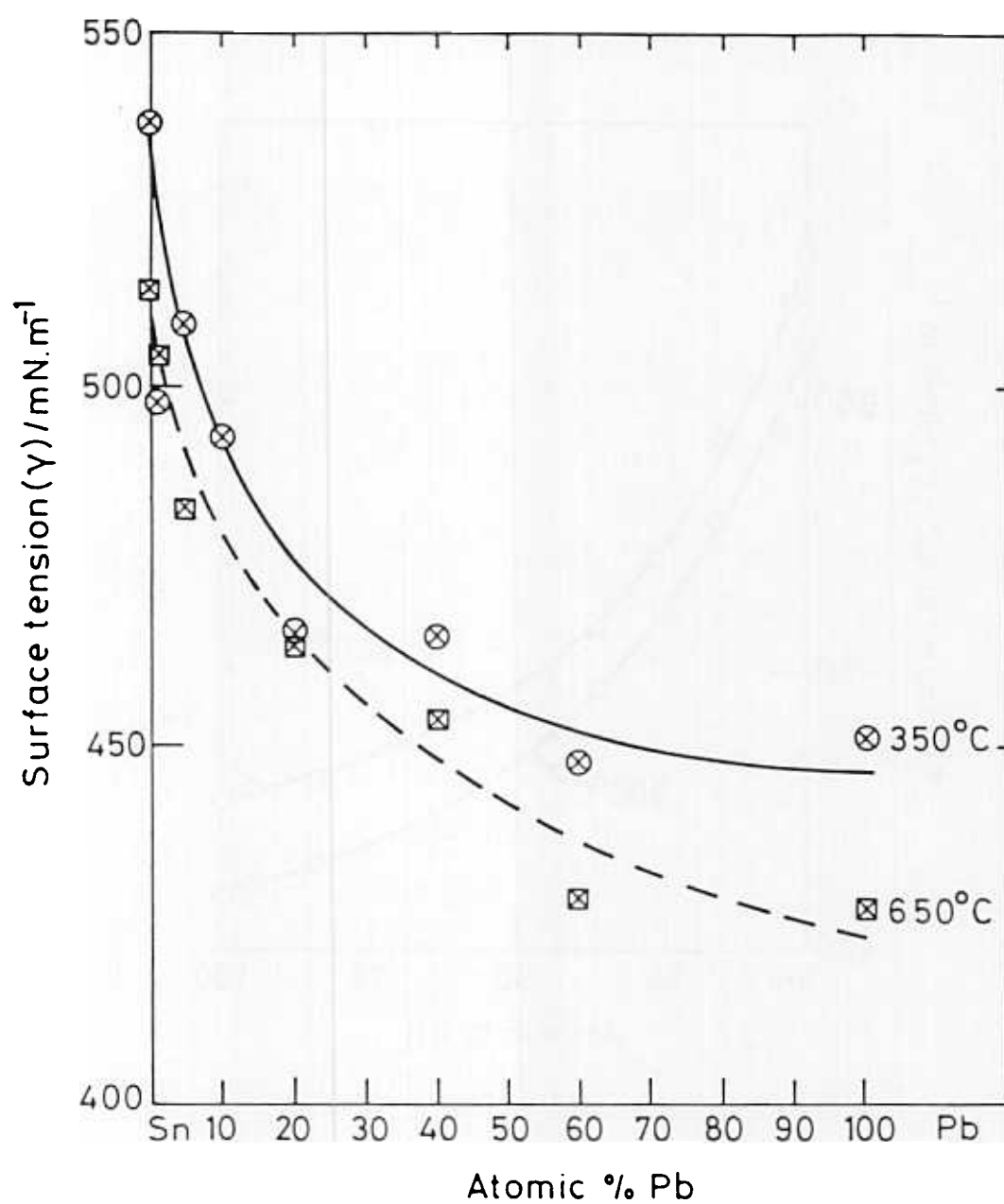


Figure 59 Effect of composition on the surface tension of Sn + Pb alloys at 350 °C and at 650 °C (Popel)⁽⁴⁸⁾.

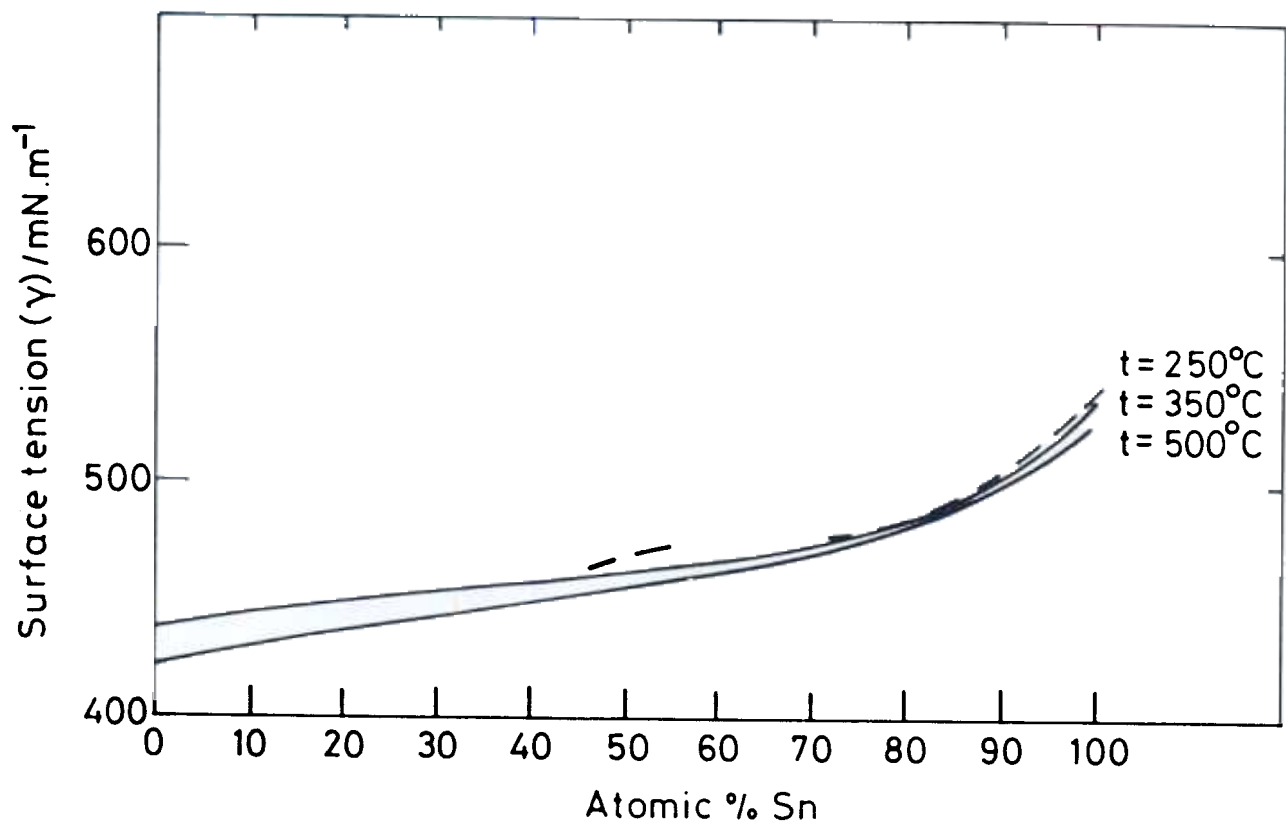


Figure 60 Variation of surface tension with composition of Sn + Pb alloys at three different temperatures (Ibragimov)⁽⁸⁾.

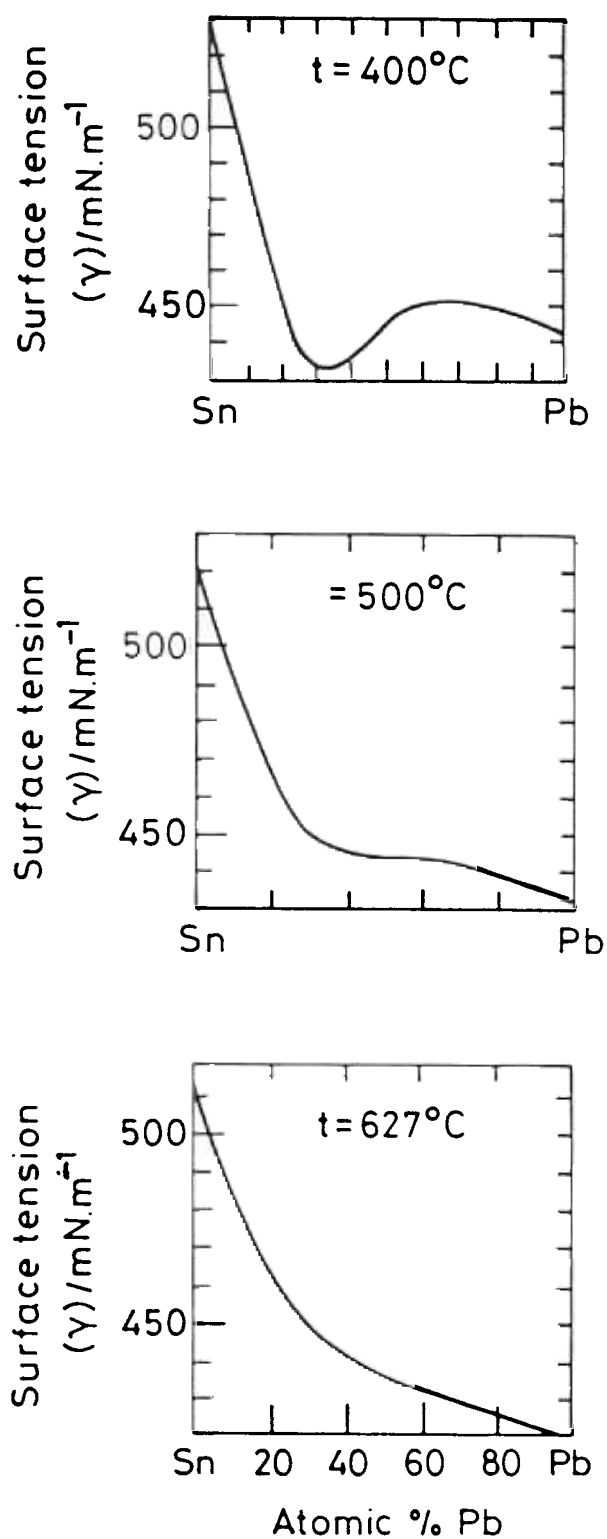


Figure 61 Variation of surface tension with composition of Sn + Pb alloys at three different temperatures (Ambrok)⁽⁴⁹⁾.

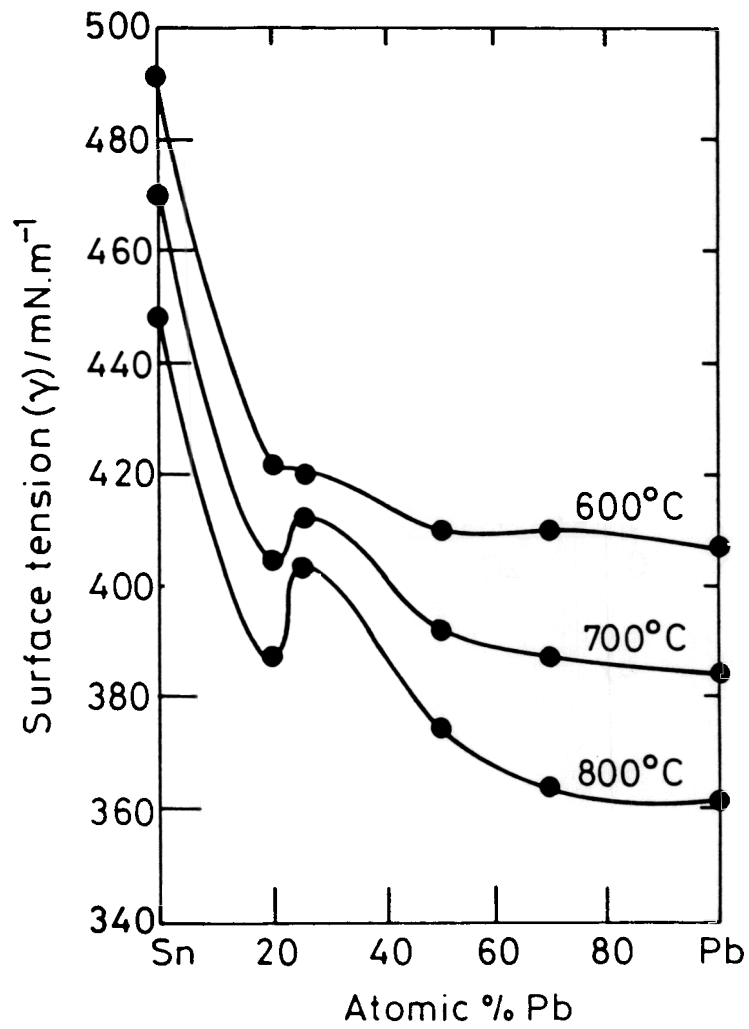
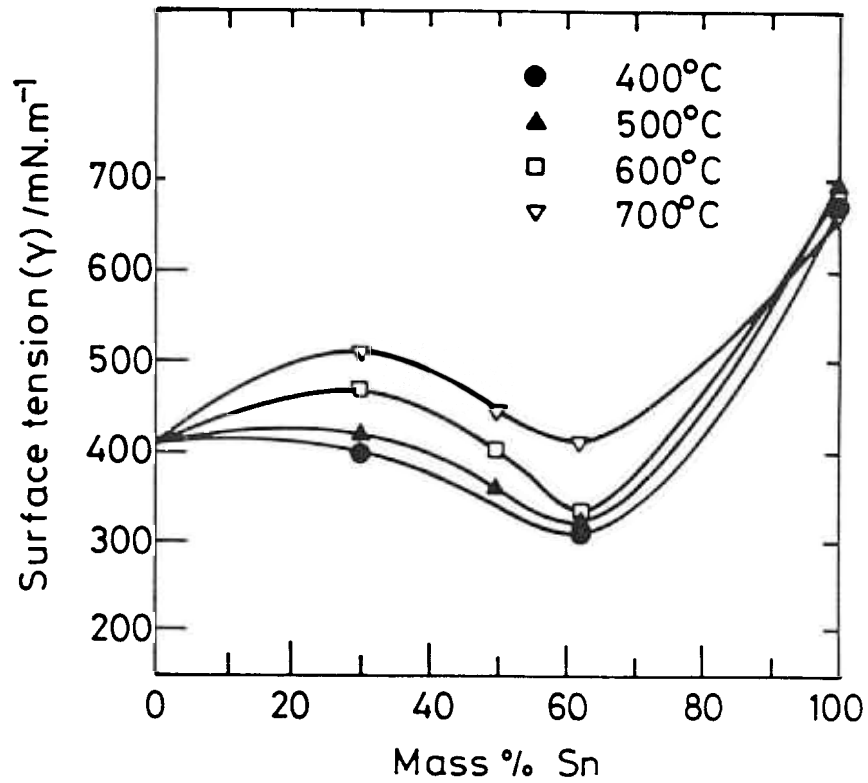
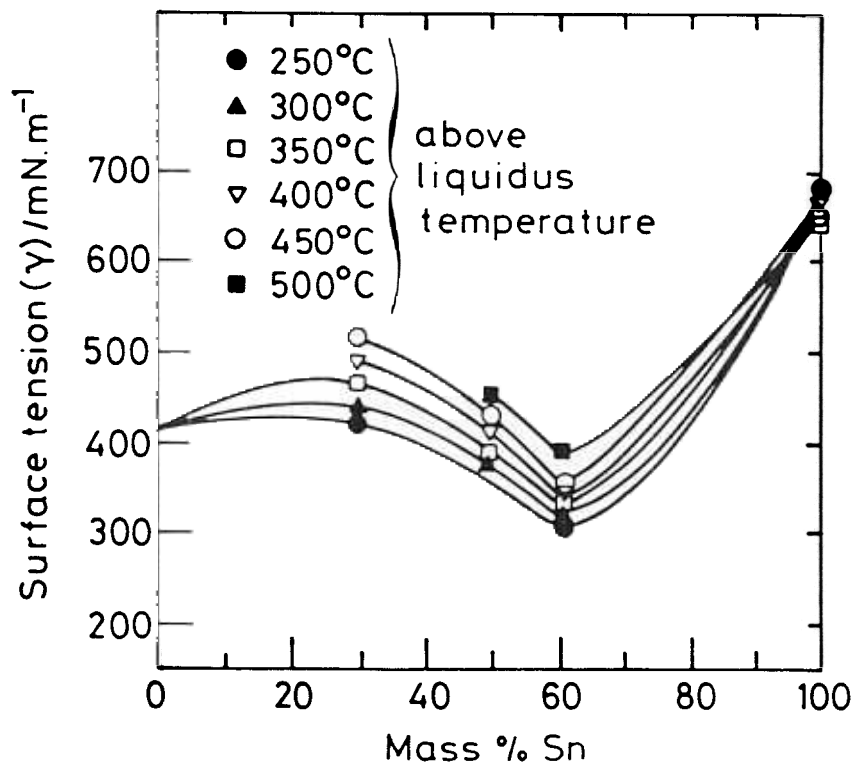


Figure 62 Variation of surface tension with composition of Sn + Pb alloys at three different temperatures (Adachi)⁽⁵⁰⁾.



a)



b)

Figure 63 Surface tension data for the Sn + Pb system given by (Demeri)⁽⁵¹⁾.

Figure (a) - variation with composition at four different temperatures.

Figure (b) - variation with composition at various temperatures above the liquidus.

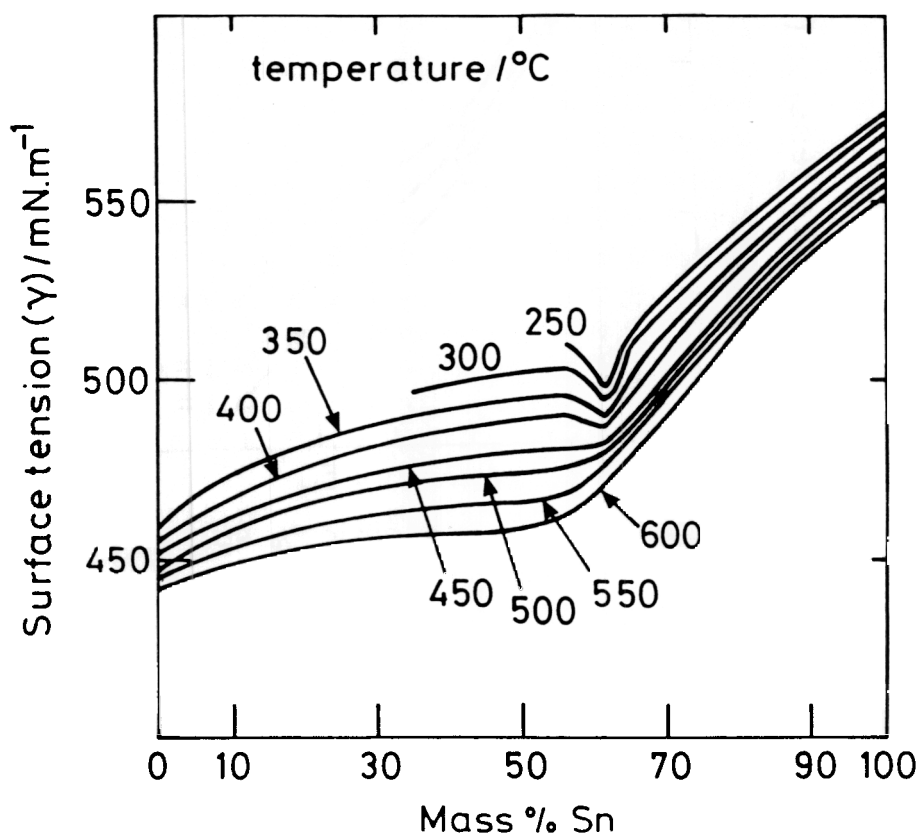


Figure 64 Variation of surface tension of Sn + Pb alloys with composition over a range of temperatures (Somol)⁽⁵²⁾.

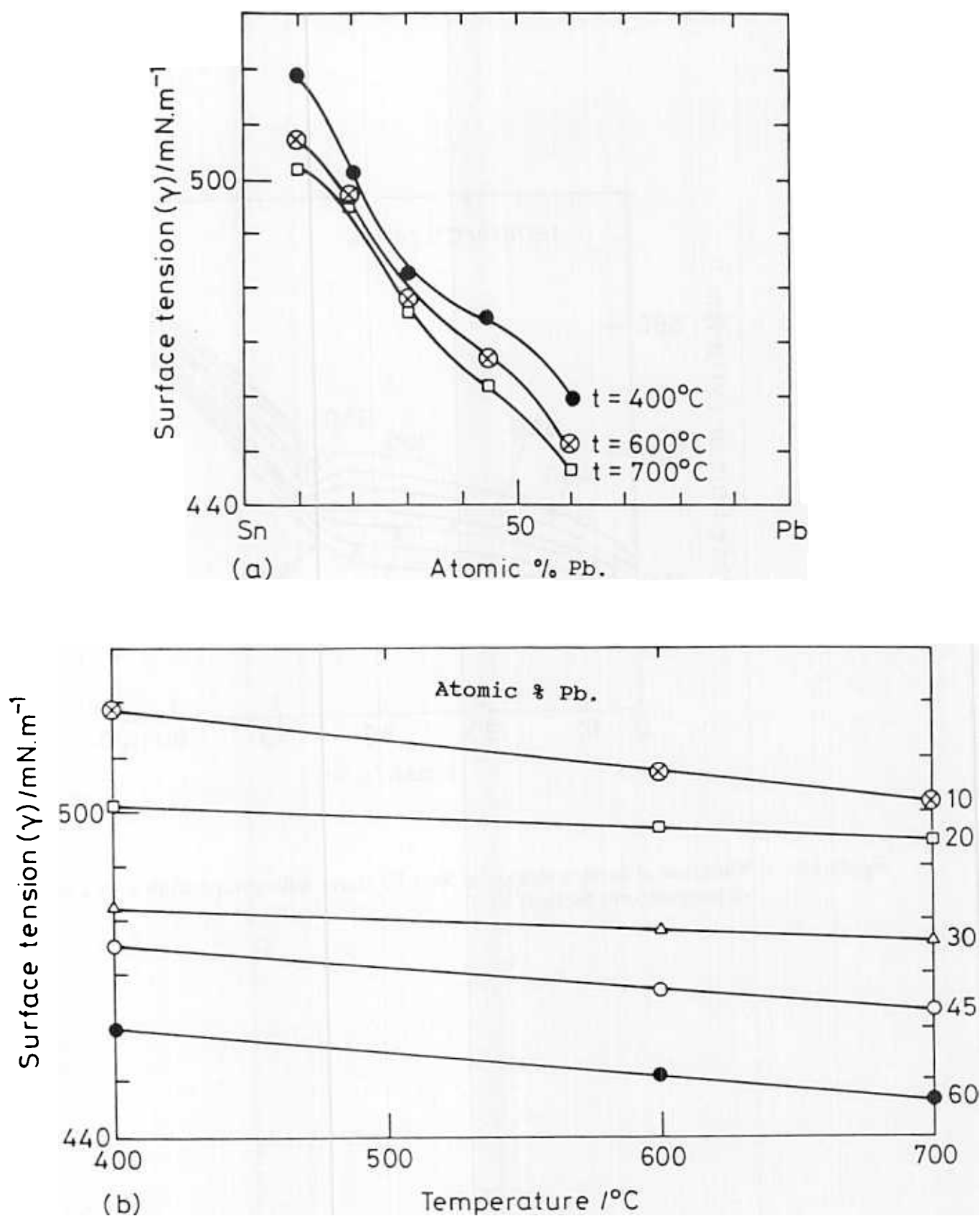
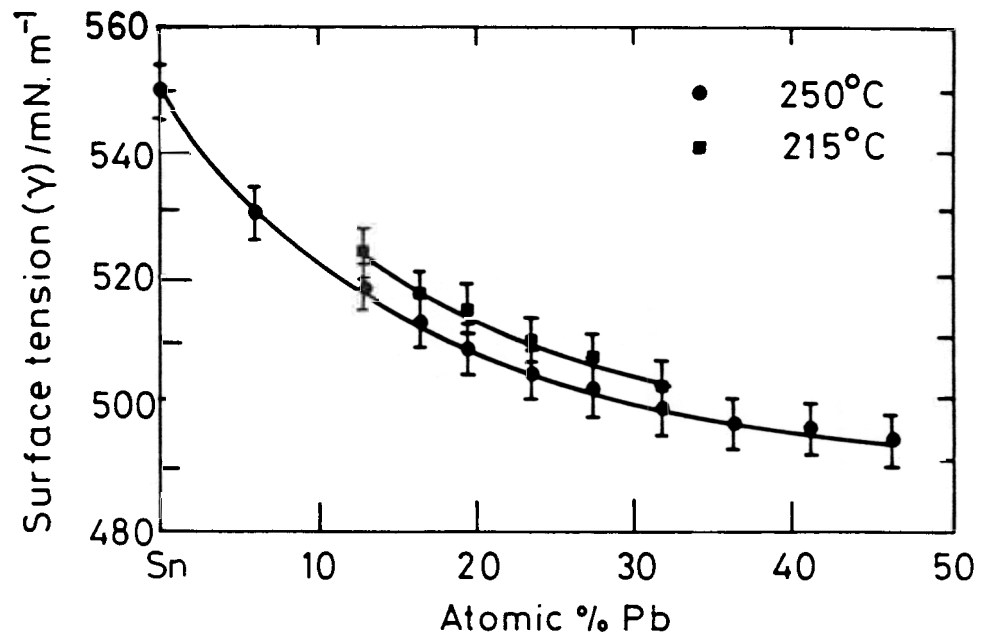
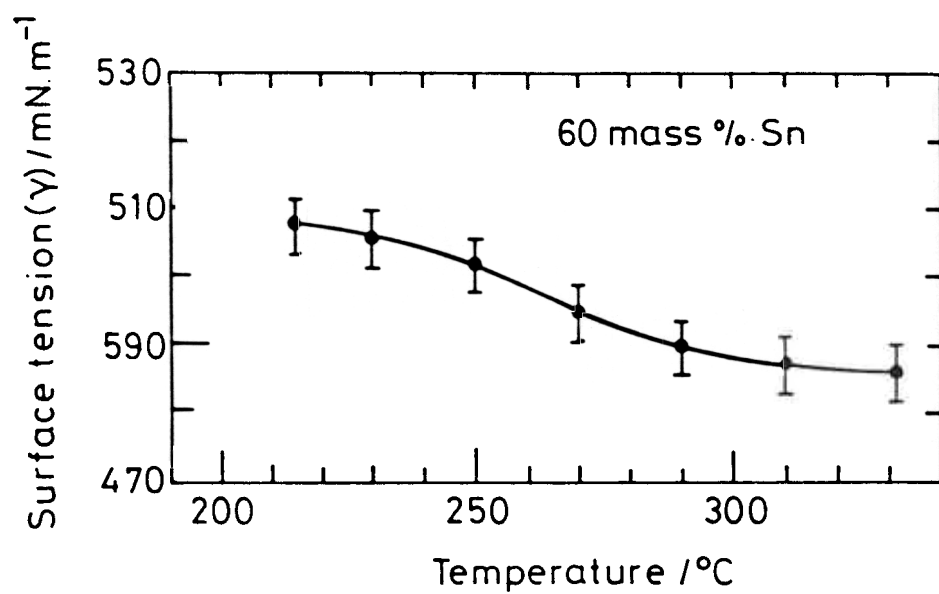


Figure 65 Effect of composition (Figure (a)) and of temperature (Figure (b)) on the surface tension of Sn + Pb alloys (Pandey)⁽⁵³⁾.



a)



b)

Figure 66 Variation of surface tension of Sn + Pb alloys at 215 °C and 250 °C (Figure (a)) and the effect of temperature on the surface tension of the alloy 60 Sn 40 Pb (mass %) (Figure (b)) (Carroll)⁽⁵⁴⁾.

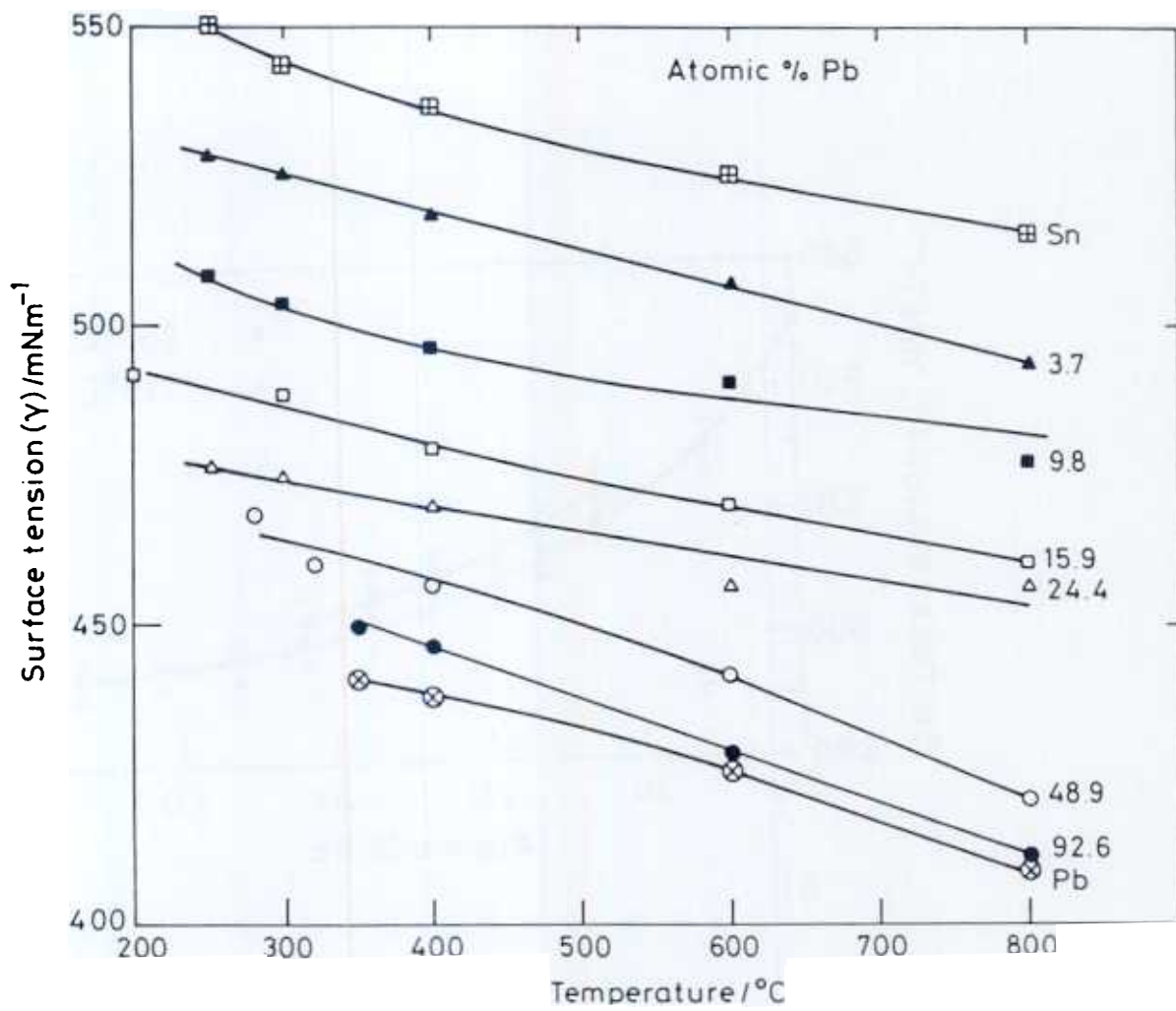


Figure 67 Variation with temperature of the surface tension of Sn, Pb and some of their alloys (Bircumshaw)⁽⁵⁵⁾.

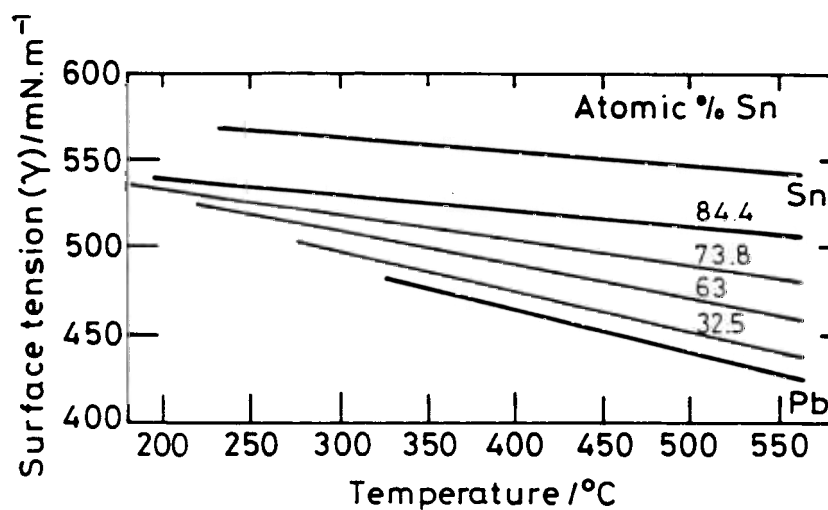


Figure 68 Variation with temperature of the surface tension of Sn, Pb and some of their alloys (Hoar)⁽⁴⁶⁾.

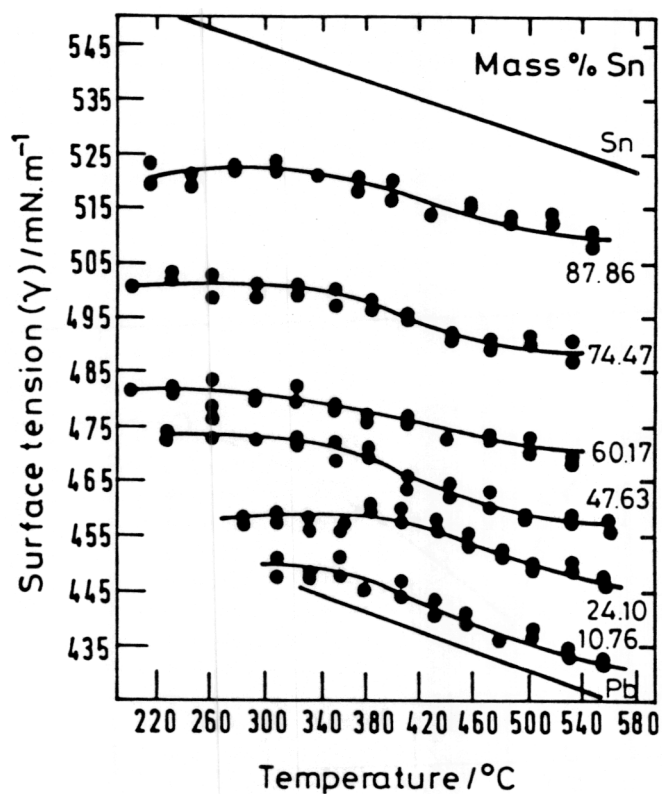


Figure 69 Variation with temperature of the surface tension of Sn, Pb and some of their alloys (White)⁽⁵⁶⁾.

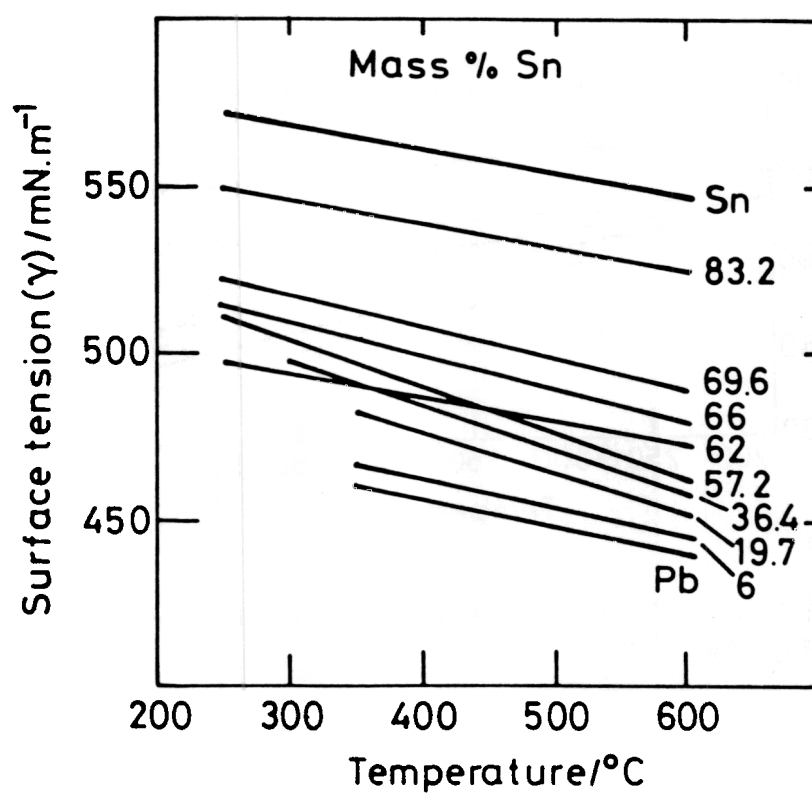


Figure 70 Variation with temperature of the surface tension of Sn, Pb and some of their alloys (Somol)⁽⁵²⁾.

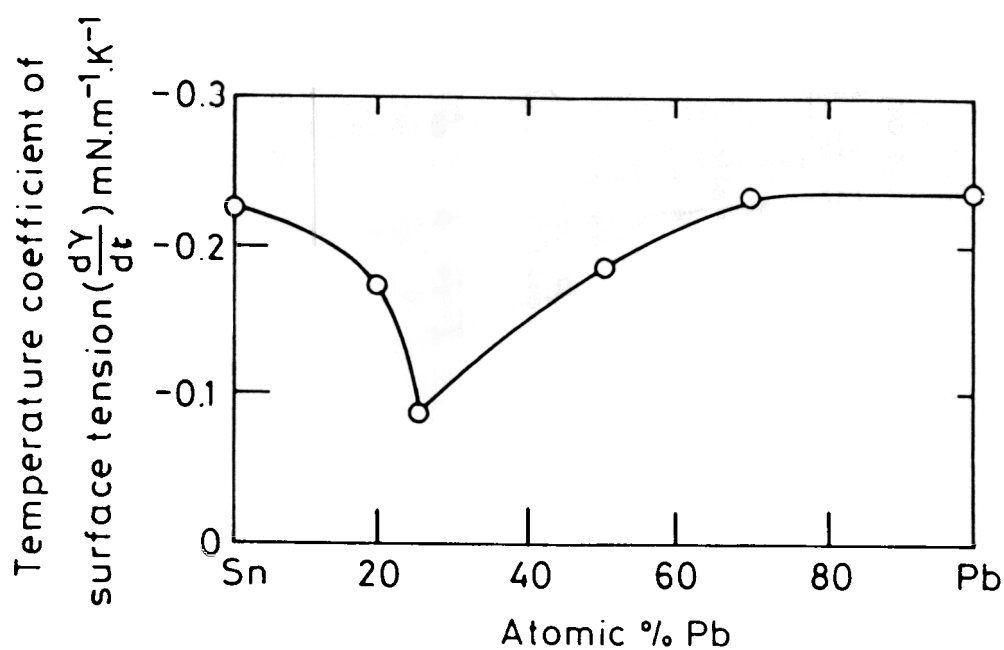


Figure 71 Effect of composition on the surface entropy of Sn + Pb alloys (Adachi)⁽⁵⁰⁾.

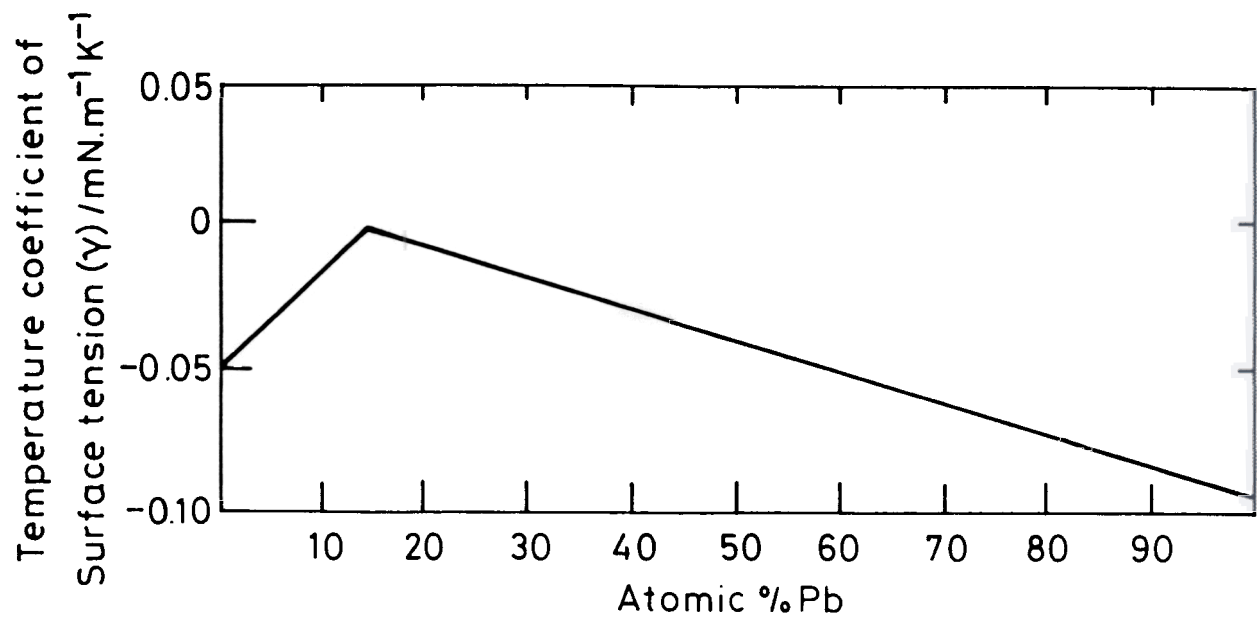


Figure 72 Effect of composition on the surface entropy of Sn + Pb alloys (Ibragimov)⁽⁸⁾.

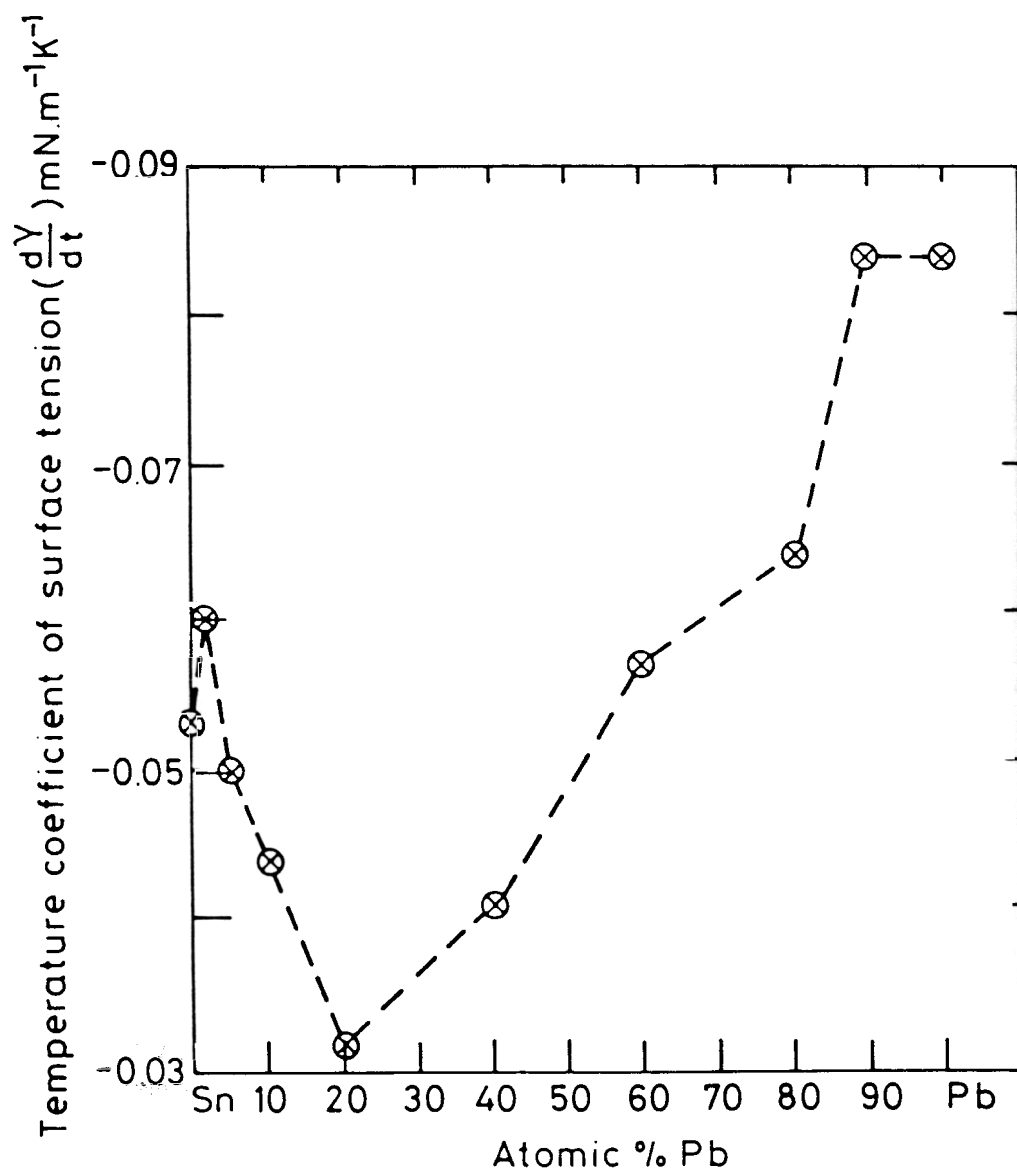


Figure 73 Effect of composition on the surface entropy of Sn + Pb alloys (Popel)⁽⁴⁸⁾.

Sn + Pd

Comments

Suggested⁽¹⁾ mean $\gamma(t)$ relation for Pd is:-

$$\gamma = 1482 - 0.279 (t-1552) \quad (t \text{ in } ^\circ\text{C})$$

The only data⁽⁵⁷⁾ for the surface tension of Sn+Pd alloys are given in Figure 74. The $\gamma([Sn])$ curve for 1000 °C, shows a continuous decrease in (γ) with increase in [Sn]. A point of inflexion was observed at around 33 at.% Sn ie around the composition of the compound Pd₂ Sn.

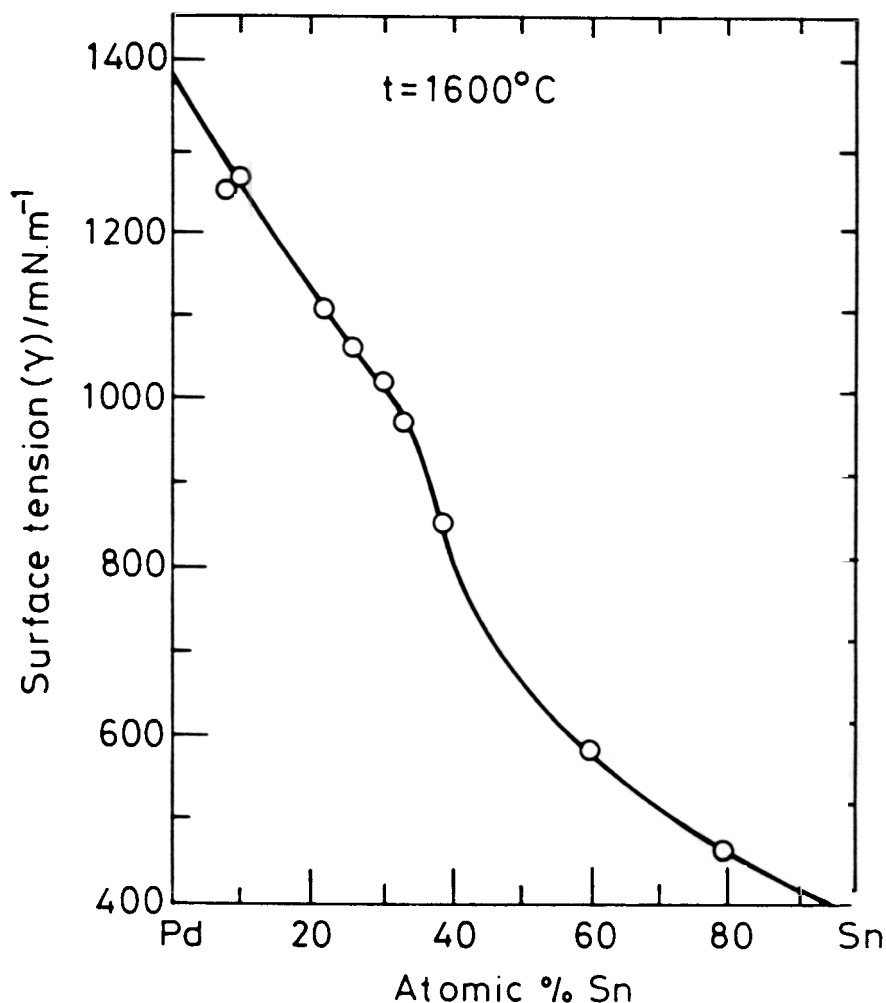


Figure 74 Effect of composition on the surface tension of Sn + Pd alloys at 1600 °C (Vatolin)⁽⁵⁷⁾.

Sn + Pt

Comments

There is a wide disparity between the extant data⁽¹⁾ for the surface tension of Pt, ranging from 1700 mN.m⁻¹ at 1800 °C to 1865 mN.m⁻¹ at 1770 °C.

The only data⁽⁵⁸⁾ for the surface tension of Sn+Pt alloys are given in Figure 75. As with the Sn+Pd system, an inflexion is apparent in the γ ([Sn]) curve at around 33 at.% Sn ie between the compositions equivalent to the compound Pt₃Sn and the eutectic at about 40 at.% Sn.

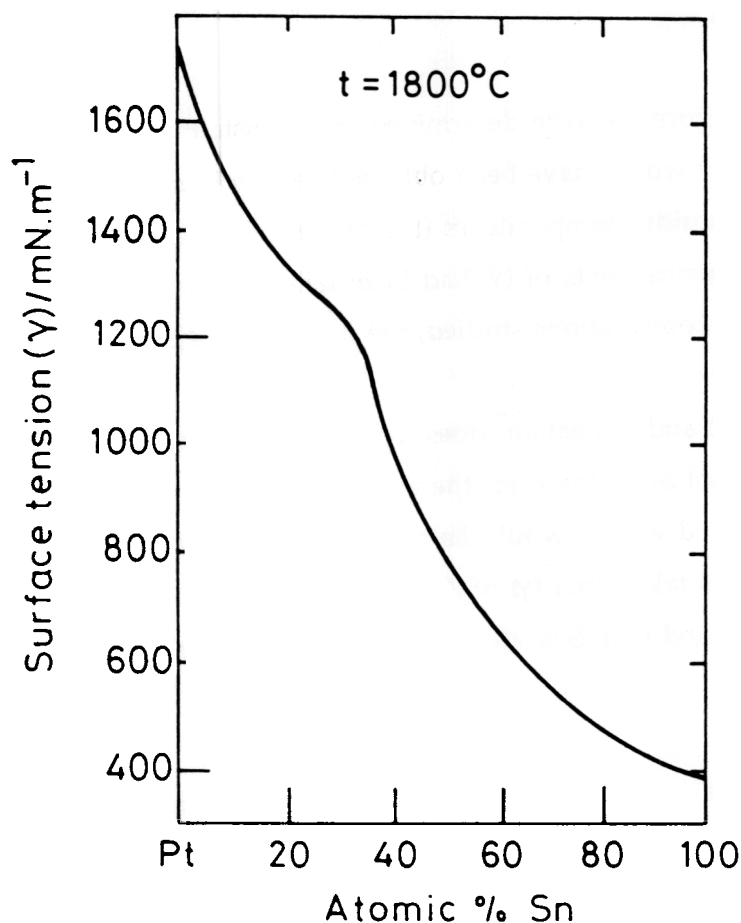


Figure 75 Effect of composition on the surface tension of Sn + Pt alloys at 1800 °C (Chegodaev)⁽⁵⁸⁾.

Sn + S

Comments

Data⁽⁵⁹⁾ for the effect of low levels of S on the surface tension of Sn are given in Figure 76. The curve shows that S is surface-active in Sn, one atomic % addition reducing (γ) by approximately 90 mN.m⁻¹. Naidich et al⁽⁵⁹⁾ quote a value for the limiting surface activity $\left(\frac{d\gamma}{d[S]}\right)_{[S] \rightarrow 0}$ as - 116 mN.m⁻¹ (at .% S)⁻¹. It is pertinent to note that the presence of

relatively low levels of S in Sn result in a substantial increase in the melting point (1 at.% S raises t_m to more than 650 °C).

The data shown in Figure 76 were determined at a constant 700 °C. It follows that the individual values of (γ) would have been obtained for a wide range of temperature levels above the respective liquidus temperatures (the degree of overtemperature decreasing with increase in [S]). If measurements of (γ) had been taken at the same overtemperature (say 50 °C) for all the alloy compositions studied, the decrease in (γ) with increase in [S] would be more marked.

The work by Bradhurst and Buchanan[~] does not quote any actual values for the effect of S on the surface tension of Sn. However, the authors observed that at 800 °C, the (γ) of Sn which was bulk-saturated with S, would be reduced by about 15.8%. If, based on the data presented in ref.(1), it is taken that (γ) of Sn at 800 °C is approximately 515 mN.m⁻¹, then material which is saturated with S would have a (γ) of around 433 mN.m⁻¹ ie a decrease of about 82 mN.m⁻¹.

There are no $\gamma(t)$ data for this system (but see comment under Sn+Se).

D H BRADHURST, A S BUCHANAN.

Austral. J. Chem. 14, 1961, 417.

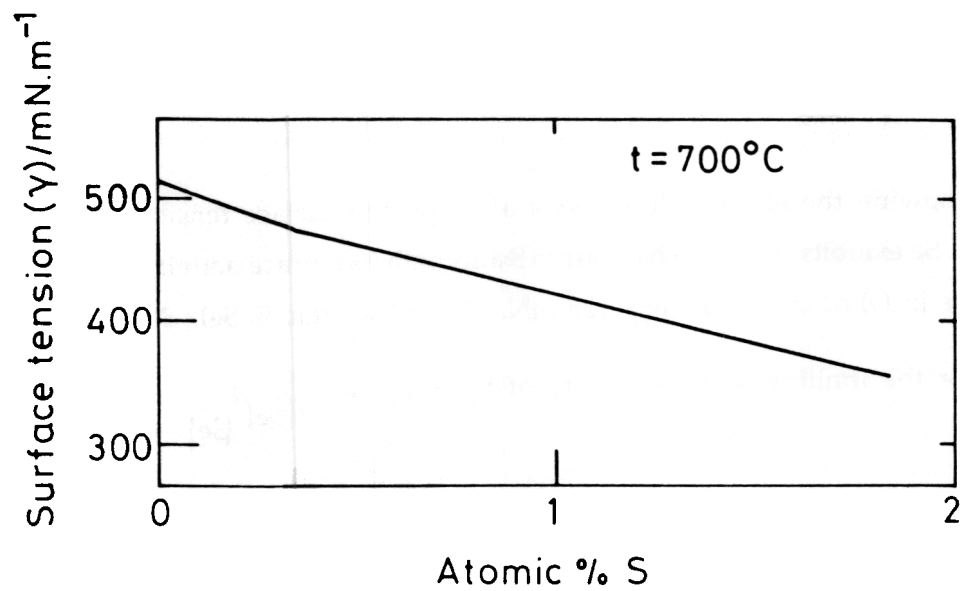


Figure 76 Effect of low levels of sulphur on the surface tension of tin at 700 °C (Naidich)⁽⁵⁹⁾.

Sn + Se

Comments

Suggested⁽¹⁾ mean $\gamma(t)$ relations for (i) Se and (ii) pure Se are:-

$$\left. \begin{array}{ll} \text{(i)} & \gamma = 103 - 0.15 (t-220) \\ \text{(ii)} & \gamma = 109 - 0.21 (t-220) \end{array} \right\} \quad (t \text{ in } ^\circ\text{C})$$

Data⁽⁵⁹⁾ showing the effect of low levels of Se on the surface tension of Sn are given in Figure 77. Se exhibits similar behaviour to S although its surface-activity is somewhat greater (a decrease in (γ) of approximately 125 mN.m^{-1} for 1 atomic % Se). Naidich et al⁽⁵⁹⁾ quote a value for the limiting surface activity of Se in Sn ie $\left(\frac{d\gamma}{d[\text{Se}]}\right)_{[\text{Se}] \rightarrow 0}$ as -210 mN.m^{-1}

(at.% Se)⁻¹.

There are no data for the effect of temperature on (γ) of these alloys, but it may be noted that for the Sn+Te system (q.v.), $\gamma(t)$ curves with positive slope have been observed over a limited range of lower temperatures. It is well known⁽²⁴⁾ that the presence of low levels of Group VI elements (O,S,Se,Te) in Fe gives rise to positive values for $(d\gamma/dt)$ and it is possible that this behaviour may apply to Sn alloys. It is also pertinent to note that the data for the Sn+Te system show that the surface-activity is greatest at the lowest temperatures (below about 450°C).

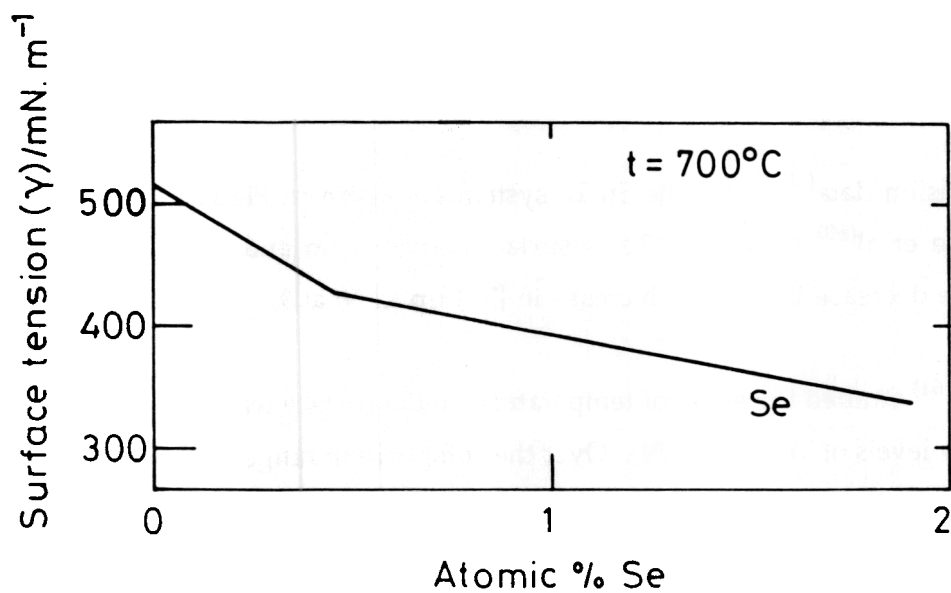


Figure 77 Effect of low levels of selenium on the surface tension of tin at 700 °C (Naidich)⁽⁵⁹⁾.

Sn + Te

Comments

Probably because of the practical difficulties in measuring (γ) of Te, the literature data⁽¹⁾ show fairly large differences ranging from 178 mN.m⁻¹ to 239 mN.m⁻¹ at 460 °C.

Surface tension data^(60,61) for the Sn-Te system are given in Figures 78-79. The results of Tsertsvadze et al⁽⁶⁰⁾ show that Te is surface-active in Sn and that at 800 °C, there is a progressive decrease in (γ) with increase in [Te] up to 50 at.%.

Pokrovskii⁽⁶¹⁾ studied the effect of temperature on the surface tension of Sn+Te alloys which contain low levels of Te (Figure 79). Over the composition range studied (0.0037-0.0364 at.% Te), positive temperature coefficients were observed for the lower temperatures. This Figure also verifies the fact that Te is strongly surface-active in Sn, particularly at the lower temperatures eg at 350 °C, the presence of 0.0364 at.% Te reduced the (γ) of Sn by about 40 mN.m⁻¹.

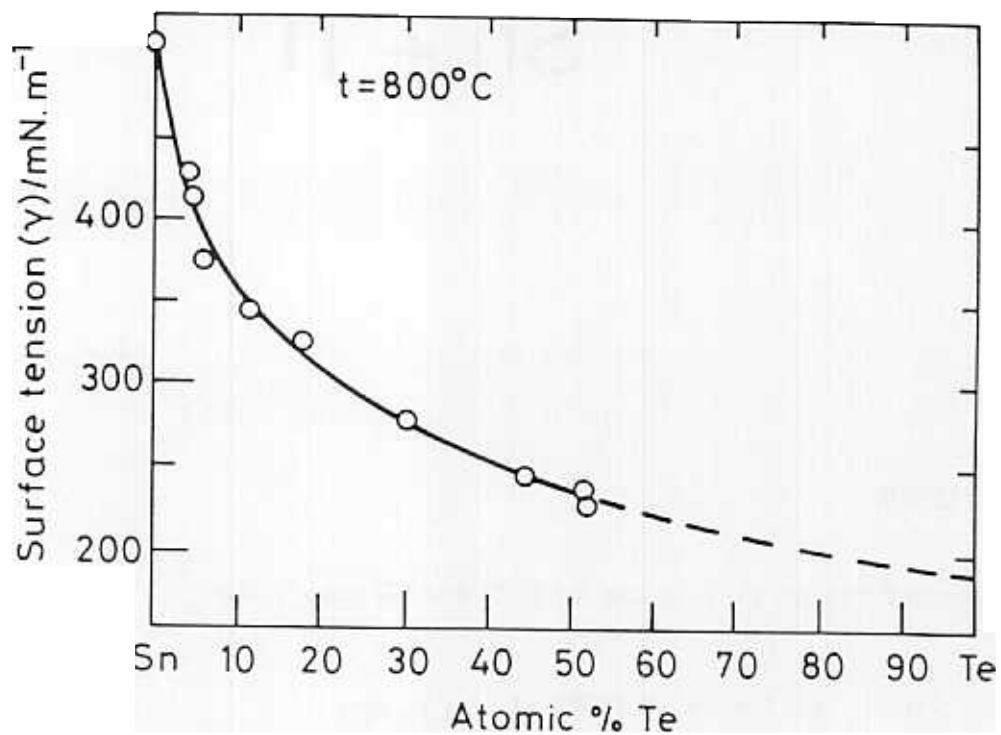


Figure 78 Effect of composition on the surface tension of Sn + Te alloys at 800 °C (Tsertsvadze)⁽⁶⁰⁾.

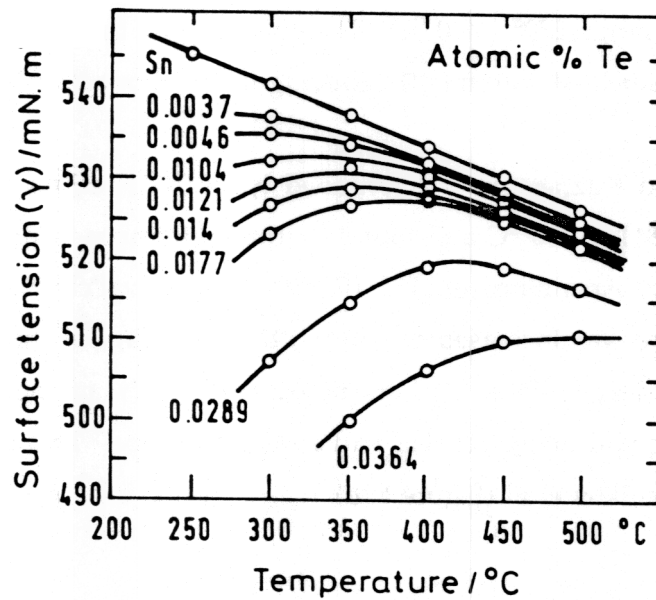


Figure 79 Effect of temperature on the surface tension of pure Sn and Sn alloys containing small amounts of Te (Pokrovskii)⁽⁶¹⁾.

Sn + Tl

Comments

Suggested⁽¹⁾ mean $\gamma(t)$ relations for (i) Tl and (ii) pure Tl are:

$$\left. \begin{array}{ll} \text{(i)} & \gamma = 459 - 0.106 (t-305) \\ \text{(ii)} & \gamma = 465 - 0.095 (t-305) \end{array} \right\} \quad (t \text{ in } ^\circ\text{C})$$

Surface tension data^(3,62,63) for the Sn+Tl system are given in Figures 80-82.

Pokrovskii and Tissen⁽³⁾ (Figure 80) studied the effect of low levels of Tl on the (γ) of Sn over a temperature range 270° - 400 °C. The curves show that Tl exhibits some surface-activity in Sn, (the presence of 1 atomic % reducing (γ) by about 19 mN.m⁻¹ at 270 °C).

Koval'chuk and Kuznetsov⁽⁶²⁾ determined (γ) of Sn+Tl alloys over the whole composition range (Figure 81) at 350 °C and found a broad minimum in the γ ([Sn]) curve, but this was not observed by Arsamikov et al⁽⁶³⁾ (Figure 82a). Koval'chuk and Kuznetsov found that if the temperature was increased to 450 °C, the minimum in the curve became broader and relatively less deep. These authors noted that the (γ) of the alloys varied linearly with temperature and all the $\gamma(t)$ curves had a negative slope. This is in general accord with the results of Arsamikov et al (Figure 82b).

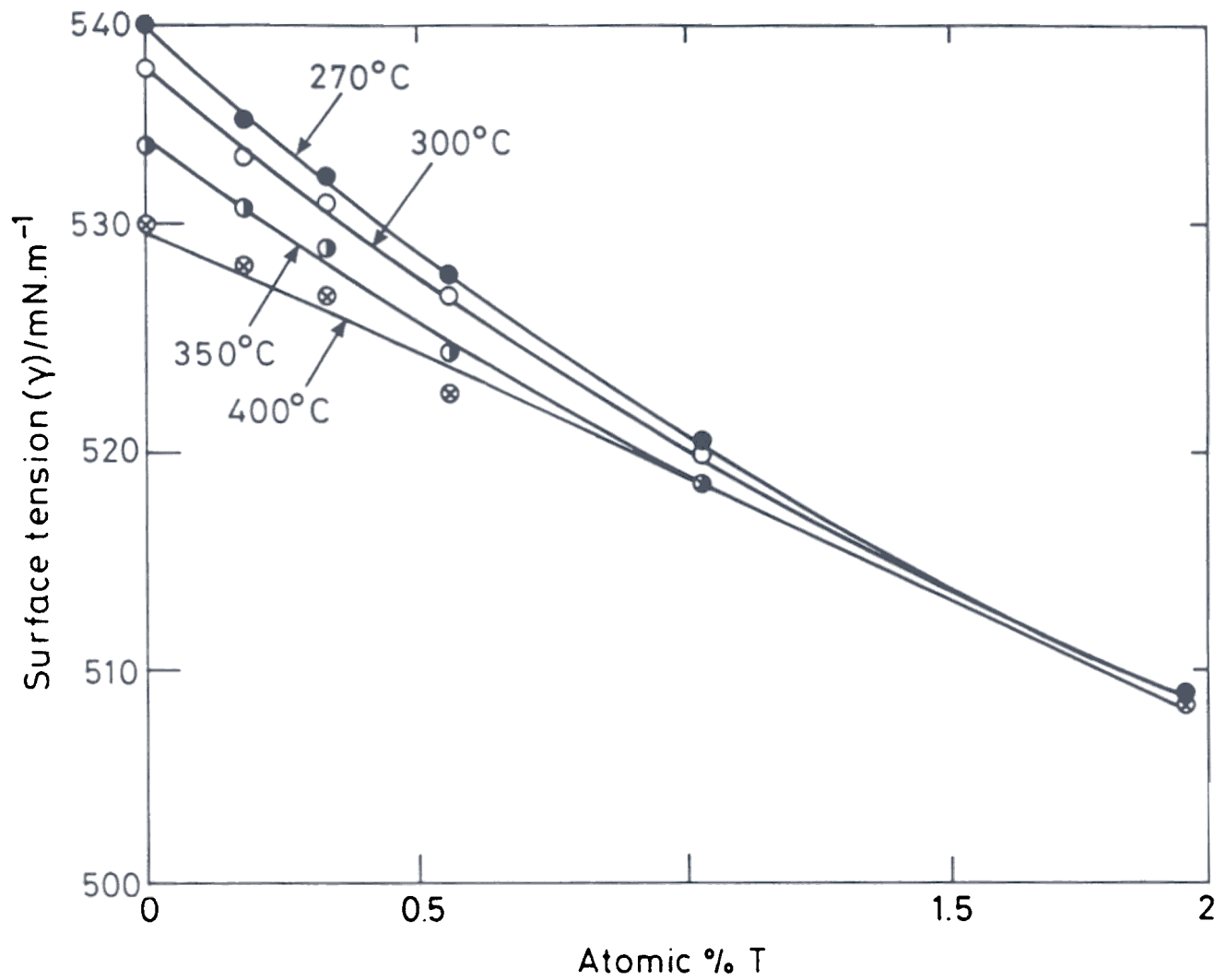


Figure 80 Effect of low levels of Tl on the surface tension of Sn at four different temperatures (Pokrovskii)⁽³⁾.

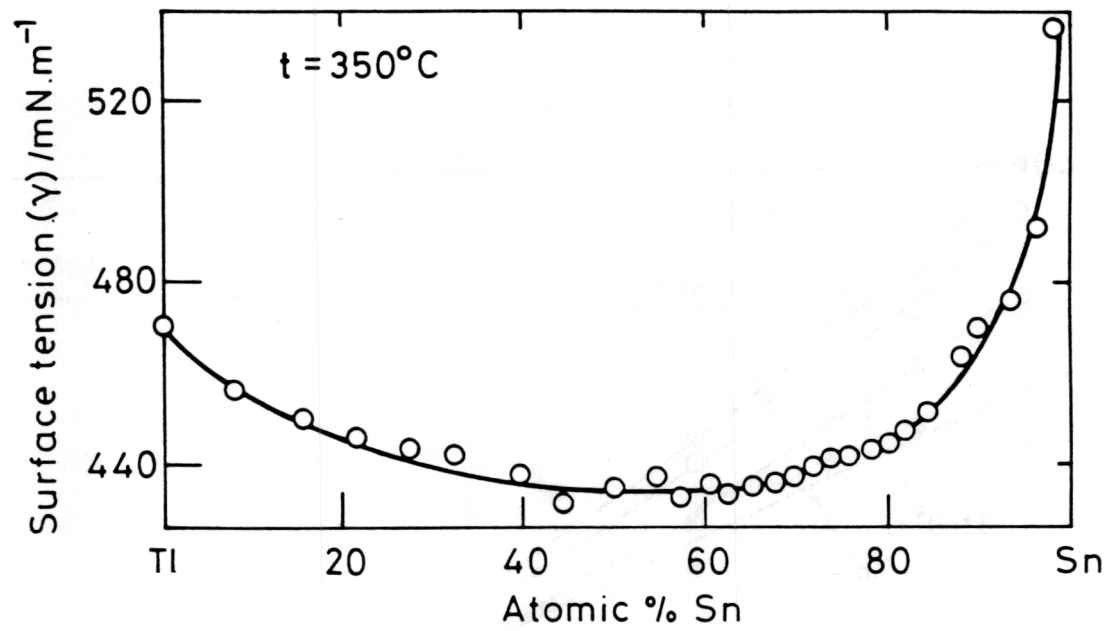


Figure 81 Variation of surface tension with composition of Sn + Tl alloys at 350 °C (Koval'chuk)⁽⁶²⁾.

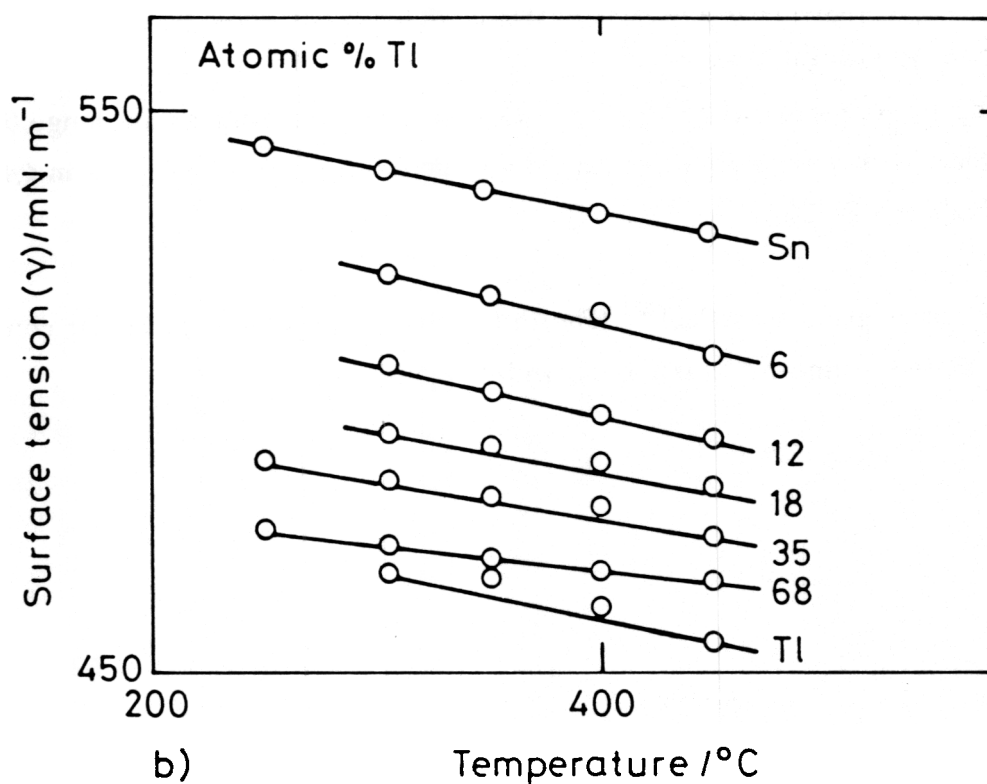
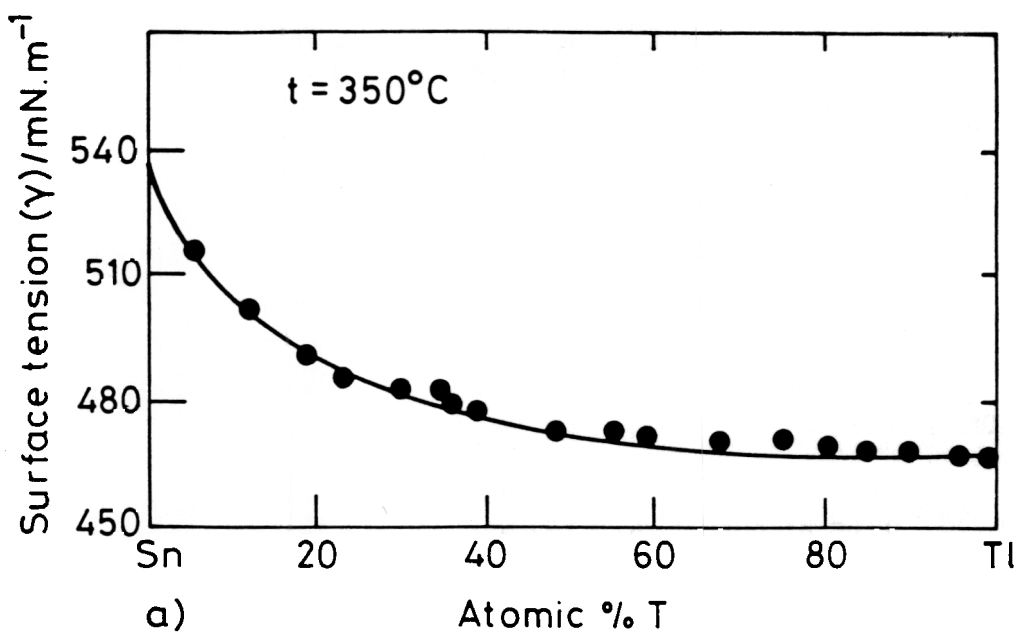


Figure 82

Variation of surface tension with composition of Sn + Tl alloys at 350°C (Figure (a)) together with the effect of temperature on the surface tension of Sn, Tl and some of their alloys (Figure (b)) (Arsamikov)⁽⁶³⁾.

Sn + Zn

Comments

Suggested⁽¹⁾ mean $\gamma(t)$ relations for (i) Zn and (ii) pure Zn are:-

$$\left. \begin{array}{l} \text{(i)} \quad \gamma = 789 - 0.21 (t-420) \\ \text{(ii)} \quad \gamma = 817 - 0.227 (t-420) \end{array} \right\} (t \text{ in } ^\circ\text{C})$$

Surface tension data^(15,64-66) for the Sn+Zn system are shown in Figures 83-86. Results given in Figures 83-85 show that relatively low additions of Zn to Sn result in a small increase in (γ) , the work of Abdel-Aziz and Aref⁽⁶⁴⁾ (Figure 83) however showing a much larger rate of increase in (γ) with Zn content.

The study by Kuznetsov et al⁽⁶⁵⁾, which covered the whole composition range (Figure 84) shows that Sn is surface-active in Zn (10 atomic % Sn giving a decrease in (γ) of about 190 mN.m^{-1} at 450°C).

The $\gamma(t)$ curves given by Pelzel⁽⁶⁶⁾ (Figure 86) show that for the particular compositions studied, there is a linear decrease in (γ) with temperature.

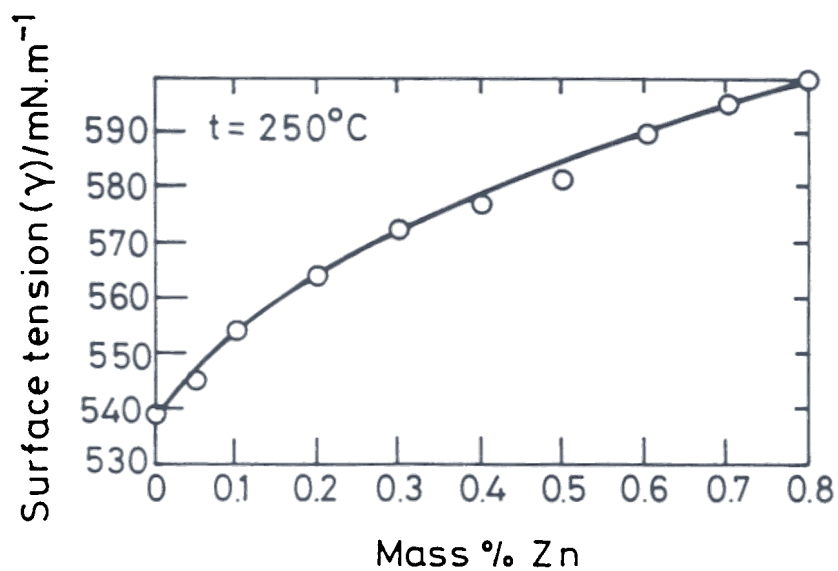


Figure 83 Effect of low levels of zinc on the surface tension of tin at 250 °C (Abdel-Aziz)⁽⁶⁴⁾.

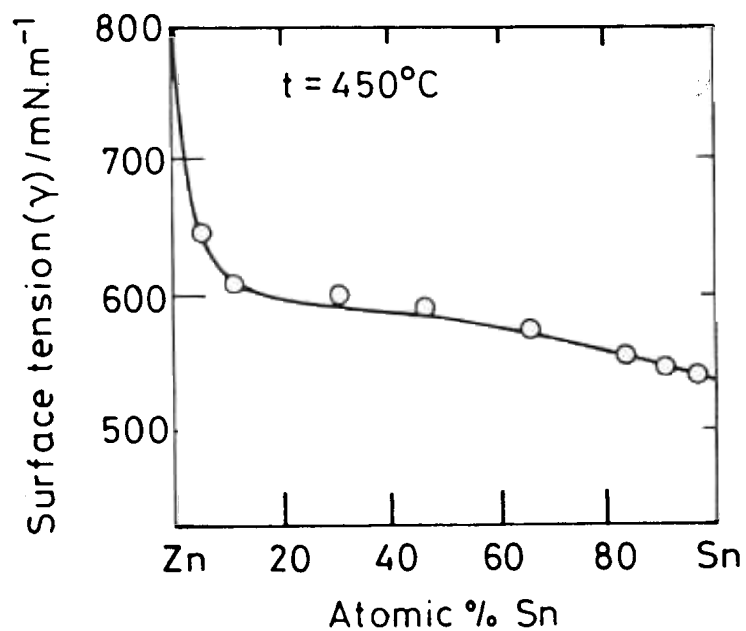


Figure 84 Variation of surface tension with composition of Sn + Zn alloys at 450 °C (Kuznetsov)⁽⁶⁵⁾.

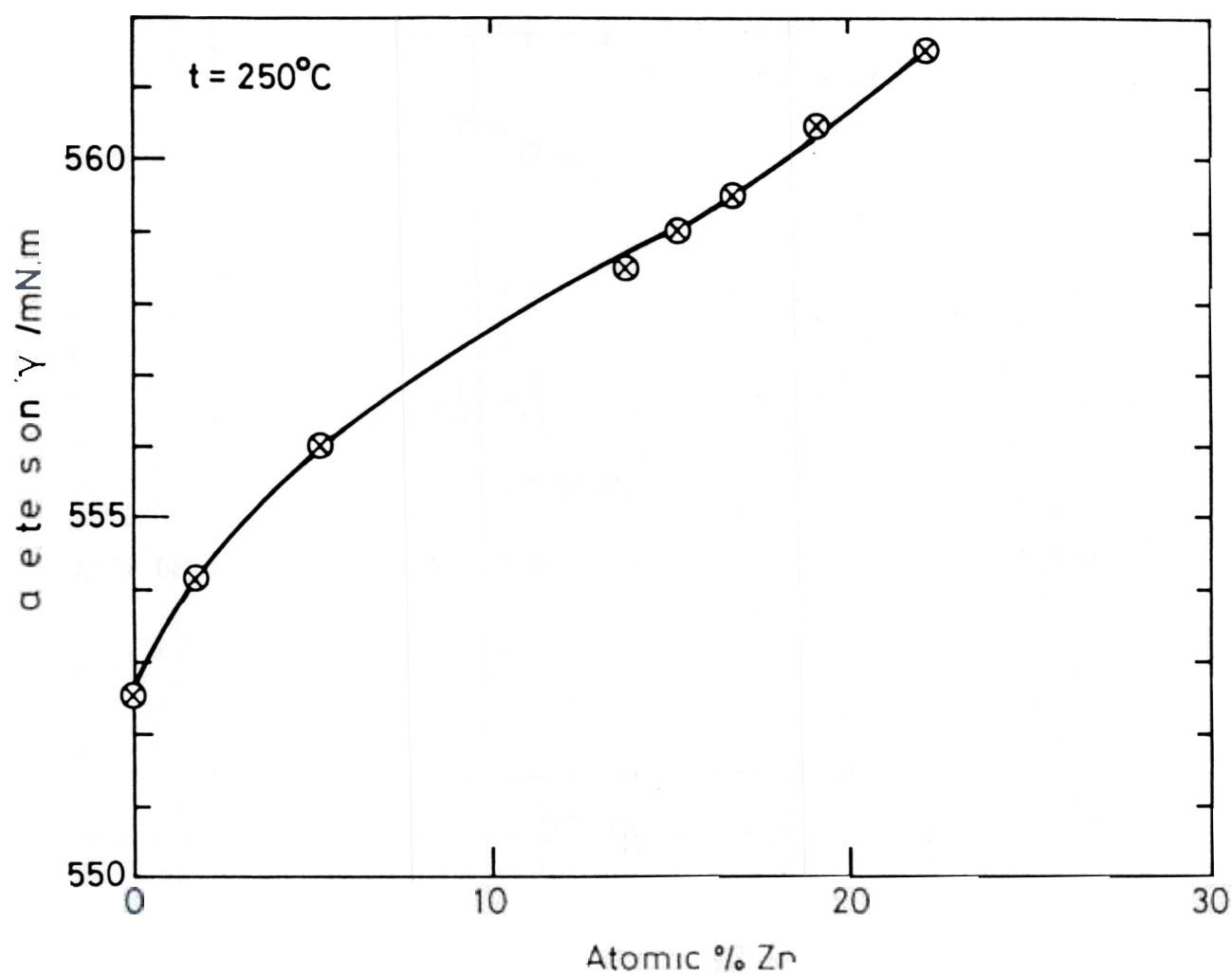


Figure Effect of composition the surface tension of Sn Zn alloys at 250 °C
(Pokrovskii)⁽¹⁵⁾

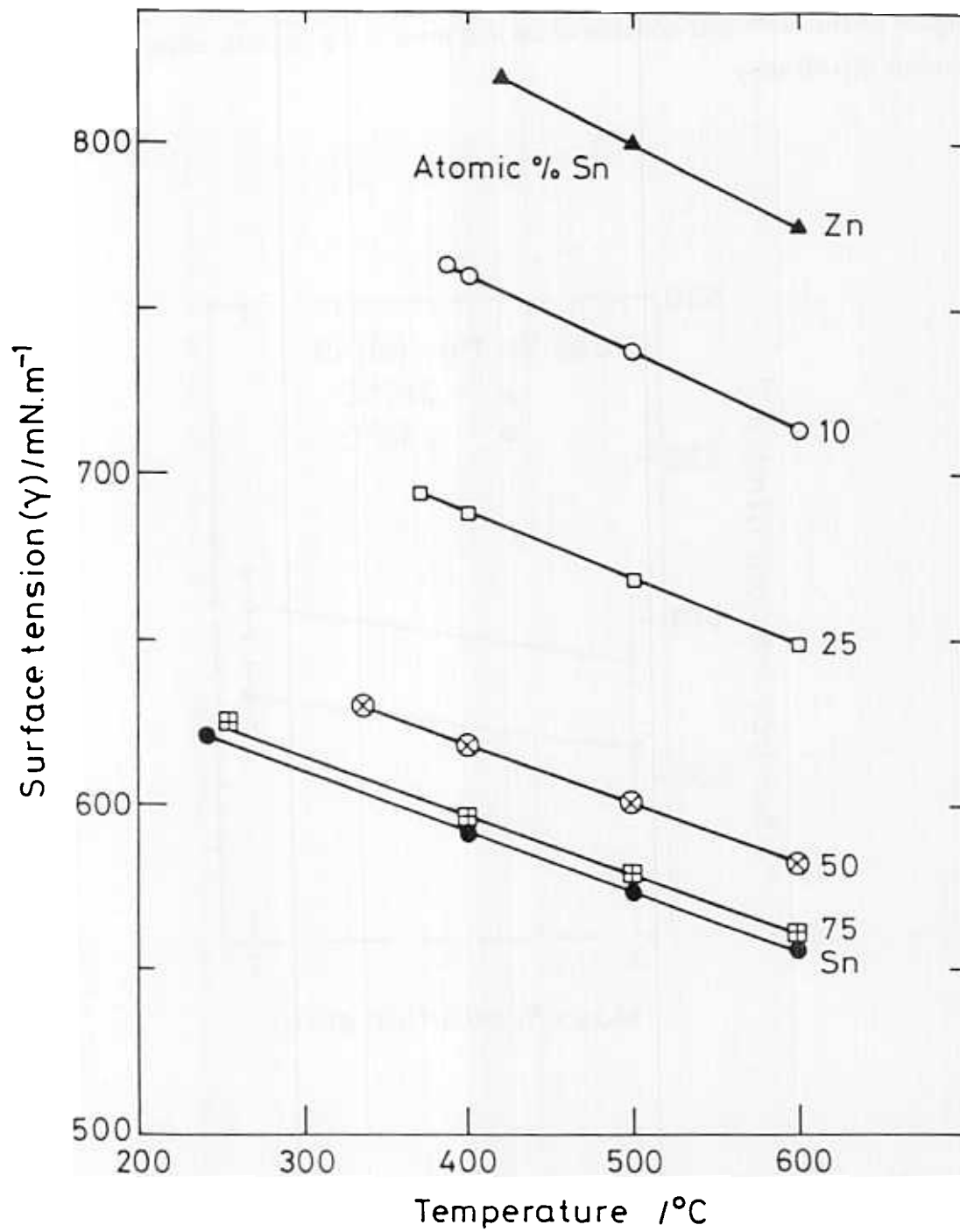


Figure 86 Effect of temperature on the surface tension of Sn, Zn and some of their alloys (Pelzel)⁽⁶⁶⁾.

Sn + Ag + Pb

Comments

Figure 87 shows⁽⁵⁴⁾ that addition of up to 2 mass % Ag has little effect on the (γ) of a near-eutectic Sn+Pb alloy.

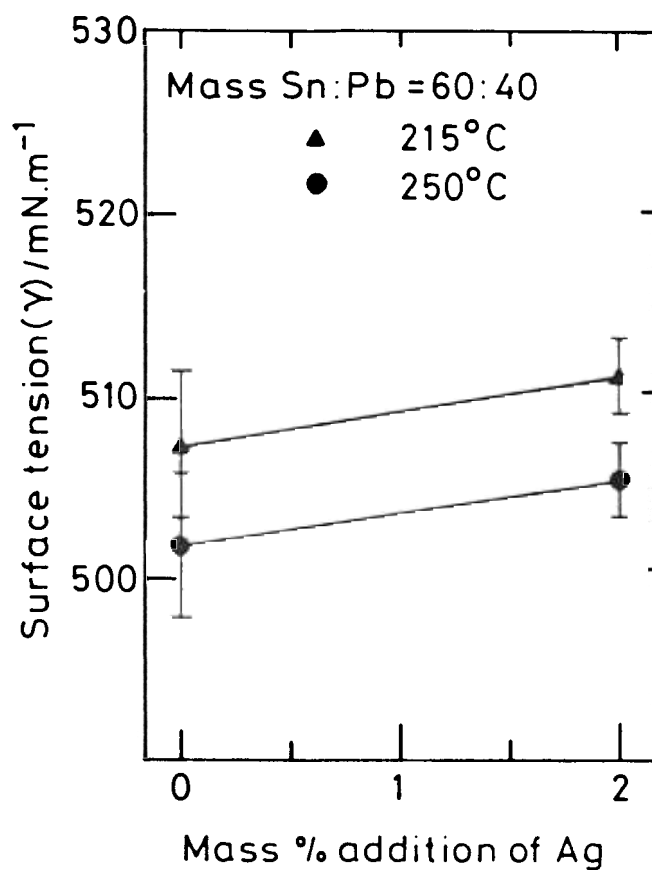


Figure 87 Effect of small additions of Ag on the surface tension of alloy 60 Sn 40 Pb (mass %) at 215 °C and 250 °C (Carroll)⁽⁵⁴⁾.

Sn + As + In

Comments

Figure 88 shows⁽⁶⁷⁾ that addition of low levels of Sn to a melt of InAs will result in a small increase in (γ) . The $\gamma(t)$ curves are linear with negative slope.

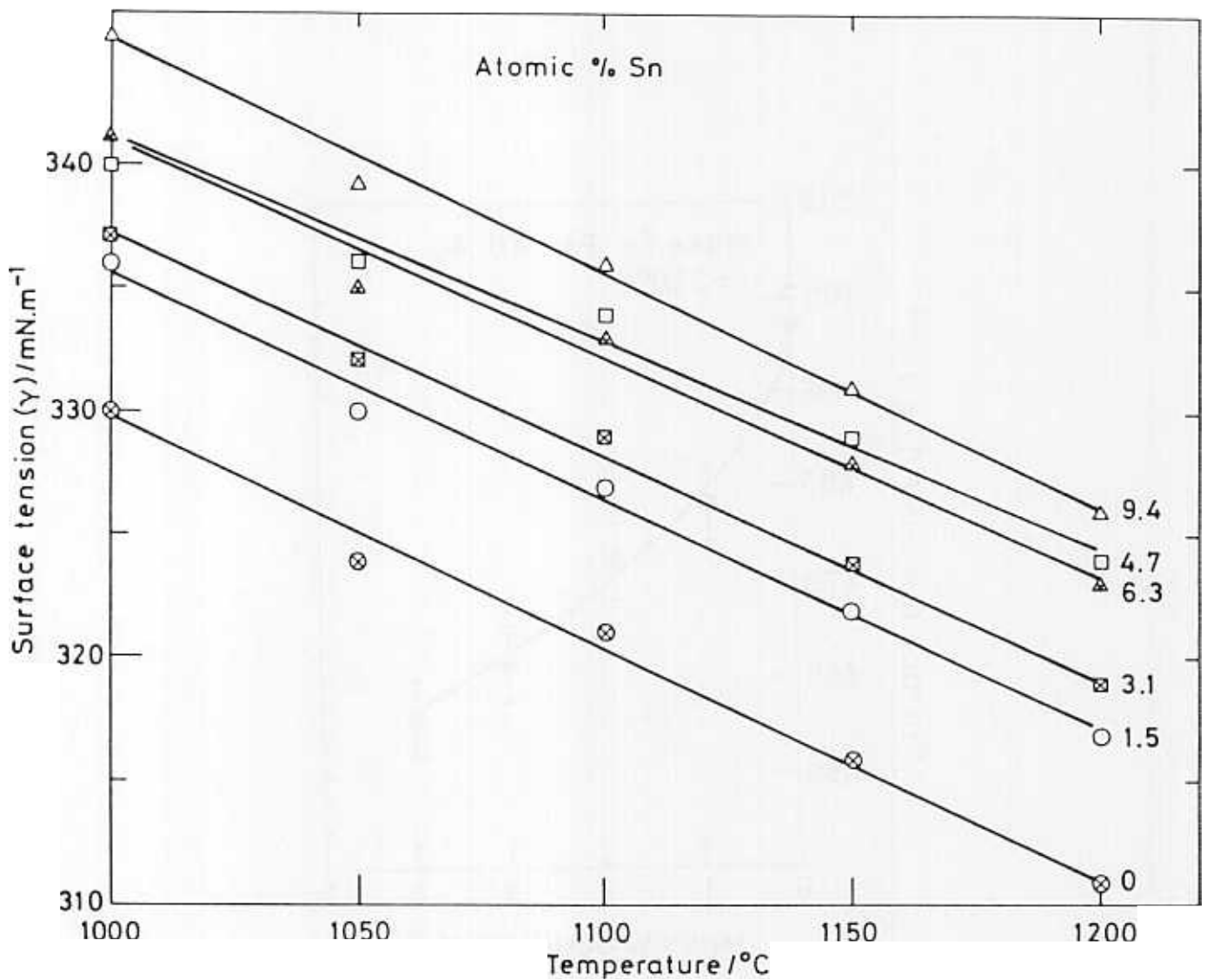


Figure 88 Effect of temperature and of additions of tin on the surface tension of InAs (Mavlonov)⁽⁶⁷⁾.

Sn + Bi + Pb

Comments

Data^(52,54) for the effect of Bi additions on the (γ) of near-eutectic alloys of Sn+Pb are shown in Figures 89-90. Both sets of data are in reasonable agreement, the presence of 4 mass % Bi decreasing (γ) by between 30 and 40 mN.m⁻¹.

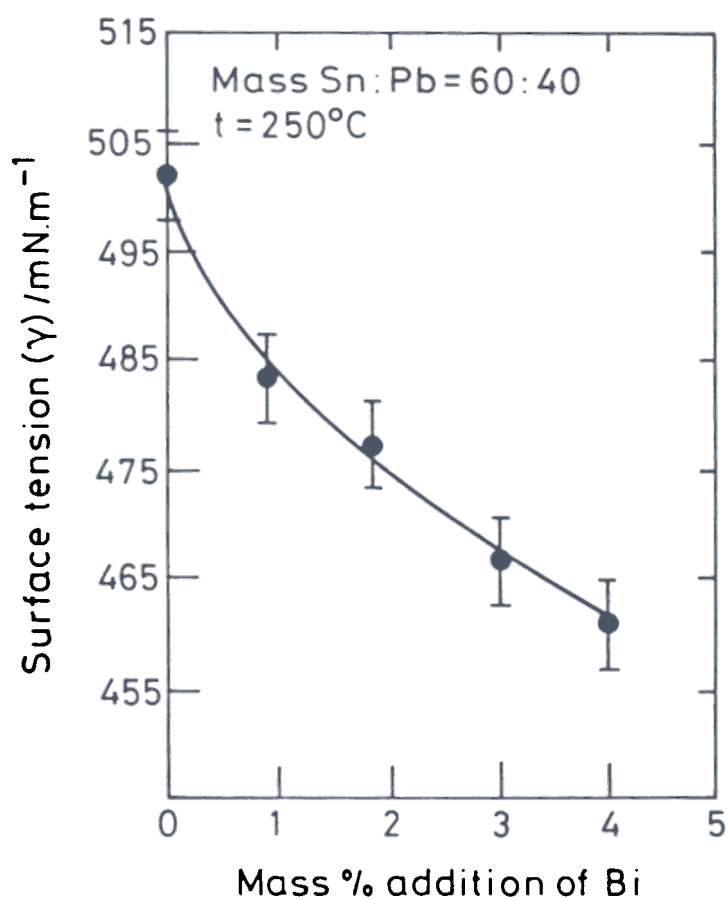


Figure 89 Effect of Bi additions on the surface tension of alloy 60 Sn 40 Pb (mass %) at 250 °C (Carroll)⁽⁵⁴⁾.

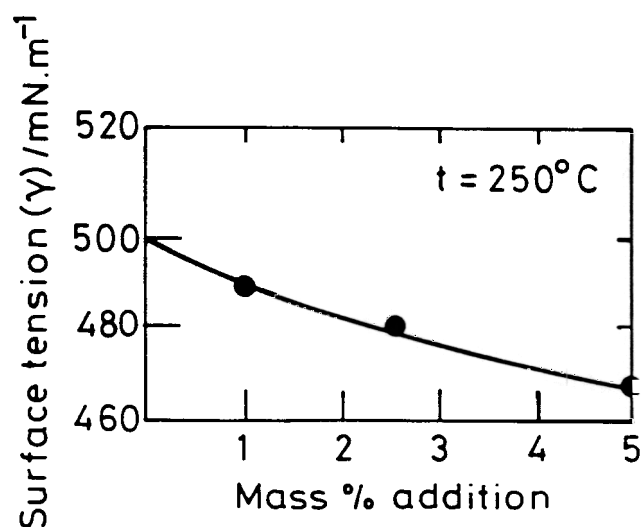


Figure 90 Effect of Bi additions on the surface tension of the eutectic Sn + Pb alloy (62 mass % Sn) at 250 °C (Somol)⁽⁵²⁾.

Sn + Cd + Pb

Comments

Data⁽⁵²⁾ for the effect of 1 mass % addition of Cd on the (γ) of the Sn+Pb eutectic are given in Figure 91, and show a small increase in (γ).

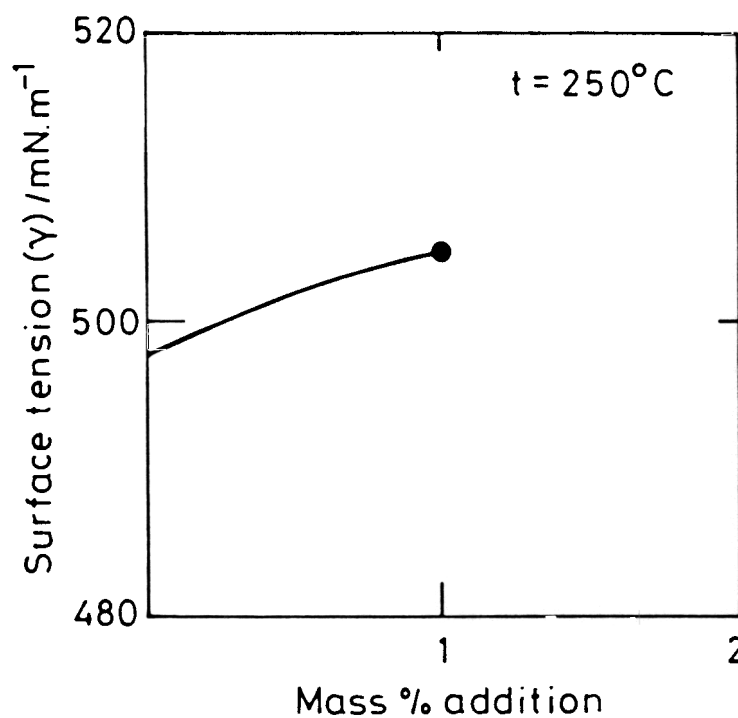


Figure 91 Effect of 1 mass % addition of Cd on the surface tension of the eutectic Sn + Pb alloy (62 mass % Sn) at 250 °C (Somol)⁽⁵²⁾.

Sn + Cu + Ni

Comments

Figure 92 shows⁽²²⁾ the effect of temperature on the (γ) of a Sn+Cu alloy and of two Sn+Cu+Ni alloys. Results indicate that the addition of 1 mass % Ni will produce a decrease in (γ) (approximately 60 mN.m⁻¹ at 850 °C).

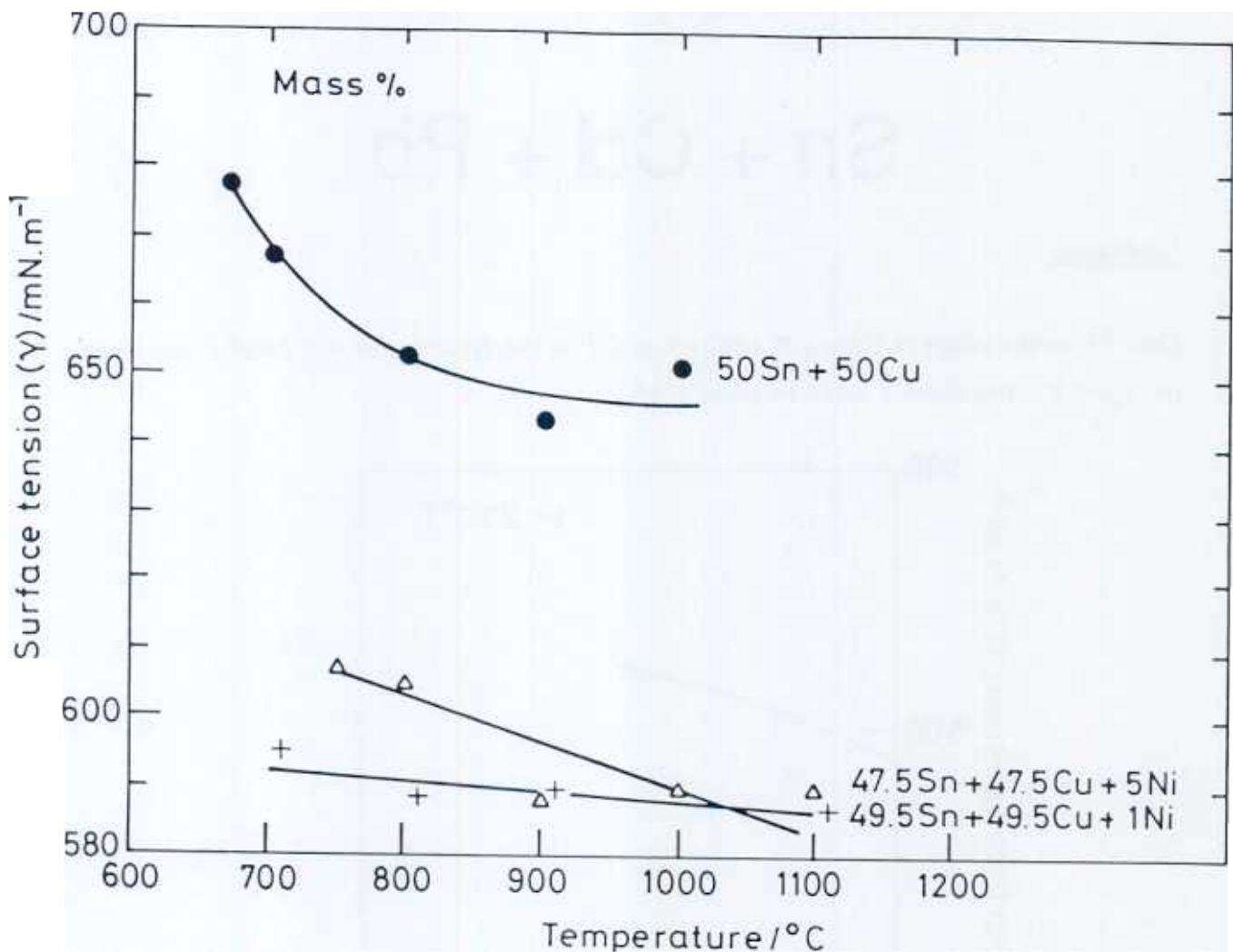


Figure 92 Effect of temperature on the surface tension of the alloy 50 Sn 50 Cu (mass %) and two of its alloys with nickel (Zagonkin)⁽²²⁾.

Sn + Cu + Pb

Comments

Figures 93-94 show the data^(52,54) for the effect of low levels of Cu on the (γ) of Sn+Pb eutectic alloys, and both sets of results are in accord in showing a small rise in (γ) with increased [Cu].

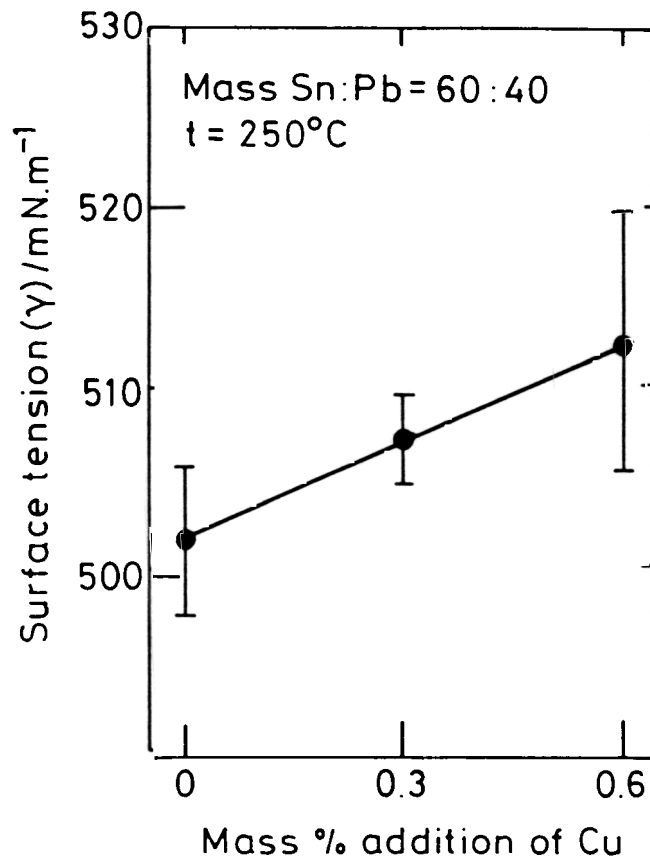


Figure 93 Effect of small additions of Cu on the surface tension of alloy 60 Sn 40 Pb (mass %) at 250 °C (Carroll)⁽⁵⁴⁾.

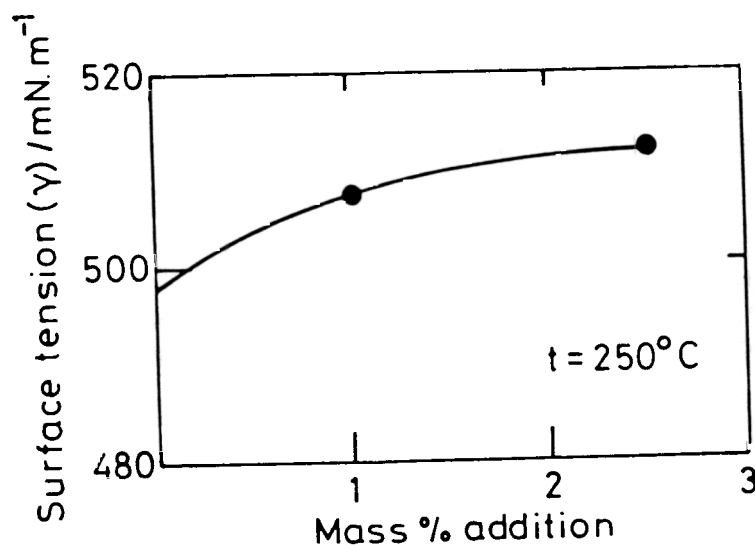


Figure 94 Effect of Cu additions on the surface tension of eutectic Sn + Pb alloy (62 mass % Sn) (Somol)⁽⁵²⁾.

Sn + Ga + In

Comments

Surface tension data^(29,68,69) of the Sn+Ga+In system are given in Figures 95-98. Figure 95 shows that Sn is slightly surface-active in Ga+In alloys, the effect being most apparent in alloys with high Ga:In ratio. Figures 96 and 97 show the isotension lines^(29,68) for the ternary system, and taking account of the temperature differences, there appears to be reasonable agreement between the two sets of data.

$t = 250^{\circ}\text{C}$

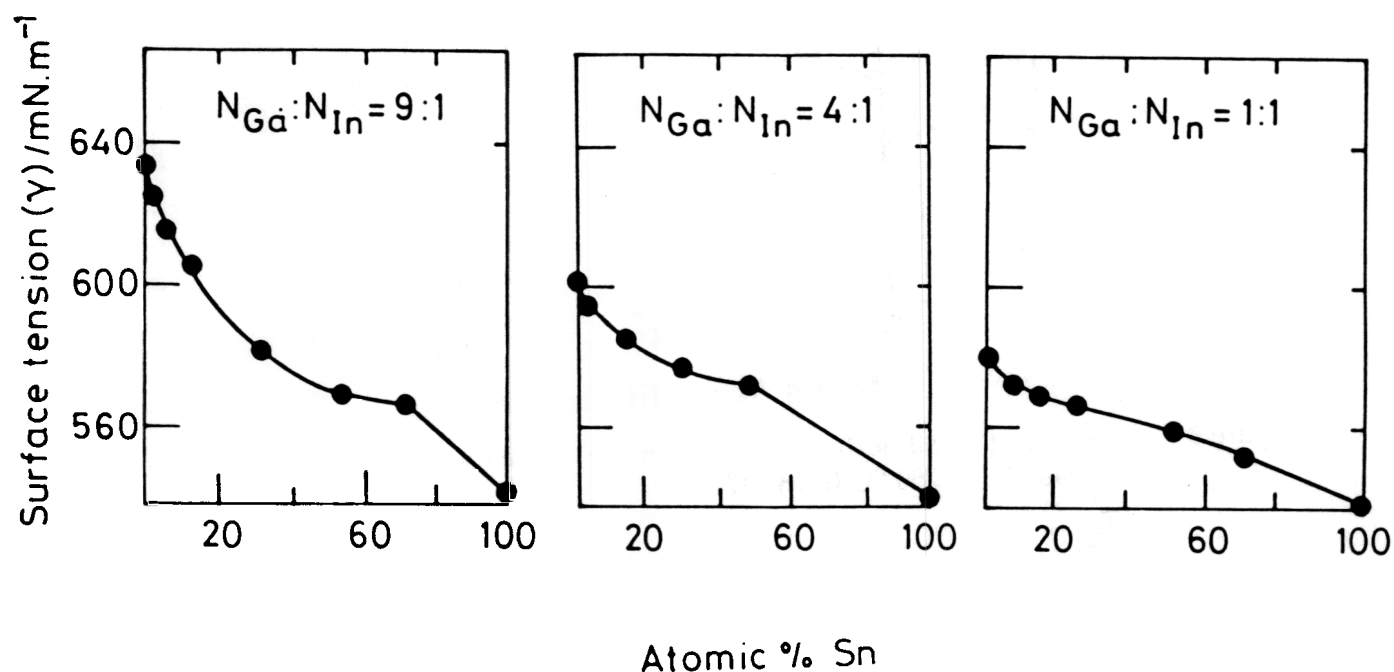


Figure 95 Effect at 250 °C, of tin content on the surface tension of Sn + Ga + In alloys, in which the atomic ratios of Ga:In are maintained constant at 9:1, 4:1 and 1:1 respectively (Kononenko)⁽²⁹⁾.

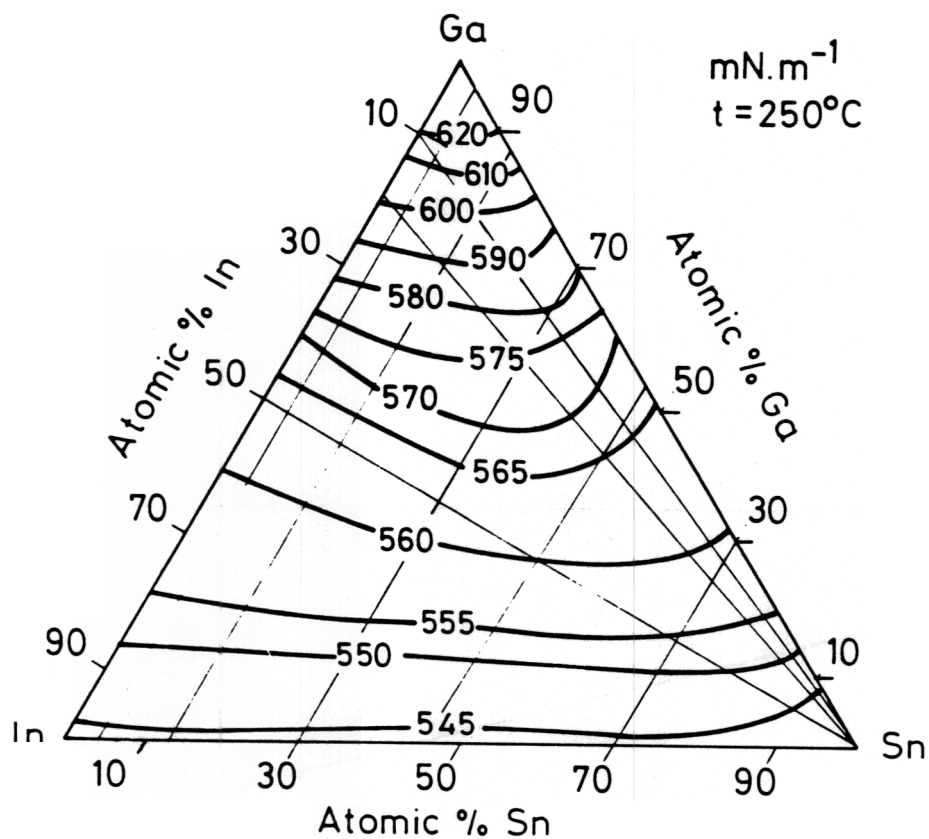


Figure 96 Isotension lines for the Sn + Ga + In system at 250°C (Kononenko)⁽²⁹⁾.

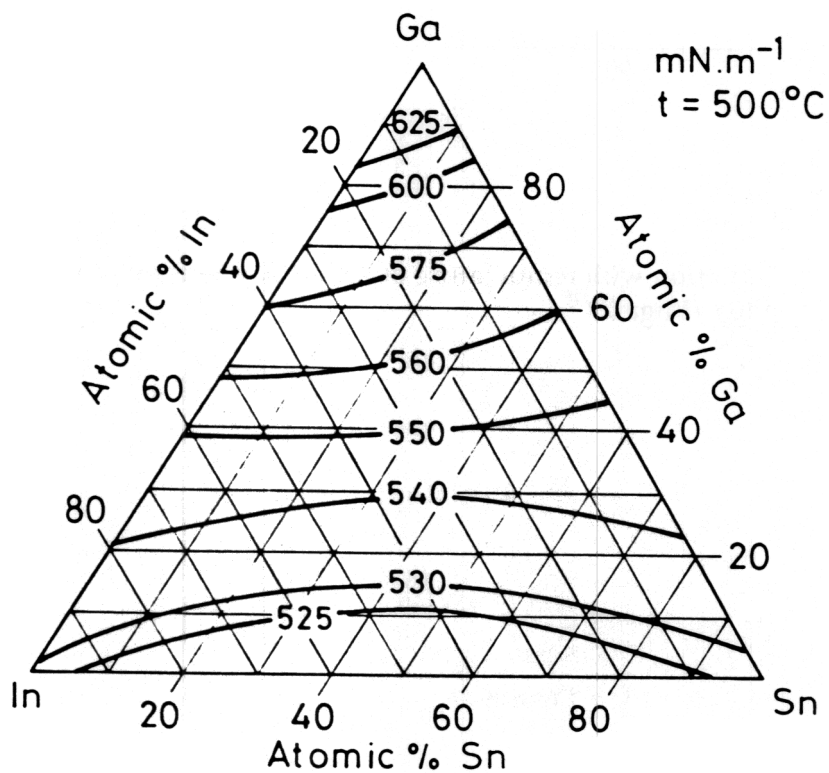


Figure 97 Isotension lines for the Sn + Ga + In system at 500°C (Ibragimov)⁽⁶⁸⁾.

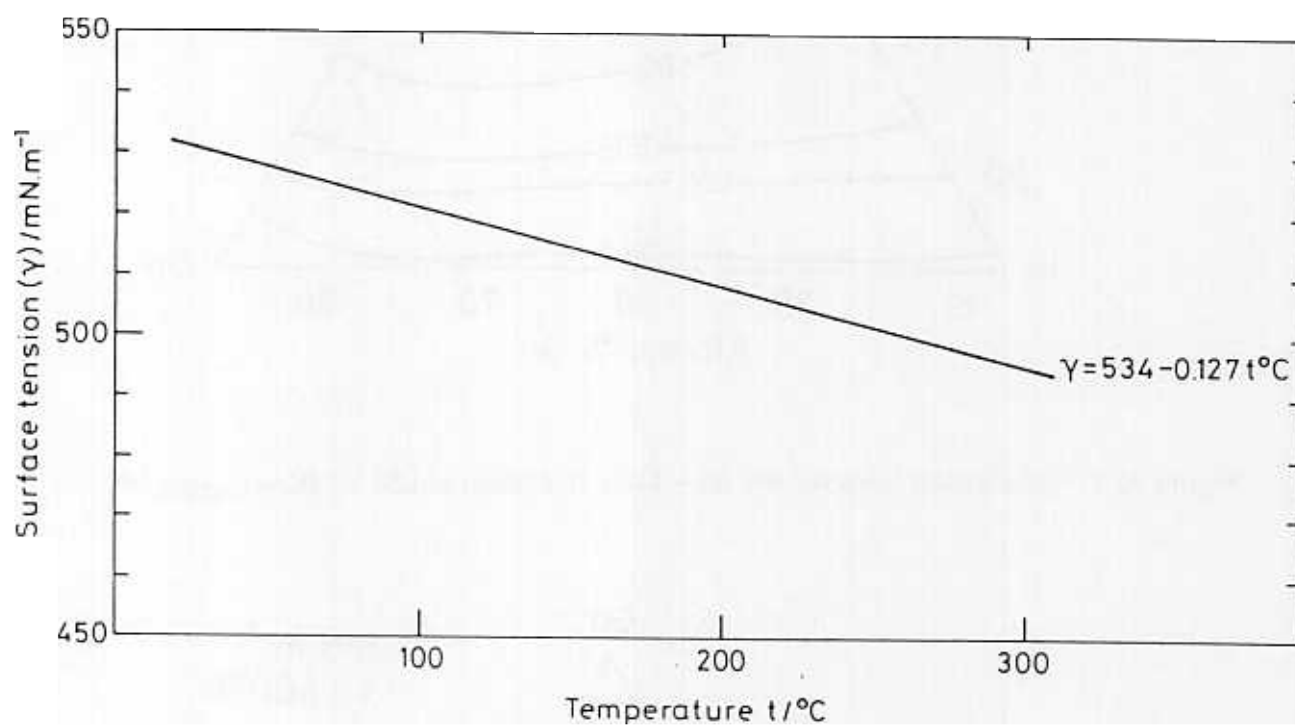


Figure 98 Variation with temperature of the surface tension of the Sn + Ga + In eutectic alloy (Migai)⁽⁶⁹⁾.

Sn + In + Pb

Comments

Figure 99⁽⁵²⁾ shows that In is not surface-active in the eutectic Sn+Pb alloy.

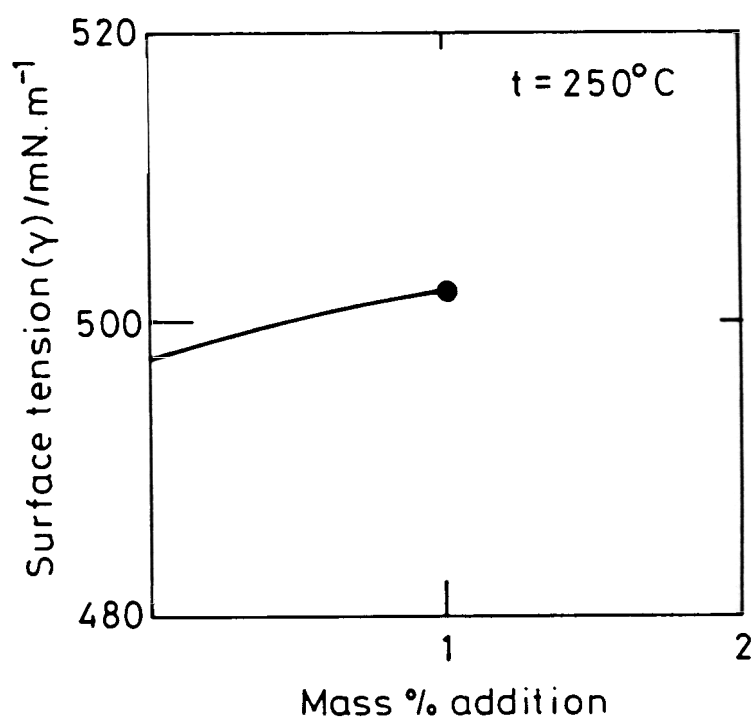


Figure 99 Effect of 1 mass % In addition on the surface tension of eutectic alloy Sn + Pb (62 mass % Sn) at 250 °C (Somol)⁽⁵²⁾.

Sn + Pb + P

Comments

Data⁽⁵⁴⁾ for the effect of P on the surface tension of a near-eutectic Sn+Pb alloy, are given in Figure 100. Small additions of P produced an increase in γ (approximately 15 mN.m^{-1} for a P content of 0.013 mass %).

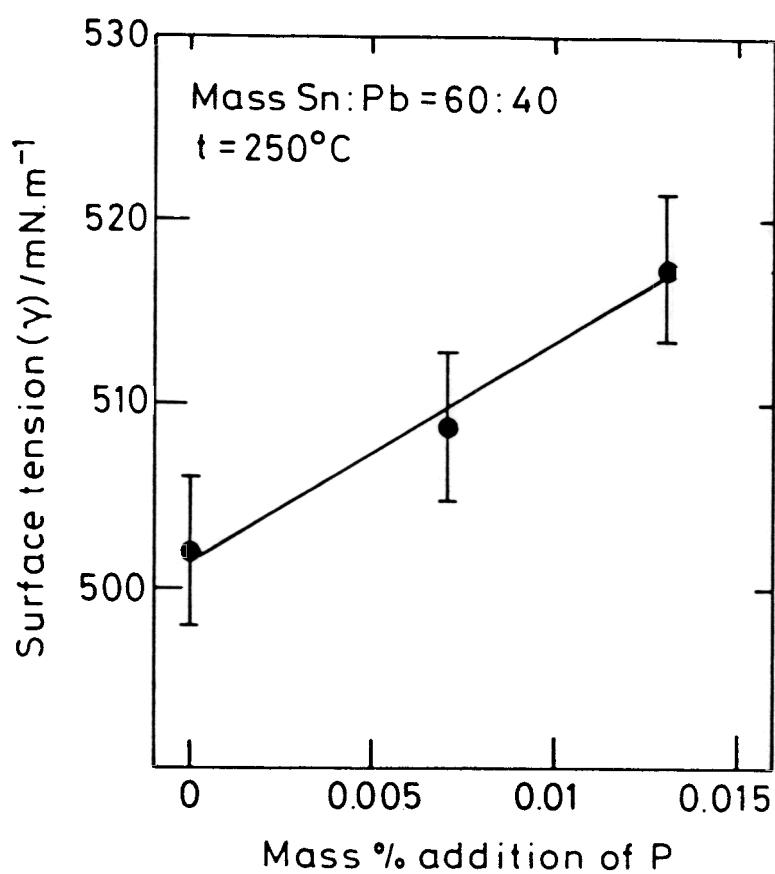


Figure 100 Effect of small additions of phosphorus on the surface tension of alloy 60 Sn 40 Pb (mass %) at 250°C (Carroll)⁽⁵⁴⁾.

Sn + Pb + Sb

Comments

The effects^(52,54) of low levels of Sb on the surface tension of Sn+Pb alloys are shown in Figures 101 and 102. The two base alloys were of similar composition, but there is some disparity between the two sets of data; that given by Carroll and Warwick⁽⁵⁴⁾ showing a higher surface-activity for Sb. (Both Somol and Beranek⁽⁵²⁾ and Carroll and Warwick⁽⁵⁴⁾, used the maximum bubble pressure technique and their data for the Sn+Bi+Pb and the Sn+Cu+Pb systems (q.v.) had shown good agreement.) One possible reason for the observed difference may be the oxygen content of the Sb used to make the ternary alloys.

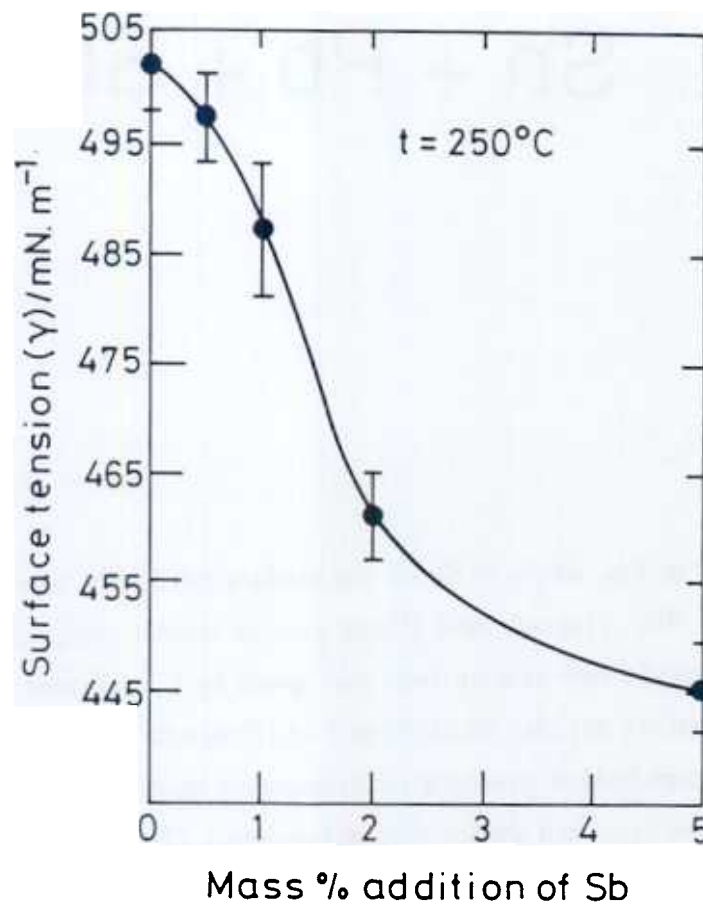


Figure 101 Effect of antimony additions on the surface tension of alloy 60 Sn 40 Pb (mass %) at 250 °C (Carroll)⁽⁵⁴⁾.

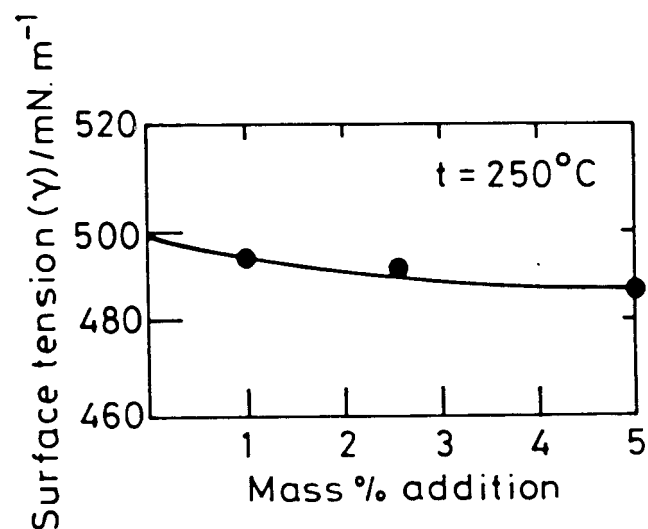


Figure 102 Effect of antimony additions on the surface tension of eutectic alloy Sn + Pb (62 mass % Sn) at 250 °C (Somol)⁽⁵²⁾.

Sn + Pb + Zn

Comments

Data⁽⁵²⁾ given in Figure 103 shows that, at 250 °C, a 1 mass % addition of Zn to the eutectic Sn+Pb alloy produces a substantial increase in γ (about 40 mN.m⁻¹).

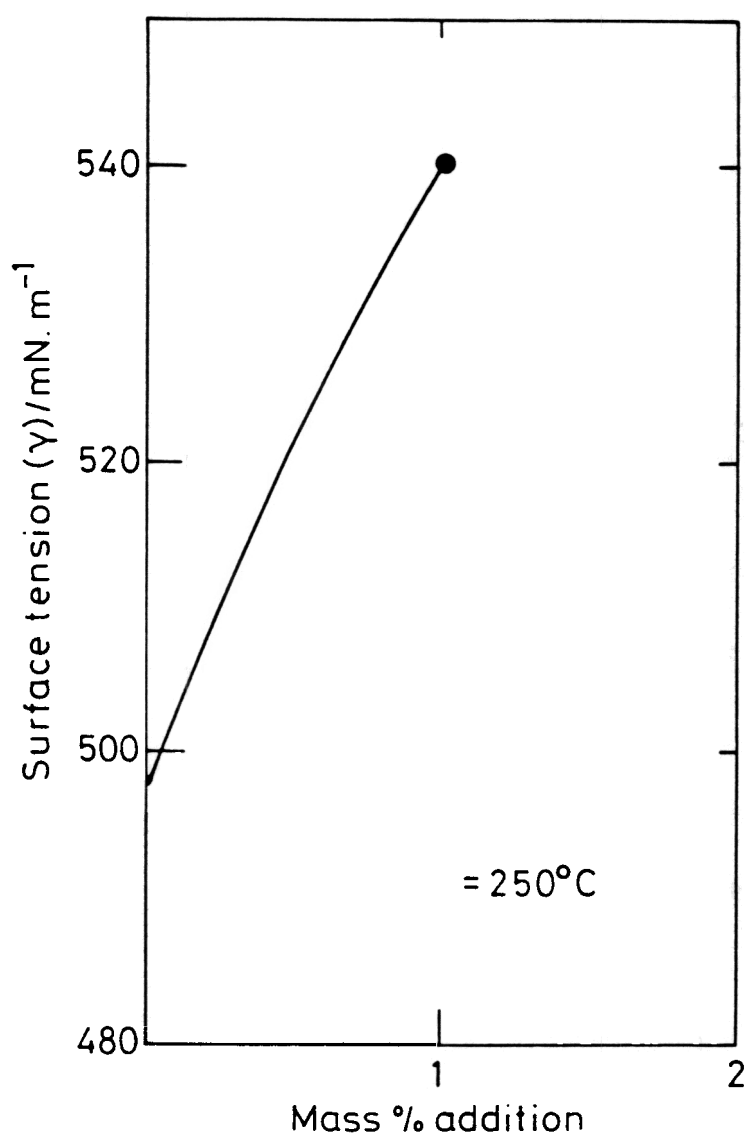


Figure 103 Effect of 1 mass % addition of Zn on the surface tension of eutectic alloy Sn + Pb (62 mass % Sn) at 250 °C (Somol)⁽⁵²⁾.

Sn + Te + Tl

Comments

Figures 104 and 105 show the effect of low levels of Sn on the surface tension of molten TlTe and Tl_2Te . In both cases, a small increase in (γ) was observed (about 2 mN.m⁻¹ per atomic % Sn).

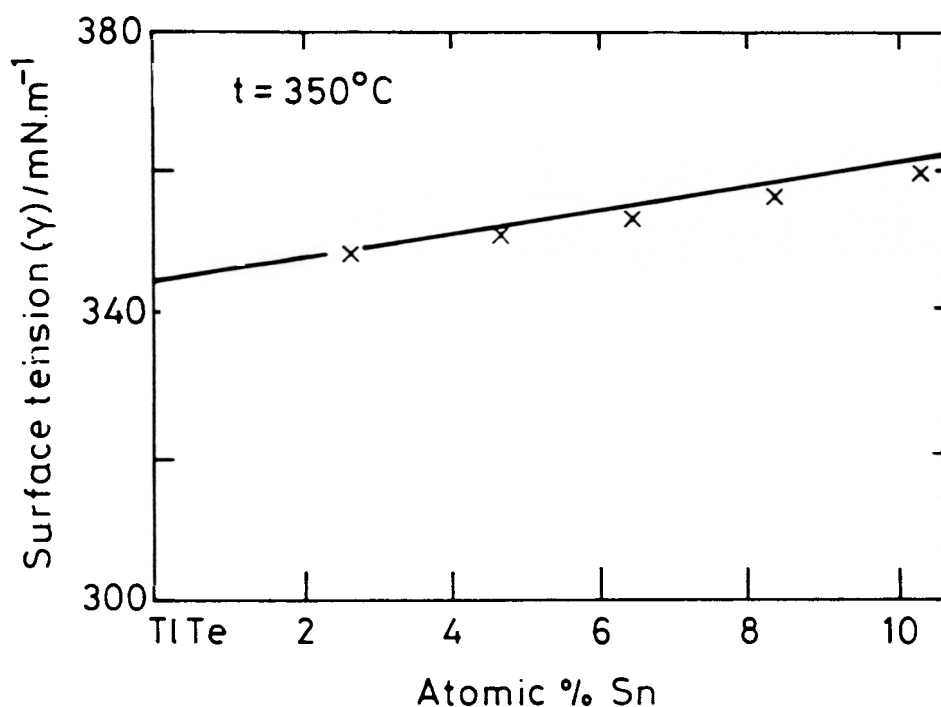


Figure 104 Effect of tin additions on the surface tension of TlTe at 350 °C (Karimov)⁽⁷⁰⁾.

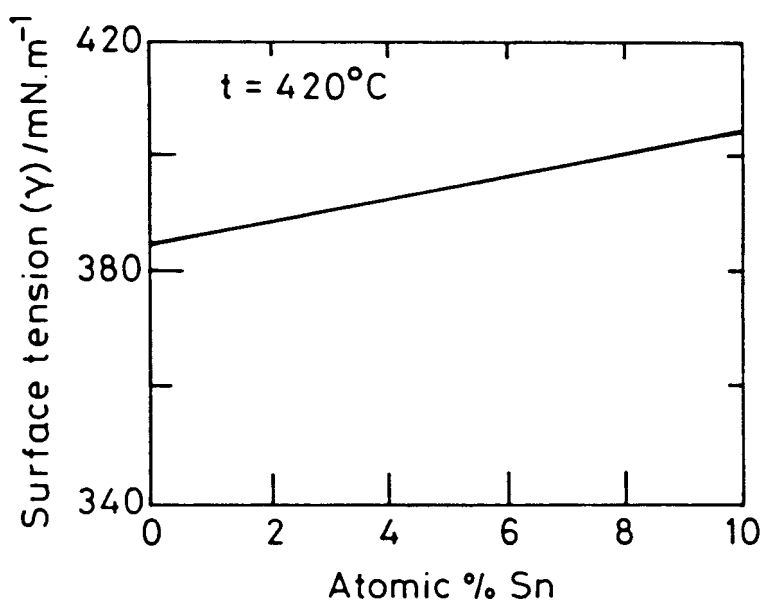


Figure 105 Effect of tin additions on the surface tension of Tl_2Te at 420 °C (Karimov)⁽⁷¹⁾.

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