The wettability of silicon carbide by Au–Si alloys

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Abstract

The wettability of SiC-monocrystals by Au–Si melts (covering the full concentration range) was studied at high temperature (1500°C). The concentration dependence of the contact angle passes through a broad minimum near 25 at.% Si. This is explained by intrinsic properties of Au–Si alloys and their interaction with SiC surface. © 1998 Elsevier Science S.A. All rights reserved.

Keywords: Wettability; Contact angle; Liquid metals; Silicon carbide

1. Introduction

The interface properties of silicon carbide–liquid metals (wetting, adhesion, contact interaction) are important in composite material technology, joining of SiC materials and semiconductor processing. Silicon carbide refractories are used in contact with metal alloys [1]. In the literature there are data about SiC-wettability by pure liquid metals [2–4] and some binary alloys [5], including that of Al–Si (19.5 at.% Si [7] and in full concentration range [8]) as well as Au–Si alloys [6]. In the Al–Si–SiC system the minimum on a contact angle isotherm has been observed at middle concentration [8]. B. Drevet et al. [6] found a minimum in the concentration dependence of the contact angle for the Au–Si–SiC system. But the authors measured wettability only for the interval 0–50 at.% Si (the temperature was 1100°C). The curve $\theta–X_{Si}$ was constructed by means of the extension (extra- and interpolation) of its part to large X_{Si} values (> 50%) until a hypothetical value of contact angle for 'liquid silicon at 1100°C' was reached. This curve passes through a minimum at $X_{Si} = 40–50\%$. The authors suggested that the minimum was conditioned by external reasons (pollution), not intrinsic alloy properties. A minimum on a contact angle isotherm is a very interesting phenomenon, theoretically and for practical purposes. Therefore, we carried out a detailed investigation of wettability in the Au–Si–SiC system for the full concentration range at 1500°C.

2. Experiments

The contact angles were measured using the sessile drop method [3] in an argon atmosphere ($P = 10^5$ Pa). Argon was purified by Mg- and Ti-getter. Silicon carbide α-SiC monocrystals 6H type ('black' and 'green' coloured) were used. The hexagonal plane (0001) was investigated. This plane was polished with diamond abrasives to a surface roughness of $\approx 0.01\,\mu$. Therefore, we did not have to take into account the Si- or C-crystallographic layers; a mixed Si and C atomic surface was studied.

We had the experience of our earlier work [9] for surface tension of Au–Si alloys in the full concentration range. Therefore, work of adhesion and interface tension can be evaluated for each alloy to make complete analyses of contact systems.

Metallic alloys were prepared by melting. Silicon of semiconductor purity and gold of 99.99% purity were used. The experiments were carried out at high temperature—up to 1500°C. High temperature promotes a diminishing or eliminating influence of possible oxide films on drop or on solid substrate surfaces. The time it took to measure each contact angle was $\approx 10–15$ min. After this time interval there was practically no change in contact angles at such high temperature. High temperature experiments provide more accuracy; the scatter in each measurement of a contact angle was less than 1–2°.
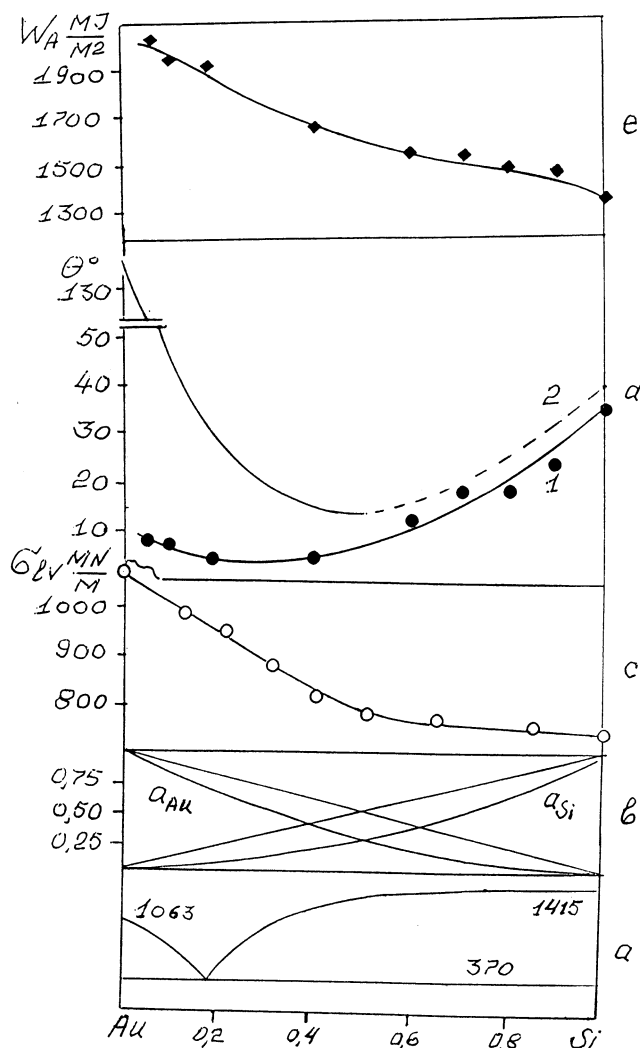
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Fig. 1. Concentration dependence of capillary properties of the Au–Si–SiC system. $T = 1500°C$. (a) Constitution diagram of Au–Si alloys (schem); (b) thermodynamic activity of components of Au–Si alloys; (c) surface tension isotherm; (d) contact angle–X_{Si} isotherm: (1) our data, $T = 1500°C$, (2) curve from [6], $T = 1150°C$, (3) work of adhesion concentration dependence.

3. Experimental results

The alloys of 0; 5; 10; 18.6; 40; 60; 70; 80; 90; 100 at.%. Si were investigated. Concentration dependence of contact angles is presented in Fig. 1(d). Typical temperature and time dependences of contact angle are shown in Table 1 (for some alloys).

Strong contact angles dropping are observed for alloys of low Si-concentration. In particular, the con-

Table 2
Time-contact angle dependence (alloy Au + 18.6 at.% Si) at $T = 1100°C$

τ (min)	0	4	7	10	15
θ (°)	40	34	22	12	12

tact angle drops from 107 to 15° when temperature changes from 1200 to 1300°C.

High contact angle values (107°) at low temperature (besides the main reasons of physicochemical nature of interface) can be conditioned by both slow kinetic process and some occasional pollution on drop surface (this factor can also influence the kinetics of spreading). High Si-content alloys are characterized by initial low contact angle values and weak temperature dependence. Contact angles of pure liquid silicon on SiC surface change in the range of 34–40° at the temperature interval 1430–1600°C.

The kinetics of wettability are also well expressed for alloys of low Si-concentration at low temperature (see Table 2).

At a temperature of $\approx 1500°C$, a time of ≈ 5–10 min is enough for the contact angles to be of stationary values.

For alloys of 10 and 18.6% Si, a black layer (probably precipitated carbon) can be seen on the drop surface after cooling. One can believe that the accuracy of the contact angle measurement is not significantly deteriorated by these carbon particles (or layer), as precipitated carbon, due to its buoyancy, accumulates in the top of the drop (away from trip line liquid–solid–gas).

No new phases are found out on the interface liquid–solid for all alloys (Fig. 4).

The Au–SiC contact system is of special interest. The wettability in this system is as follows:

T (°C)	t (min)	θ (°)	d (mm)
1100	60	138	0.71
1200	60	126	0.93
1500	20	108	1.27
	>20	? (Drop starts to move and is partly dispersed), where d is the diameter of the drop base	

As usual, this system is considered to be equilibrious, nonreactive and nonwetting. It is true for low tempera-

Table 1
Temperature influence on contact angles

T (°C)	1100	1150	1200	1300	1450	1500	
θ (°)	110	—	107	15	–	7	Alloy Au + 10% Si
θ (°)	20	17	15	—	12	12	Alloy Au + 60% Si

tures (1100–1300°C). Under these conditions $\theta = 130$–120°, but at a high temperature ($T = 1500$°C) the system manifests unexpected, reactive behaviour. At 1500°C golden drop, resting on the SiC surface, undergoes an explosion-like action. It results in spraying, dispersing part of the melt into little droplets, which cover the rest of the surface of SiC similar to rain. Sometimes the drop leaves its place suddenly and moves quickly along the SiC surface. When this occurs it is impossible to measure the contact angle. A typical contact interaction in an Au–SiC system at 1500°C is shown in Fig. 3.

4. Discussion

The contact angle–concentration dependence curve in the system of Au–Si–SiC can be divided in two parts:
5–100 at.% Si
In this region there is a minimum on the curve at ≈ 40 at.% Si. The descending part of the θ–X_{Si} curve in the silicon-rich interval is clearly expressed (dropping θ from 35° to 4–5°). The decrease in contact angle in the gold-rich concentration interval (when silicon content increases from 5 to 40 at.%) is substantial at low temperature 1100–1200°C (see below).

$T = 1100$°C

at.% Si	Contact angle, θ°
0	138
5	102
10	107
18.5	12

The values of the contact angle measured in this work at 1100°C are in agreement with previous results [6]. At high temperatures (1500°C) the decrease in the contact angle is lower.

The descending part of the θ–X_{Si} curve in the silicon-rich region should be considered as an important fundamental result of the investigation. This part of the curve agrees with the hypothetical curve [6] for this concentrating interval (see Fig. 1).

Surface tension of Au–Si alloys decreases monotonously from 1070 mN m^{-1} for gold to 735 mN m^{-1} for silicon at 1500°C [9] (see Fig. 1).

Thus, Au additions to an Si melt induce a decrease of the contact angle, despite the fact that the surface tension of Au is higher than that of silicon. Calculations show that the work of adhesion increases from 1360 mJ m^{-2} for liquid silicon to 1750 mJ m^{-2} for alloy 40% Si. The minimum on the θ–X_{Si} curve and the drop in the contact angles when a component with a high surface tension (Au) is added to Si demand special attention and explanation.

According to reference [6], low contact angle values of Au–Si alloys on the SiC surface at 40–50 at.% Si, and

the fact that it is impossible to predict and describe the minimum on the θ–X_{Si} curve [10], means that the minimum must be caused by some additional, external reasons, in particular, by oxygen dissolved in the melt (from gas media), which promotes wettability.

Theoretically, oxygen can be adsorbed at a metal–ionic substrate interface (oxides, salts) due to coulomb interaction of the O^{-2} ion (through metallic cation) with electro charged surface, and it seems there are no reasons why oxygen should be segregated at a covalent solid–liquid metal interface. Additionally, it is unlikely that a gas media would have such a specific influence, acting only on alloys but not on pure components.

The wettability of SiC has been measured experimentally [6] using the alloy Au + 31 at.% Si ($T = 1100$°C) under different conditions and it was found that replacing the molybdenum furnace resistor (or alumina furnace) with a graphite furnace resistor led to higher contact angle values—from 0–20 to 59°. This was attributed to lower oxygen pressure: 10^{-30} Pa (graphite heater) compared with 10^{-9}–10^{-12} Pa (molybdenum or alumina furnace). But high contact angles (59°) measured in the graphite resistor can be conditioned by carburization of the samples. Therefore, we carried out the complementary experiments, in which extra low oxygen pressure was reached without using carbon getter.

SiC wettability using alloy Au + 40 at.% Si was measured (in addition to our basic data for purified argon media, tungsten heater) under conditions of high vacuo 8×10^{-4} Pa, but a specimen was inserted in a closed cell with porous titanium walls. In this case the contact angle can be obtained on solidified drop after the experiment.

The data received for stationary contact angles were as follows:
Alloy Au + 40 at.% Si
Basic experiment (argon media)

T (°C)	θ (°)	t (min)
1150	22	5
1200	16	5

Complementary experiment No. 1 (vacuo)

$T = 850$°C

t (min)	0	4	10	20
θ (°)	38	35	35	33

$T = 1100$°C

t (min)	0	4	10	20
θ (°)	23	21	21	20–21

$T = 1300$°C

t (min)	0	10
θ (°)	16	16

Complementary experiment No. 2 (vacuo, Ti closed porous cell).

$T = 1150°C$; $t = 60$ min; $P = 10^{-19}–10^{-20}$ Pa; $\theta \leq 10°$.

Thus, the data of our complementary experiments are in good agreement with the basic data for argon media. It may be considered that partial oxygen pressure in vacuum experiments, especially in experiments with titanium cell, was essentially lower than that for argon media, i.e. lowering oxygen pressure does not lead to an increasing contact angle. This is in agreement with the accepted point of view (for high temperature study of capillary properties) that oxygen pressure $\approx 10^{-10}$ Pa is low enough to provide a reliable contact angle value and oxygen influence will not be significant at such low pressure $10^{-10}–10^{-20}$ Pa.

Taking into account the above mentioned theoretical reasoning and data of complementary experiments, we can conclude that the minimum on the $\theta(X_{Si})$ curve observed in the present work for the Au–Si–SiC system should be considered to be caused by intrinsic properties of Au–Si alloys and their interaction with SiC. A similar contact angle–X_{Si} dependence (minimum on the isotherm) has been found in Al–Si–SiC system ($T = 1600–1700°C$) in our earlier work [8] (Fig. 2). The constitution diagram of the Al–Si system is similar to that for Au–Si alloys (Fig. 1a, Fig. 2a). In this system Al additions to the Si melt also result in decreasing contact angles; the surface tension of Al and Si being practically equal at 1600–1700°C.

0–5 at.% Si

At high temperatures (1500°C) pure gold–SiC is an unusual anomalous contact system, which is characterized by sufficiently strong, but specific interaction of Au with SiC. One can believe that Au at high temperature, when Gibbs potential of SiC decreases, can decompose SiC due to Au–Si interaction (similar to Cu–SiC system). Gold–silicon interatomic bonds are strong enough. The temperature required to dissolve Au in Si is high (28 KJ mol^{-1}) [14]. A number of Au–Si compounds such as Au$_n$Su were found at high rapid cooling of Au–Si melts by X-ray analysis [11–15].

Thus, when the interaction between Au–SiC takes place, the compounds (or solutions) Au–Si are formed and free carbon is precipitated; black carbon film can be observed on the surface of solidified drops on the SiC surface (Fig. 3). Thus, the equation of this chemical reaction can be written as:

Au + SiC → Au$_n$Si + C↓; $n = 3–5$ [15]
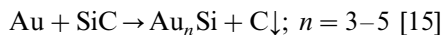
The 'explosive' character of this reaction may be associated with selective Au–Si interaction, the penetration of Au atoms along the Si layer in SiC monocrystal, followed by the cracking of the entire C-atomic plane in SiC (Fig. 4).

A small addition of Si (5 at.%) to gold, lowering the partial molar free energy of Si dissolution in gold, prevents 'explosive' Au–SiC interaction, and the process of 'normal wetting' is observed. The interval 0–5 at.% Si should be investigated in detail in the future.

As for theoretical description of the contact angle concentration isotherms for binary alloys, one can say that calculations based on the model of ideal or regular solutions ([10], in particular) qualitatively explain only simple cases of the minimum on θ isotherms, by the relation between surface tension and work of adhesion of alloy components (in the energetic equation of these theories, term of macro surface properties of component: surface tension and work of adhesion differences work, but not the micro atomic interaction term). For example the addition of Al (adhesion active element) to Sn in contact with Al$_2$O$_3$ [19] or AlN [20] causes an increase in the work of adhesion and contact angles decrease. On the other hand, the addition of surface active element Sn to Al decreases the surface tension of alloys and the contact angle decreases.
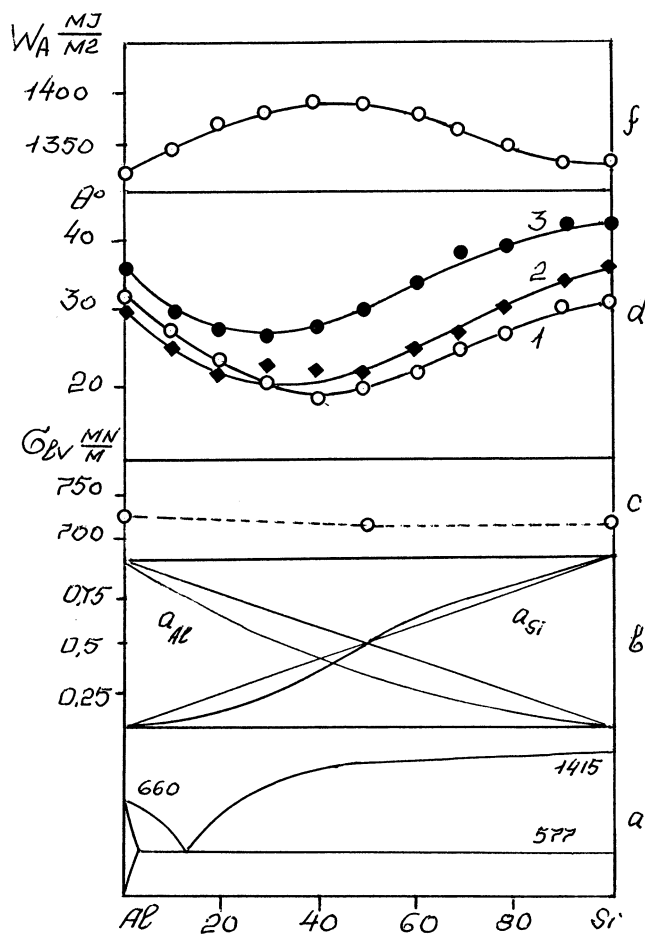

Fig. 2. Concentration dependence of capillary properties of Al–Si–SiC system from work [8]. (a) Constitution diagram of Al–Si alloys; (b) thermodynamic activity of components of Al–Si alloys [18] at $T = 1700°C$; (c) surface tension of Al–Si alloys; (d) contact angle–X_{Si} isotherms; (1) 1650°C; polished hexagonal plane, (2) 1770°C; natural hexagonal plane, (3) 1650°C; natural hexagonal plane.

Above mentioned theories are not applicable to Au–Si–SiC and Al–Si–SiC systems. More general and complete theories [21–23] operate with real solutions, thermodynamic activity in the bulk and surface of solutions, difference between molar volumes and molar surface of components and their dependence on composition. One of the first and most widely used is the
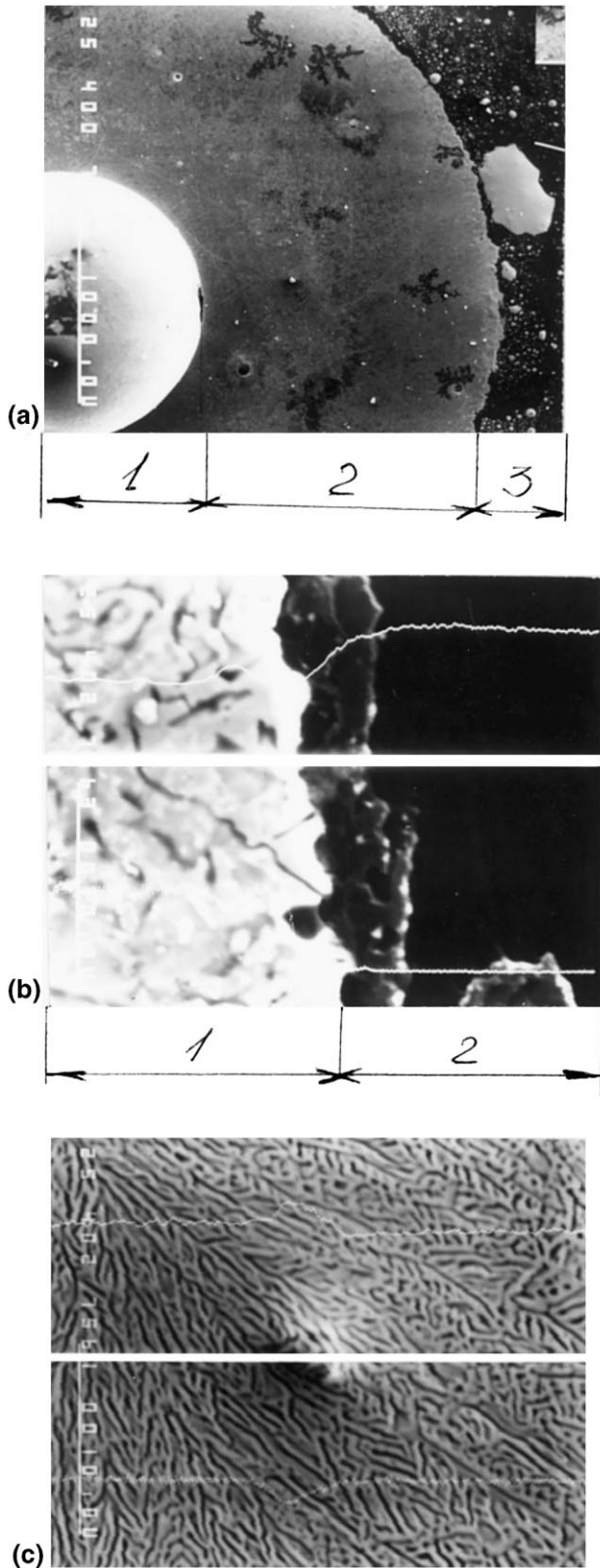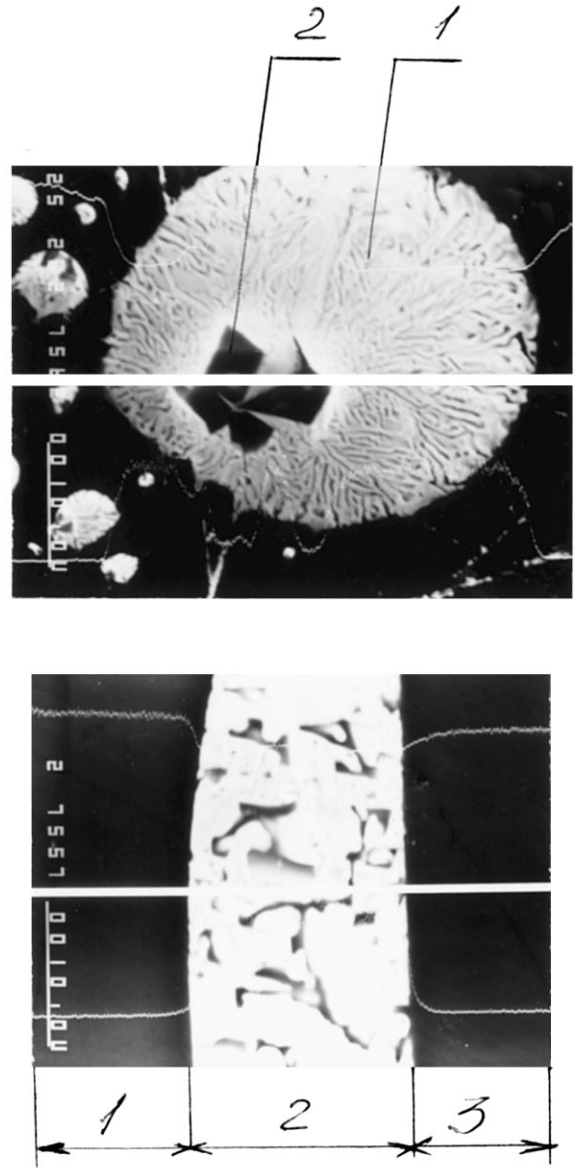

(a)

(b)

(c)

Fig. 3.

Fig. 4. Cross section of interface of Au + 10 at.% Si alloy and SiC × 500; (after heating at 1500°C; $t = 10$ min). (1) Primary Si crystal; (2) Au–Si eutectic; (3) SiC.

Fig. 3. Details of contact interaction of Au melt with SiC. Picture is after 1100°C, 60 min, then 1200°C, 60 min and 1500°C 20 min. (1) Au drop on SiC surface (from above view; × 24); region 1, Au drop; region 2, surface spreading of melt (diffusion zone?); region 3, SiC surface with Au droplets. (2) Boundary of diffusion layer on SiC surface; (from above view, × 2250); region 1, spreading melt layer; region 2, SiC surface. (3) Central part of spreading melt layer surface Au–Si alloy (from above view; × 2250). (4) Small Au droplet on SiC surface (after 'raining') × 150. (a) Au–Si eutectic structure; (b) primary Si crystals.

Joucovitsky theory of surface tension of solutions [21] and then the Popel-Pavlov theory [22]. In principle, these theories predict the special points on the surface property isotherms (including the minimum) but they were developed for boundary liquid–gas (S. Ono [24] constructed the theory for interface liquid–solid, but for regular solution model). In point of view of these theories, one case when we might wait for the minimum on the interface tension isotherm will be realized for systems with positive deviation of bulk thermodynamic activity from Raul's law (weak interaction between different components). But thermodynamic activity of elements in Al–Si alloys at 1700°C is of negative deviation from ideality for Al and only light positive deviation for Si in the range of 0.5–1 atomic fracture of Si [18] (Fig. 2b), heat of mixing for this system is negative.

The Au–Si system is also characterized of negative deviation of thermodynamic activity from concentration [16,17] (Fig. 1b); heat of mixing is negative. The more complicated case of the minimum on θ isotherm can be realized at strong interaction between different components of the alloy; but it can not be calculated now due to lack of data concerning activity of components in the surface layer. Therefore, the 'minimum' can only be qualitatively explained.

It is possible that the addition of silicon to gold increases the interaction (decreases interfacial tension and contact angle) of alloy–SiC due to silicon bonds with carbon of SiC. On the other hand, the addition of Au to Si can promote wettability because of bonding of gold with silicon of SiC. Joining Si and Au results in the maximum wettability at the intermediate concentration of alloy.

Below, the attempt to explain the 'minimum' on θ isotherms in (Au–Si)–SiC and (Al–Si)–SiC systems has been done on the basis of atomic-electron structural notions as follows: Au–Si (and Al–Si) atomic interaction is probably strengthening Si–SiC bonds: electroaffinity of Si = 3.32 Ry (affinity of electron to atomic skeleton-energy of joining of one s-electron in Rydberg's units), much more than for Al (2.09 Ry), and Au (0.68 Ry) [25]; consequently in Al–Si and Au–Si alloys (alloys of Si with an essentially metallic element) there must be a transition of valent electros in the direction of Si atoms. The strength of the covalent bond must be higher if electron density per unit bond ($N \cdot e/Z$) will be more. (N is the number of valent electrons; Z is the coordinate number). According to Gladishevsky's work on the crystal and electronic structure of Si-containing compounds [26], electronegative ionization of Si atoms due to the presence of the metallic atoms, promotes the creation of strong covalent bonds between Si atoms, or we can say between Si atoms and exterior substrate (SiC). Consequently, the presence of metallic atoms in Si melt can increase the ability of Si atoms to settle

covalent bonds. This can explain the increase in wettability when Au (or Al) is added to the Si melt.

Comparing the behaviour of Au–Si–SiC and Al–Si–SiC systems, it can be seen that the 'activity' of Au is more expressed than with Al: when Au is added to Si, the contact angle decreases from 35 (liquid silicon) to 5° (min of θ value); $\Delta^{\theta} \cong 30°$. For the Al–Si–SiC system when Al is added to Si, the contact angle decreases from 32 to 19°; $\Delta\theta \cong 12°$. This is in agreement with greater 'metallicity' of Au (electro-affinity 0.68 Ry mol^{-1}) than for Al (2.08 Ry mol^{-1}).

5. Conclusion

A decrease in the contact angles in the liquid silicon–SiC system, induced by Au additions was found. It is in agreement with the influence of Al in the Al–Si–SiC system investigated earlier.

The minimum on $\theta-X_{Si}$ isotherm in the Au–Si–SiC system should be considered to be caused by electronic properties of Au–Si alloys and their interaction with SiC.

Acknowledgements

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