JOURNAL OF MATERIALS SCIENCE 20 (1985) 3597–3604

Surface phenomena at the interfaces of the tungsten–liquid Cu–Sb alloy system

JACEK SENKARA, WŁADSŁAW K. WŁOSINSKI
Institute for Technology of Electronic Materials, Konstruktorska 6, 02-673 Warsaw, Poland

This paper describes phenomena occurring at the interfaces of the solid tungsten–liquid Cu–Sb alloy. Model experiments, such as the measurement of surface energy of the liquid, the wettability of tungsten in the equilibrium conditions, kinetics of wetting and structural investigations have been carried out within the temperature range 1373 to 1573 K and in the range of antimony concentration up to 35 at% in the liquid. On the basis of the results obtained and thermodynamic calculations it has been demonstrated that antimony is surface-active at all interfaces of the system.

1. Introduction

The subject of this study is connected with industrial needs in the range of contact composite materials designed for use in the quickly developing and promising domain of the vacuum switching technique. Surface phenomena at the interfaces, linked with simultaneous presence in the system of a liquid and a solid phase, lie at the foundations of the technology of composites, particularly of liquid phase sintering and infiltration. They are also of great importance during the work of electric contacts.

In the available literature there is practically no information on surface phenomena occurring in the W–Cu–Sb system, contrary to the model system of W–Cu metals, insoluble in one another, which has been examined fairly well in this respect [1–3]. Little is known of the Sb–W phase equilibrium system, except for the suggested possibility of a weak chemical reaction of these elements [4].

In this paper we have attempted to describe and interpret the surface phenomena occurring at the interfaces of the above-mentioned system, within the range of antimony concentrations reaching 35 at %.

2. Experimental procedures and results

2.1. Test materials and conditions

The following materials were used: 99.999% pure copper, 99.99% pure tungsten sheet and 99.9999% pure antimony. The Cu–Sb alloys were obtained by melting the ingredients in graphite crucible in a laboratory induction vacuum furnace Balzers VSG-02. The tungsten plaques were polished: the average height of surface irregularities was smaller than 0.1 μm.

A pure atmosphere of flowing hydrogen of maximum pressure of H_2O 0.26 Pa (dew point −70° C) and O_2 0.1 Pa (ca. 1 ppm) was used. Most of the experiments were carried out in a surface phenomena testing device of our own design, described earlier [5]. Both phases (liquid and solid) were separately heated, and the tungsten surface was refined prior to its contact with the liquid. Fig. 1 shows two variants of phase contact applied: the liquid drop is pressed out from the crucible on the tungsten substrate (a), or the tungsten plate is slowly lowered on to the top of the drop resting on the non-wetting graphite substrate (b).

2.2. Surface energy of liquid Cu–Sb alloys

The surface energy, ω_{LV}, of liquid Cu–Sb alloys was examined by the "large drop" method [6], in 19 mm diameter crucible of spectrographically pure graphite. The ratio of drop radius to its height was greater than 2.0. Calculations were carried out according the Porter improved procedure [7] on the basis of drop parameters

0022–2461/85 $03.00 + .12

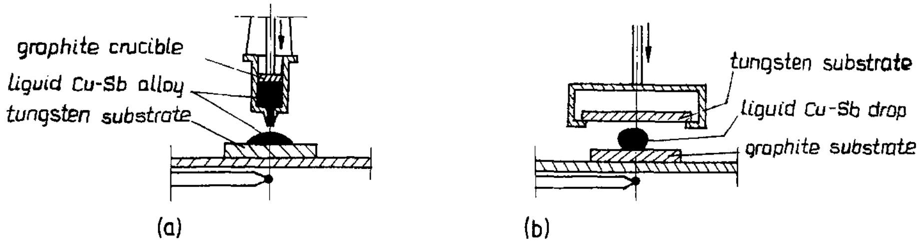

Figure 1 Two variants of wetting of a tungsten surface by Cu–Sb alloys: (a) by placing a liquid drop on immobile substrate, (b) by slow contact of tungsten substrate with an immobile drop.

measured on photographs. The results of the calculations are shown in Fig. 2.

The shape of the isotherms indicate a strong relationship of ω_{LV} for low antimony concentrations. The effect of temperature on the surface energy of alloys investigated is rather insignificant.

2.3. Wettability in the equilibrium conditions

The equilibrium contact angle was assumed to be a measure of wettability. The angle was determined on the basis of the measurements made on a photograph of a sessile drop of the Cu–Sb alloy on the flat tungsten surface. The wetting act was carried out according to the diagram shown in Fig. 1a. The results are presented in Fig. 3. Each datum point is an arithmetic mean for three samples.

From the figure, it can be seen that antimony exerts a significant effect on the degree of wettability in the system under examination. Addition of antimony to copper lowers the θ value which reaches a minimum for $x_{Sb} = 0.02, \ldots, 0.04$. For higher antimony concentrations the wettability becomes much poorer.

2.4. Kinetics of wetting

The experiments were carried out according to the variant from Fig. 1b. The liquid phase drops all had the same volume of 0.2 cm^3. The contour

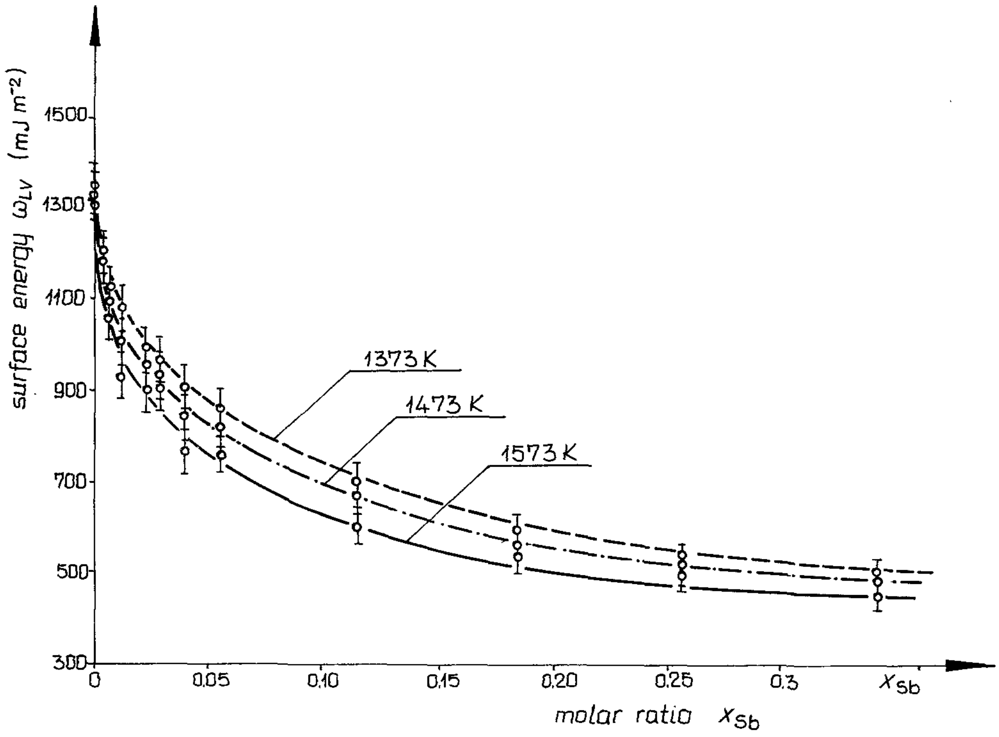

Figure 2 Surface energy, ω_{LV}, of liquid Cu–Sb alloys in a hydrogen atmosphere as a function of composition and temperature.

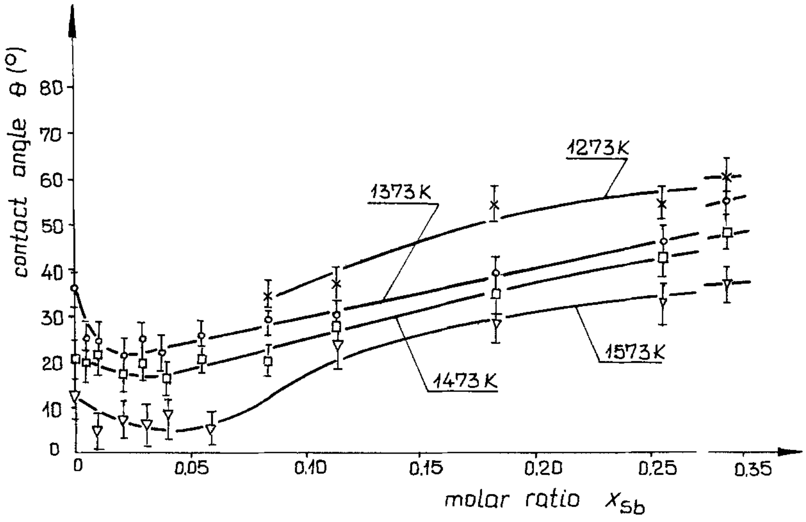

Figure 3 Equilibrium contact angles of tungsten by Cu–Sb alloys depending on solution composition and temperature.

of the spreading drop was filmed on 16 mm cine-film at a speed of 2000 frames $\sec^{-1}$. The diameter of the wetted surface and the dynamic contact angle were measured. Fig. 4 presents the relation of the wetted surface area to the time and the rate of spreading to the composition of the Cu–Sb alloy.

It is seen from the figure that the relationship of wetted surface to time is of a linear character, except for the Cu–34.3 at % Sb alloy. The diagrams embrace the interval up to approximately 10^{-2} sec, and within that time the spreading ability of this alloy is stopped, whereas alloys of other compositions spread at an unchanged rate.

2.5. Structural investigations

The experiments were carried out using the X-ray Jeol JXA-50A microanalyser. Areas near the W–Cu–5.5 at % Sb alloy interface were analysed. The composition of the alloy was chosen based on the wettability results: for this composition the strongest interfacial reaction could be expected. Test samples were prepared by immersing the pieces of tungsten sheet, previously surface-refined, in the liquid alloy, keeping then there for 6 h at 1373 and 1573 K, followed by rapid cooling. In Fig. 5 typical distributions of tungsten and antimony concentrations, perpendicular to the interface, are shown.

No formation of a new phase within the seal, diffusion of antimony into tungsten or solubility of tungsten in the Cu–Sb alloy, can be observed. On the other hand, a distinct growth of antimony concentration in the vicinity of its boundary with tungsten, on the Cu–Sb solution side, can be noticed. These phenomena will be tested in greater detail by isotopic methods in the future.

3. Discussion of results

The results were discussed from the point of view of explaining the effect of antimony on surface phenomena occurring in the investigated system.

A measure of the activity of the element at the interface is its excess calculated for the two-component solution according to Gibbs' equation [8]:

$$\Gamma_{\mathrm{Sb}}^{\mathrm{Cu}} = -\frac{a_{\mathrm{Sb}}}{RT}\left(\frac{\mathrm{d}\omega}{\mathrm{d}a_{\mathrm{Sb}}}\right)_T \qquad (1)$$

where: $\Gamma_{\mathrm{Sb}}^{\mathrm{Cu}}$ is the antimony adsorption while the surface excess, according to Gibbs' convention, is equal zero; ω is the surface energy; a the thermodynamic activity; R the gas constant; and T the temperature.

The results of ω_{LV} measurements (Fig. 2) suggest the antimony surface activity on liquid copper ($\mathrm{d}\omega_{\mathrm{LV}}/\mathrm{d}a_{\mathrm{Sb}} < 0$). To determine the derivative in Equation 1, the relation of ω_{LV} to a_{Sb} (not quoted in this paper) had been plotted. The diagrams were constructed on the basis of the published data on antimony activity in the Cu–Sb solution [11]. After graphic differentiation, the $\Gamma_{\mathrm{Sb}}^{\mathrm{Cu}}$ values were calculated and are presented in Fig. 6.

An attempt was also made to estimate the composition of the surface layer for antimony concentrations in the solution corresponding to extremal adsorption. The results of the calculations are shown in Table I.

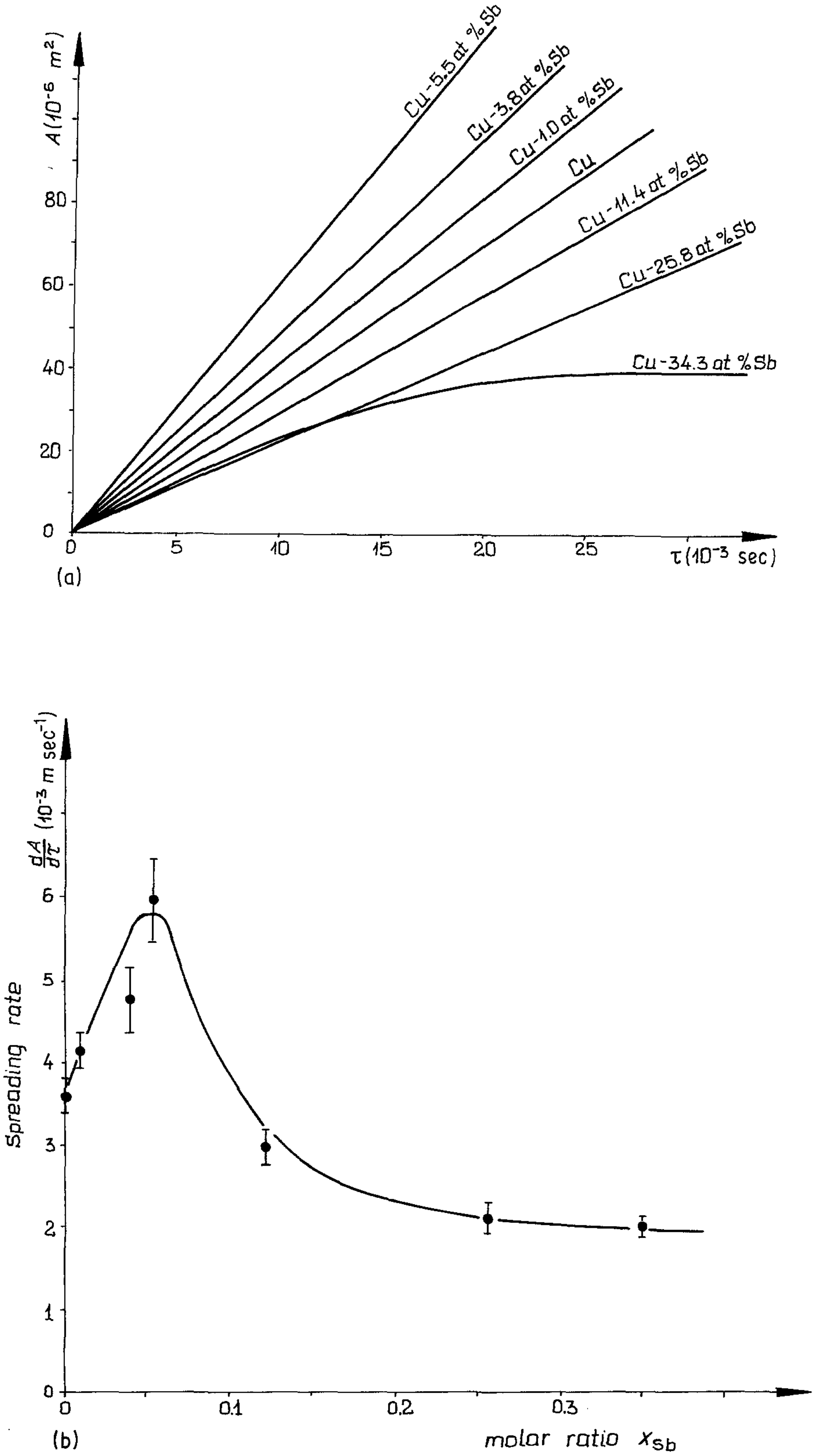

Figure 4 (a) The area of tungsten surface wetted by Cu–Sb alloys at 1373 K, as a function of wetting time. (b) Spreading rate depending on antimony concentration in liquid solution.

TABLE I Calculated composition of the surface layer in liquid Cu–Sb alloys

Quantity	Symbol	Unit	1373 K	1473 K	1573 K
Sb concentrations corresponding to the max. adsorption	x_{Sb}^{E}	–	0.20	0.18	0.14
Max. surface excess	Γ_{Sb}^{Cu}	$10^{-5}\,\mathrm{mol\,m^{-2}}$	6.5	5.7	4.0
Sb concentration in surface layer	x_{Sb}^{ω}	–	0.80	0.78	0.73

From the above considerations (Fig. 6 and Table I) it results that antimony is strongly active at the liquid Cu–Sb alloy–hydrogen interface within the temperature range 1373 to 1573 K and x_{Sb} concentrations from 0 to 0.35. The maximum surface excess Γ_{Sb}^{Cu} of the order of 4 to 6.5 × $10^{-5}\,\mathrm{mol\,m^{-2}}$ and the corresponding concentration of antimony in the surface layer can be taken as a measure of this activity. The estimated value of this concentration is four times higher than in the bulk phase.

The initial shape of diagrams in Fig. 3 suggests antimony activity also at the solid–liquid interface; however, the wettability greatly decreases with further increase in x_{Sb}. From Young's equation:

$$\cos\theta = \frac{\omega_{SV} - \omega_{SL}}{\omega_{LV}} \qquad (2)$$

it results that this is possible when $\omega_{SV}\downarrow$ or $\omega_{SL}\uparrow$ (ω_{SV} and ω_{SL} are, respectively, solid–vapour and solid–liquid energy). It is improbable that ω_{SL} would increase with the growth of antimony content: this is indicated both by the shape of the first range of curves $\theta = f(x_{Sb})$, and by the theoretical calculations of the ω_{SL} value for W–Cu and W–Sb according to Miedema and Broeder's model of the solid–liquid interface [9].

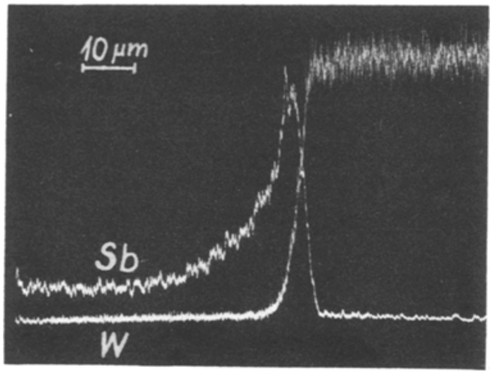

Figure 5 Linear distribution of tungsten and antimony concentrations perpendicular to the W–Cu–5.5 at. % Sb interface after 6 h contact at 1573 K.

It results from the calculations that $\omega_{W-Cu} = 961\,\mathrm{mJ\,m^{-2}} > \omega_{W-Sb} = 751\,\mathrm{mJ\,m^{-2}}$ for 1373 K; thus it is highly improbable that the addition of antimony to liquid copper would increase ω_{SL}, and to such a great extent as to cause an increase in angle θ with a decrease in ω_{LV} (Fig. 2).

The deterioration of tungsten wettability by Cu–Sb alloys with a higher antimony content can be explained by the decrease in ω_{SV} due to the adsorption of the atoms of this element on the tungsten surface from the gaseous phase. To support this conclusion, the pressure of saturated vapours over the Cu–Sb solution was calculated, using the literature data on vapour pressure of the two pure components [10], and copper and antimony activity in the solution, as well as taking into account the equilibrium constants for the $Sb \rightleftharpoons Sb_2 \rightleftharpoons Sb_4$ reactions

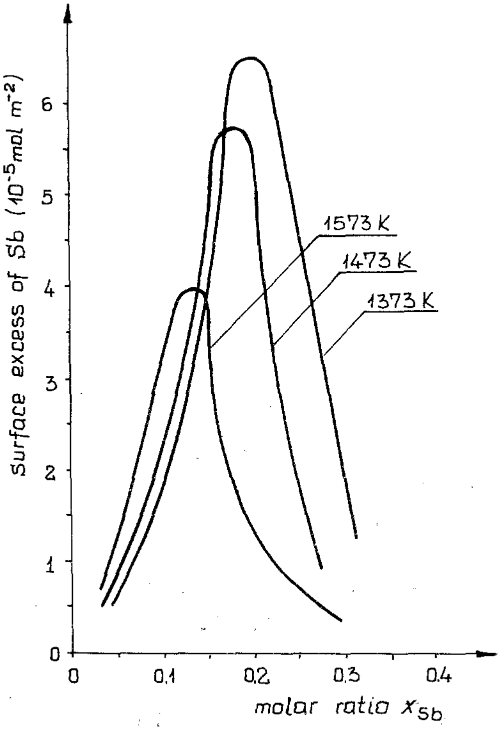

Figure 6 Surface excess of antimony at the liquid Cu–Sb alloy–hydrogen interface as a function of solution composition.

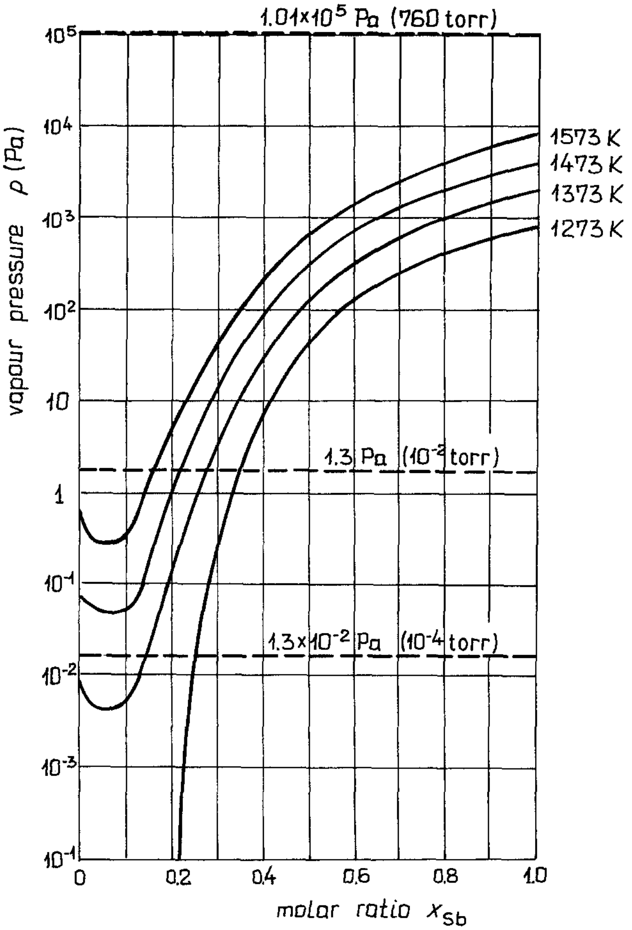

Figure 7 Pressure of saturated vapours above the Cu–Sb solution as a function of its composition and temperature.

in the gaseous phase [11]. The results are presented in Fig. 7.

There is a correlation between the deterioration of wettability and the increase in vapour pressure above the solution. In Table II a few other data, also confirming this hypothesis, are presented. In column ω_{SV}, the content of tungsten surface energy, calculated from Equation 2, in the presence of copper and antimony vapours, is given. The previously calculated values on the basis of Miedema and Broeder's model have been substituted for ω_{SL}; the remaining data are the results obtained in the present study (the additional measurement of ω_{LV} for antimony and the contact angle in the W–Sb system at 1373 K have been carried out, obtaining results of 350 mJ m^{-2} and 62°).

TABLE II Specification of data concerning the adsorption of copper and antimony vapours by tungsten (1373 K)

A–B system	ω_{SV}^{AB} (mJ m^{-2})	$\Delta H^\circ_{ads.A-B}$* (kJ mol^{-1})	$-\Delta H^\circ_{ev.B}$† (kJ mol^{-1})
W–Cu vapour	2050	315 [12]	336 [10]
W–Sb vapour	918	440 [12]	264 [10]

*Standard enthalpy of adsorption.
†Standard enthalpy of evaporation.

ω_{SV} is much higher in the W–Cu (vap.) than in the W–Sb (vap.) system, not to mention ω_S of tungsten in a vacuum (2830 mJ m^{-2} at 1773 K [1]). Thus, there is no doubt from the thermodynamic point of view that the adsorption of antimony atoms on tungsten will take place. The difference between the value of the energy of ω_S and $\omega_{W\text{-}Sb\,(vap.)}$ is so high, that this process should occur at a high rate.

Adsorption enthalpy can approximately be regarded as a criterion of the course of the process (the correct criterion is ΔG°). $\Delta H^\circ_{ads.}$ for antimony on tungsten is greater than $\Delta H^\circ_{ads.}$ for copper on tungsten, which indicates the tendency of antimony atoms towards adsorption in the first place. $\Delta H^\circ_{ads.}$ for antimony on tungsten is much higher than $-\Delta H^\circ_{ev.}$ for antimony whereas for copper these two values are comparable.

In the first case it certainly testifies to the stability of the adsorbed layer at the surface of the substrate ($\Delta H^\circ_{\text{ads.}} = -\Delta H^\circ_{\text{des.}}$).

In the light of the discussion of the results of the wettability experiments, the symptom of antimony activity in the investigated system can be a decrease in θ within the x_{Sb} concentration range in the solution to approximately 0.06, on the one hand, and a considerable reduction of ω_{SV} leading to a great deterioration of wettability within the range $x_{\text{Sb}} > 0.06$, on the other. Antimony surface excess at the tungsten–solution interface, calculated from Equation 1, can be a criterion of surface activity for the first range. In our case this value cannot be determined, because the relationship of ω_{SL} to a_{Sb} is not known. The values of ω_{SL} are usually calculated from Equation 2. This equation can be applied if the functional relation of ω_{SV} to the pressure of antimony vapour is known. However, based on the information collected, a semi-quantitative conclusion can be formulated. Since $\omega_{\text{W-Cu}} \rangle \omega_{\text{W-Sb}}$ (the difference being 22%), the function $\omega_{\text{SL}} = f(a_{\text{Sb}})$ is of a decreasing character, thus $\Gamma \rangle 0$. A small difference in the interface energies testifies to a significant, although not very high, activity of antimony at the W–liquid Cu–Sb interface.

The kinetics of spreading and wettability is a result of the action of two opposite factors: the driving force of the process resulting from the tendency of the system towards equilibrium and the kinetic resistance forces. In view of the high speed of the processes (the estimated Reynolds number $Re \rangle Re_{\text{crit.}}$), the classical laws, especially Young's equation, cannot be used to describe them. At the initial stage of spreading, the distance between the periphery of wetting and the centre of the drop is small, and therefore the liquid transportation processes play an insignificant role, and the kinetic resistance forces connected with the formation of the interatomic bonds between the liquid and the solid are decisive. Thus, the rate of spreading can be simply a criterion of the affinity of phases.

The increase in the rate of spreading (Fig. 4) with the growth of x_{Sb} to approximately 0.06, indicates a distinct activity of antimony on the solid–liquid interface and an affinity higher than copper to tungsten. A further increase in antimony concentration in the solution results in a drop of the spreading rate, this being undoubtedly connected with the adsorption of this element on the tungsten surface. The appearance of antimony adsorption on the solid–gas interface in the course of kinetic tests confirms the conclusion about its occurrance from the gaseous phase, because for such short periods of contact between the phases, other mechanisms (such as surface diffusion from the liquid) are hardly probable.

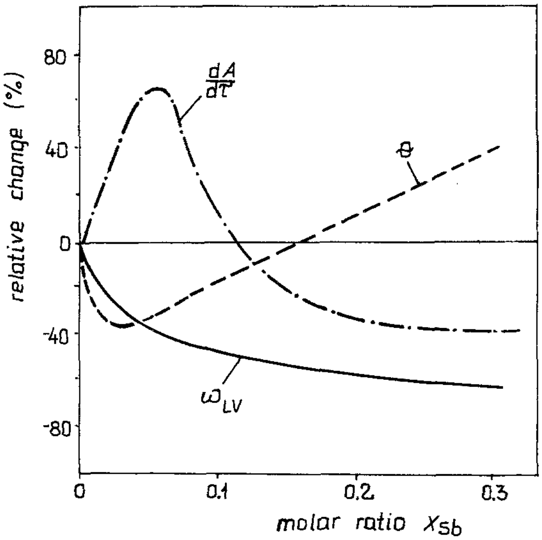

Figure 8 The relative change of measured values in relation to pure copper as a function of antimony concentration in the Cu–Sb solution, at 1373 K.

X-ray microanalysis has revealed a distinct increase in antimony concentration in the interfacial area on the liquid side, which can indirectly indicate the inter-phase activity of this element. The result of the analysis testifies to the absence of a strong chemical reaction between antimony and tungsten; nevertheless, because of the high absorption coefficient of the characteristic antimony X-radiation by tungsten, it cannot be completely excluded.

Fig. 8 sums up considerations about the role of antimony in the system under investigation. In the figure, the results of experiments of the surface energy of the liquid phase, the equilibrium contact angle and the kinetics of spreading have been presented jointly, for a temperature of 1373 K, in one coordinate system. On the X-axis the values of the composition of the Cu–Sb alloy have been marked and the relative change of the given value in relation to pure copper has been put on the Y-axis. A distinct correlation between the shape of the curves and the curve for 1373 K in Fig. 7 can be noticed.

4. Conclusions

1. Antimony is surface-active at all interfaces of the W–Cu–Sb system within the temperature range 1373 to 1573 K and x_{Sb} up to 0.35.

(a) At the LV interface it reduces the surface energy as a result of adsorption (the calculated maximum surface excess is $6.5 \times 10^{-5}\,\mathrm{mol\,m^{-2}}$, and antimony concentration in the surface layer is four times greater than its concentration inside the solution).

(b) At the SV interface, within the range of $x_{\mathrm{Sb}} > 0.06$, it greatly reduces the surface energy by way of adsorption from the gaseous phase (the estimated value $\omega_{\mathrm{W-Sb\,vap.}}$ is three times smaller than the value of $\omega_{\mathrm{W-vacuum}}$).

(c) At the SL interface it reduces the value of the interfacial energy and, for $x_{\mathrm{Sb}} < 0.06$, it improves wettability both in the equilibrium and kinetic aspect (in relation to pure copper the extreme value of angle θ is about 40% smaller and the spreading rate, $\mathrm{d}A/\mathrm{d}\tau$, is higher by about 60%).

2. The presence of antimony in the liquid phase does not result in a significant chemical reaction between the phases.

References

1. E. N. HODKIN, M. G. NICHOLAS and D. M. POOLE, *J. Less-Common Metals* **20** (1970) 93.
2. M. G. NICHOLAS and D. M. POOLE, *J. Mater. Sci.* **2** (1967) 269.
3. Yu. W. NAIDICH, Y. A. LAVRINENKO and W. A. EVDOKHIMOV, *Sov. Powder Met.* **4** (1977) 43.
4. F. A. SHUNK, "Constitution of Binary Alloys. Second Supplement" (McGraw Hill, New York, 1969).
5. Polish Patent No 115 102, 30 June (1982).
6. Yu. W. NAIDICH, "The Contact Phenomena in Liquid Metals" (Naukova Dumka, Kiev, 1972) in Russian.
7. W. MISSOL, "The Energy of Interfaces in Metals" (Śląsk, Katowice 1974) in Polish.
8. A. W. ADAMSON, "Physical Chemistry of Surfaces" (Interscience, New York, 1960).
9. A. R. MIEDEMA and F. J. A. den BROEDER, *Z. Metallkde* **70** (1979) 14.
10. O. KUBASCHEWSKI and C. B. ALCOCK, "Metallurgical Thermochemistry" (Pergamon Press, Oxford, 1979).
11. T. AZAKAMI and A. YAZAWA, *Can. Met. Quart.* **15** (1976) 111.
12. A. R. MIEDEMA and J. W. F. DORLEIJN, *Surf. Sci.* **95** (1980) 447.

Received 16 July
and accepted 20 November 1984