УДК 532.64:666.3/7:669

Y. V. Naidich[*]

ADVANCE IN THE THEORY OF CERAMICS/LIQUID METAL SYSTEMS WETTABILITY. PECULIARITY OF CONTACT PROCESSES FOR TRANSITION AND NON—TRANSITION METALS

Abstract

The review and some general comments devoted to scientific problems of high temperature wetting and adhesion in systems liquid metals—solid ceramic materials were done including the analysis of data received in a last time. The theoretical treatment of high temperature wetting processes and mechanism based on traditional thermodynamic notions and new approach on atomic and atomic-electron level were developed. As ceramics various substrates namely substrates with predominated ionic interatomic bonds (oxides for example) which usually hardly wetted by liquid metals are considered first of all.

The contribution of nonequilibrium and equilibrium parts of adhesion to wetting process are considered and analysed.

The "active" metals viz metals with high enough chemical affinity for solid phase atoms or iones were divided on transition metals (d-electron orbitals are partly occupied by electrons) and nontransition metals (d-orbitals are empty or completely full by electrons).

[*] Ю. В. Найдіч — професор, завідуючий відділом, Інститут проблем матеріалознавства ім. І. М. Францевича НАН України, Київ.

The wettability in first case (transition metals) is much more intensive than that for nontransition metals inspite of thermodynamic factors (chemical affinity of metal for atoms of solid phase are closed). Many experimental data illustrate these regularity.

The Ligand field theory is proposed to explane and to give treatment on electron level superiority of transition metals in adhesion activity.

An adhesion activity of nontransition metals to solid substrates (oxides) is much low or moderate and dewetting phenomena are frequently observed in this case. This especial feature is explained by formation at the interface nonstable of intermediate valency compounds which can be subjected to reaction of disproportionation.

Some practical recommendations related to regulation and governing wetting processes in various technological procedures were done.

Keywords: *high temperature wettability, adhesion, ceramics, transition and nontransition metals, d-electron orbitals and ligand field theory, dewetting, reaction of disproportionation.*

Introduction

The wettability of ceramic materials by liquid metals is important factor for high technology development in various area of advanced materials manufacture including composites processing, ceramic—to—metal joining, many metallurgical problems. The wettability, as a part of surface and interface phenomena is important for developing of nanosystems science.

Ceramics (ionic or ionocovalent substrates) — metal systems as the most contrasted in viewpoint of difference in interatomic bonds nature in contact pair are of special.

The wettability and adhesion at liquid metal—ceramic interfaces are intensively studied in the last thirty or forty years. The data received before 1980 are discussed in the review [5]. In the last time numerous

new data were obtained, which were considered at the International Conferences on High Temperature Capillarity (HTC-94, -97, -2000, -2004, -2007, -2009, -2012) and at the NATO workshop (1997).

That demands further development of a theoretical concept describing high temperature wettability processes, taking into account that a number of wettability process peculiarities remain not clear or hardly understandable and debatable; and in the last HTC-international conferences and in the most publications generalized review or special invited lectures devoted to the problem questions of the high temperature capillarity discipline are practically absent.

The aim of this paper is to consider some key questions in the theory of high temperature wettability and interface structure for liquid metal-solid nonmetal substrates and make further step to the better understanding of high temperature wettability phenomena. The new approach is proposed to consideration of interface processes and adhesion mechanism including treatment of wettability process on atomic—electron level.

Some general comments

The classic thermodynamics of surface phenomena [1—4] is a background for high temperature wettability processes.

Among the interface parameters which describe the contact systems solid-liquid-gas, namely surface energies at the boundary

$$
\begin{aligned}
&\text{liquid—gas} &&\sigma_{lg} \\
&\text{solid—gas} &&\sigma_{sg} \\
&\text{liquid—solid} &&\sigma_{ls},
\end{aligned}
$$

only liquid—gas surface tension σ_{lg} and contact angle θ can be measured experimentally with sufficient accuracy. As to σ_{sg} and σ_{ls}, we have to recognize that numerous attempts to obtain them were in the whole not

successful in the case of rigid solids, and now, unfortunately, in the most scientific works no attention is paid to this important question.

The difficulty in obtaining of solid (rigid!) surface energy consists in not only absence of accurate reliable experimental method but also in complexity of the very notion of the surface energy of solids. A solid phase barierred by surface in the most cases is not in the state of thermodynamic equilibrium (in difference from liquid phase). Also we must account the specific solid surface structure, phenomena of relaxsation of surface atoms after surface arised, formation of specific surface crystal lattice and symmetry differented from bulk structure [23, 24]. Now these processes are under intensive study — theoretically (ab initio calculations) [26, 28] and experimentally — e. g. Low energy electronic diffraction method (see foot-note as well in page 5).

As to the experimental methods of solid surface energy obtaining by microscopic studies of the morphology of an interface area closed to triple junction liquid—solid—gas with dihedral angle measurements (or so colled ”sine rule“) like in earlier Kingery's team works (see e. g. [45]) in which the measurements of σ_{sg} for Al_2O_3 and ZrO_2 ceramics and interfacial energies of these ceramics contacted to liquid Ni were carried out or in the last separated works [61—63], we can say that all these measurements have drawbacks inasmuch as we cannot have garantee, that equilibrium state of contact system is reached and interface solid/gas remains flat up to the triple line of liquid drop (this late relates especially to [62, 63]).

Nevertheless the scientific works in this important direction (solid surface energy obtaining) should be continued. Perhaps it is necessary to performe systematic investigations of separated stage of complicated methodology for measuring the surface energy of solid body.

Some examples of such investigations can be the works [64, 65] where dihedral angles formation processes were studied experimentally

and analyzed for couples of metal$_{solid}$ — metal$_{liquid}$ (policrystal Ni and Pb, and bicrystal Mo — NiMo alloy [64]. Such systems are of more simple (it is lightly to reach equlibrium state) than ceramic – metal systems. But even in these (metal/metal) systems (Fe/Mn—Cu [65]) surface energy of solid substrate could be evaluated with the aid of some theoretical calculations.

At the same time σ_{lg} and contact angle θ values allow to calculate work of adhesion using Young's equation

$$W_A = \sigma_ж \, (1 + \cos\theta). \tag{1}$$

It is work of adhesion can be related directly to solid—liquid attraction forces and bonding energy. W_A value is always positive, some attraction between solid and liquid always exists. So called "work of immersion": product $\sigma_{lg} \cdot \cos\theta$ (really "adhesion tension" — the parameter and terminology introduced by Freindlich in 1924 to describe the behaviour of a liquid in capillary space), is sign changed value and, we should consider, not suitable to characterize the liquid—solid energetic processes of bonding and interaction as it proposed to be considered in some works [6—8].

But of course we should note that due to complication of atomic structure of a solid surface, particularly the "relaxation" of the surface atoms after surface is formed, in some theoretical works (ab initio calculations) correction of W_A is performed by introduce definition W_A-separation (W_{sep}). In the last time both W_A values are calculated (see first of all Finnis works [27, 28].

There are many difficulties when transferring the classical capillarity concepts, which are stated on and operate in low temperature equilibrium systems, to high temperature reactive systems area. For nonequilibrium systems and nonreversible contact processes in many

cases one can believe that the equilibrium (pcevdoequilibrium) is reached in narrow interface region and thermodynamic consideration can be applied. [*]

Ceramics are usually badly wetted by liquid metals, substances with high values of surface tension, which cannot be overcome to spread by weak physical van der Waals liquid—solid interaction. A commonly accepted point of view is that a good enough wettability is realized in contact systems which are deviated from equilibrium state and conditioned by chemical forces, chemical interface reactions. Historically this assertion was pointed out in different forms by many authors: A. Levin (1952 [9]), Kingery, (1956 [10]), our investigation (1954—1958 [11, 12]), Jordan and Lane (1962 [13]), Zhuchovitsky (1964 [14]), Ono and Kondo (1960 [15]) , Aksay, Hoge, Pask (1974 [16]).

A classification of the contact systems liquid metal/solid, dividing them on equilibrium and nonequilibrium ones and analyses of wetting process in each type of the systems were done in [12] (1968). According to [12] for any contact systems

$$W_A = W_{A\ nonequil} + W_{A\ equil}, \qquad (2)$$

where $W_{A\ nonequil} = f\left(\mu_i^L - \mu_i^S\right)$; $\mu_i^{L,S}$ is chemical potential of i-component in liquid and solid phases, and $\mu_i^L \neq \mu_i^S$ for nonequilibrium contact systems. $W_{A\ equil}$ is function of difference in nature and properties of phases, which are in contact: P_L and P_S, $W_{A\ equil} = \varphi(P_L - P_S)$; the difference of phase properties is the very reason for positive interface tension. $W_A =$ is equal $W_{A\ equil}$ for the case when the phase L a phase S are closed on chemical nature and are in

---

[*] The thermodynamic of nonequilibrium processes can be used if system deviates not far from equilibrium state (linear Onzager equations); But these theory is developed not enough for use it in real contact systems.

conditions of thermodynamic equilibrium at their contact (of course temperature and pressure in each phases mean to be equal). [*]

Chemical interface reaction gives directly an energetic contribution to wettability and adhesion. This last assertion is sometimes debatable and only the role of a new intermediate phase which are formed at the interface is declared [17—19]. But free energy of chemical reaction is identically equal to the energy of chemical bonds established (in our case interfacial bonds). So this assertion as a matter of fact is evident and confirmed by many experimental data, namely by the correlations between wetting and energy change ΔG (Gibbs potential change when reaction occurs) for various systems. Let us consider some examples.

On Fig. 1 data for simple (monocomponent) solid (carbon—graphite)/liquid metal systems wettability are presented [25]. The wettability was measured for alloys, containing transition metals Ti, Ta, Nb, V, Cr, Mn dissolved in Au, and Ge. The enumerated elements are characterized by high enough (but different!) chemical affinity for carbon and form carbide layers at the interface.

There is a good correlation between wettability and ΔG for reaction of carbide formation $Me + C \rightarrow MeC + \Delta G$. The more ΔG value the better wettability degree. (Action of nonequilibrium, reactive contribution to W_A value). Separate deviations from strict succession in ΔG — contact angle dependence can be explained by influence of different thermodynamic activity of elements Ti, Ta, V, Nb, Cr, Mn in a solution of these metals in Au, Ge. The data for thermodynamic activity in many cases are not known, but cunsideration of corresponding phase diagrams of alloys allows to remove some contradiction.

---

[*] For values of P_L and P_S various characteristics of liquid and solid phass (tipe of chemical bonds — e. g. share of ionicity of bonds, electronegatiuty, electrocouductivity, equlibrium concentration of one of components at given temperature of phase diagram, e. c.) can be taken.
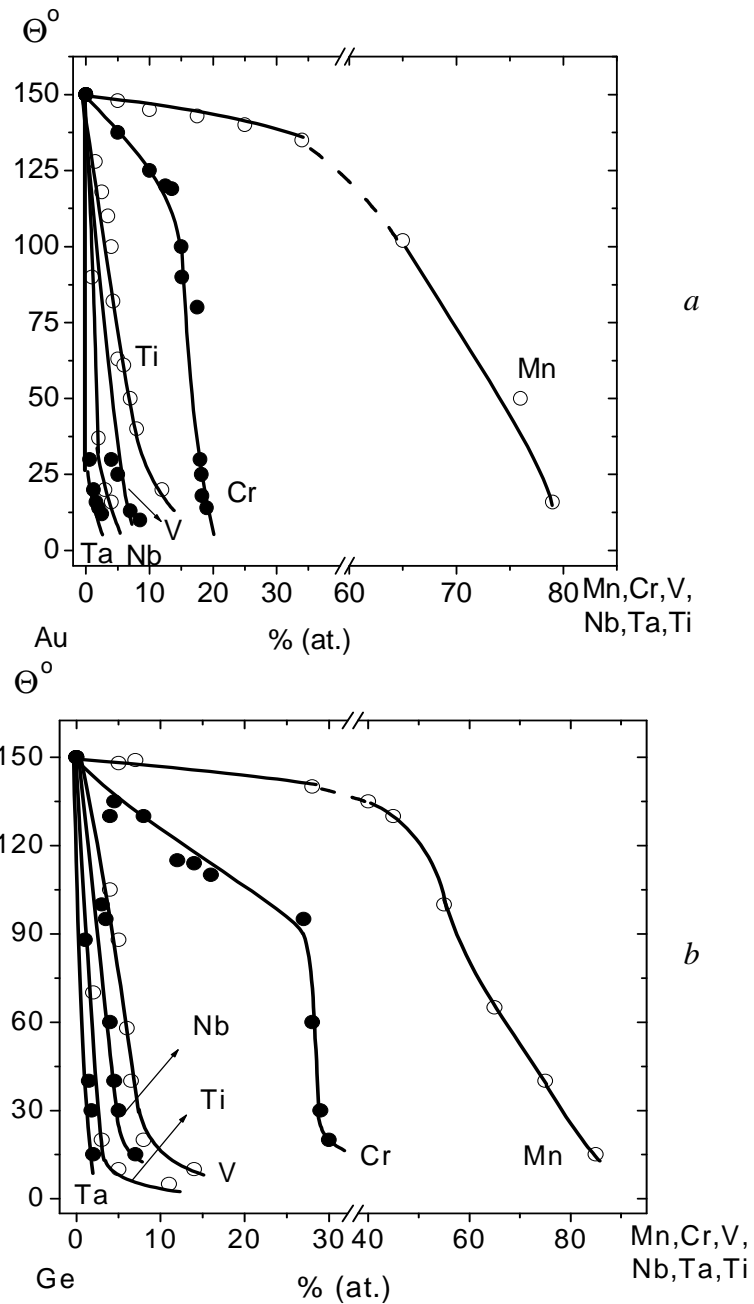
Fig. 1. Wettability of graphite by Au—melts (*a*) and Ge—melts (*b*): concentration dependencies of contact angle. $T = 1200$ °C. Gibbs potential changes when metal—carbon reaction occurs and carbides are formed $-\Delta G_{kJ/g\text{-}at\ C}$: for Mn (3,5), Cr (12), V (27), Nb (32), Ta (36), Ti (47)

(Thermodynamic activity of Mn in Mn—Au alloys is available, and a_{Mn} at concentration region $0 \cong 30\%$ (at.) is very low and corresponding curve for Mn in Fig. 1, *a* will be really displaced to left and down in Fig. 1, but succession of ΔG^o values for different metals and corellation wettability — ΔG^o will be nevertheless observed).

It should be added that adhesiactive elements investigated form at the interface alloy/graphite the layer of <u>metallike</u> carbides, which itself can be wetted by liquid metals (action of equilibrium part in total W_A). But in this case it is hard to find the correlation (if it do exists) between wettability degree and properties of corresponding carbide. As a rule thermodynamically stable carbides (like TiC) are wetted worse than chromium or tungsten carbides.

Another example clearly shows important role of reactive nonquilibrium part of W_A (see table 1 [25, p. 62—64]).

The metals of VIII group of periodic systems — Ni, Co, Fe and Pt, Pd wet graphite surface only due to dissolution process of carbon in these metals.

The dissolution of carbon in liquid Ni and other enumerated metals is chemical process, chemical reaction and while it occurs high enough wetting degree takes place. The metals saturated by carbon up to limit concentration (at the given temperature conditions) don't wet graphite surfaces ($\theta > 90°$). In this case the chemical potentials of carbon in liquid and solid phase are equal and contribution of nonequilibrium term in the total work of adhesion is zero. Ni, containing ~12% (at.) C (T ~1500 °C) is hardly closed on properties to pure graphite so that equilibrium term to W_A total cannot be significant (it is possible — on the level of van der Waals energy interaction).

The next point. It was revealed [58] that metal melt spreading (alloy $Cu_{46}Sn_4Ti_{30}$ and other Ti-containing melts) on graphite surface is very

T a b l e 1. **Wettability of graphite by liquid metal—pure and saturated by carbon [25]***

Liquid metal	T, °C	θ°	Liquid metal saturated by carbon, % (at.)	T, °C	θ°
Fe	1550	**37**	Fe + 15,7 C	1550	**107**
Co	1500	**48**	Co + 15,5 C	1550	**120**
Ni	1500	**45**	Ni + 13 C	1550	**115**
Pd	1560	**44**	Pd + C**	1560	**116**
Pt	1800	**87**	—	—	—

* Experiments were performed by sessile drop method in high vacuum with the aid of special set up, which allows to heat metal sepcimen and graphite without contact of one to another to temperature we need and then to place drop on graphite surface. Experiments were performed with G. A. Kolesnichenko.

**Carbon concentration is closed to saturation one.

fast process. After the moment of liquid—solid contact occurs, wetting angle dropping from 160—180° to 20—30° takes only ~10^{-2} sec (experiments were performed with the aide of super high speed photo camera: 1500—5000 frames/sec). In such case it is hard to expect formation of 3D layer of titanium carbide. One can say about adsorption process of titanium on the graphite surface. In [19] the process of chemical adsorption of one of component of liquid phase on solid substrate surface is treated as essentially different from chemical interface reaction. But chemical bonds (including "adsorption" bonds)

are formed in both cases, and energy of these bonds gives direct contribution to the total adhesion at the liquid/solid contact.

Further the most contrast systems as to nature of interatomic bonds namely liquid metals and ionic solid phases (oxides with predominated ionic bonds) will be considered.

In liquid metal—oxide contact systems when oxidation-reduction interfacial reaction produces a layer of a new intermediate oxide (oxide of liquid metal phase) the greatest wettability degree will take place for oxides in which metallic properties are the most pronounced. In particular for Ti-containing melts contacted to oxides Al_2O_3, MgO, SiO_2 this is clearly illustrated experimentally [30]. Data are presented on Table 2. If TiO oxide is formed at the interface (group I in the Table 2) adhesion is the much more (circa by factor 2) than adhesion in case of Ti_2O_3 formation (group II in the Table 2). Simple explanation of the fact is as follows: TiO-oxide is the more metallike compound in comparison with Ti_2O_3-oxide (last compound is closed to semiconductive substrate, in which electroconductinity of metal type is manifested at high temperature. The change of Gibbs potential for TiO formation ($-387,7$ $^{kJ}/_{g.at.O}$) only some more than that for Ti_2O_3 ($-380,0$ $^{kJ}/_{g.at.O}$); so that in this case one can talk about significant role in wetting process of equilibrium part of total W_A.

Nevertheless at consideration on the whole dependence of contact angles on Ti concentration (system $Cu—Ti/Al_2O_3$) one can observe intencive action of nonequilibrium, reactive factor as well. Moreover there is possibility to divide the action of nonequilibrium and equilibrium factor in wetting process. This illustrates Fig. 2, where wettability — Ti concentration dependence is presented for systems $CuTi—Al_2O_3$ and $CuTi—TiO_{1,14}$. [*] For $CuTi—Al_2O_3$ total contact angle dropping when Ti-

_____

[*] $TiO_{1,14}$ oxide has been specially synthesised, this substrate is closed on composition to TiO oxide.
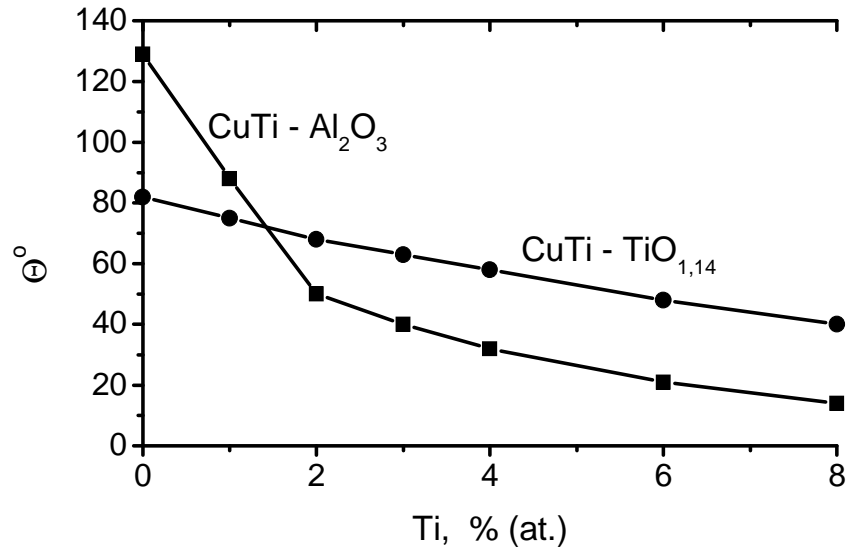
Fig. 2. Wetting of Al_2O_3 and $TiO_{1.14}$ by CuTi alloys, $T = 1150\ °C$

concentration increases from 0 to 8% (at.) is of $129 - 15 = 114°$, it is caused by action of both factors—reactive and equilibrium ones.

For pure Cu contact angle wetting of $TiO_{1,14}$ is $82°$ viz the contact angle dropping (comparatively to Al_2O_3) is $129 - 82 = 47°$ and such a contact angle change must be conditioned by action of equilibrium factor. Further not so significant contact angle dropping as we can see on the Fig. 2 for CuTi—$TiO_{1,14}$ system can be explained by some remaining reactivity ($TiO_{1,14}$ contains some more oxygen than TiO) and changing liquid phase composition from pure Cu to Cu—Ti alloys. We should pay attention, that steepness of the curve of contact angle dropping for reactive systems CuTi— Al_2O_3 in interval 0—2% (at.) Ti is much more than that for Cu—$TiO_{1,14}$ systems, closed to equilibrium one.

In sum as to Eustathopoulos point of view [17] that reactiv term role in adhesion and wettability is negligible one can say that such assertion cannot be accepted. Authors [17] insists that … "irreversible contribution to wetting would be effective only in the case of very

intensive reactions locallised at the triple line" (linear boundary liquid—solid—gas). Such formulation causes many questions and containes vagueness. For example: there are to much conditions for manifestation of irreversible contribution to wetting process.

Besides author in [17] evaluate the action of reactive factor by thickness of interface layer — Ti_2O_3 arised at the liquid/solid boundary in system CuPd—Ti(15% (at.)) contacted to Al_2O_3, mullite, SiO_2; 1475° K. But it is clear that thickness of an intermediate layer in experiment [17] and on the whole, say e. g. thickness of oxide phase on an solid metal surface at oxidation of metal is "kinetic" factor, determined (excluding may be for noble metals) by diffusion mobility of components in compounds, structure of and defects in solids substrate (new and base one) and cannot be cryterium of reactive, chemical "ability" of components at the interface.

So at the end we need to take account of the both contributions to wetting processes: nonequilibrium (reactive) contribution and equilibrium one.

It should be noted that the processes considered above for Ti-containing melts—oxide systems are especial interested. Titanium is a transition metal, that is metal in which its atoms are characterized by partly filled d-electron orbitals. Only transition metals can form the oxides with significant share of metallic interatomic bonds and metallic properties.

The question about the role of d-electron orbitals in the adhesion processes for contact systems metal melt—solid oxides will be discussed below in details on atomic—electron level.

T a b l e 2. **The work of adhesion at the interface of liquid—solid in systems Ti — containing melts (2% (at.) Ti) — Al$_2$O$_3$, MgO, SiO$_2$ and chemical composition of interface layer [30]**

Group	Systems	T, °C	W$_A$, mJ/m^2	Interface layer	Method of identification of interface compound
I	Cu—Ti—Al$_2$O$_3$	1150	**2100**	TiO	x — ray*
	Cu—Ti—MgO	1150	**1894**	TiO	visual**
	Cu—Ti—SiO$_2$	1150	**2185**	TiO	visual
II	Au—Ti—Al$_2$O$_3$	1150	1100	Ti$_2$O$_3$	x — ray
	Ni—Ti—Al$_2$O$_3$	1500	1220	Ti$_2$O$_3$	x — ray
	Ni—Mo—Ti—Al$_2$O$_3$	1500	<1500	Ti$_2$O$_3$	x — ray
	Sn—Ti—SiO$_2$	1150	867	Ti$_2$O$_3$	visual

∗ The identification of different Ti oxides was performed by investigation of its crystallographic structure with the aid of x-ray debyegramms which were received on sapphire and other oxides as solid phase. The seamples of oxides were prepared in shape of cylindrical pivots ($\varnothing$ ~1 mm, 10—15 mm long) with well polished surface. Such pivots were immersed in metal melt and then extracted from one. Temperature—time—high vacuum regime was the same in the all manipulations. Due to not full wettability of solid surface covered by TiO or Ti$_2$O$_3$ oxide layer by metal melt (θ ~30—40°), after pivot extraction surface of seamples was bared and "dry". Then seample (cylindrical pivot) is placed in x-ray camera and debyegramm was produced at revolving of seample.

** The colour of TiO and Ti$_2$O$_3$ is strongly different. So identification of such oxides can be perfomed by visual observation as well.

The atomic mechanism of interface bonds formation in metal melts/solid substrates (mainly—oxide compounds)

The oxides surfaces[*] randomly oriented are formed mainly by oxygen ions, which are of significantly more dimensions and higher polarisability than that for cations.

When crystal is breaking on some plane the cations on surface due to its low dimention and more mobility under action of force field of crystal are displaced beneath the geometrical crystal surface level, in the depth of crystal. It means that liquid metal at contact to oxide surface interacts mainly with oxygen (anion) on oxide surface. All these assertions are based on many works, beginning with Madelung [20], Dent [21], Weyl [22], Adam [4]. Really the surface atoms due to lack of neighbors and under action of force field of crystal are displaced from its position in a bulk of crystal. These phenomena as mentioned above are known as atomic relaxation and surface reconstruction (see e. g. [23, 24]).

The formation of interfacial strength bonds can be imaged of follows.

Terminal metal atoms of liquid phase contacting directly to solid surface (oxides) have to participate <u>simultaneously</u>: a) in the ionic bonds to the oxide, giving a part of their valent electrons to p-level of oxygen in initial solid oxide (oxidation-reduction chemical process which leads to formation of a new oxide, viz oxide of metal of liquid phase) and b) in metallic bonds to other, more deeply positioned liquid metal phase atoms.

This last bond will be weakened because of no participation in it of electrons leaving terminal metal atoms and accepted by oxygen of solid phase. The resultant bond at the interface liquid metal/solid oxide and

---

[*] We talk about so called ''common oxides''— like Al_2O_3, MgO (oxides of nontransition metals). It is possible to enlarge these considerations on the other ionic or ionocovalent substrates, viz galogenides (fluorides), some sulfides, soltlike compounds.

wettability will be conditioned by weak link in the chaine: metal atom in the depths of melt — terminal metal atom — oxygen in solid oxides, and two cases can be realized:

i. If metal of liquid phase is of low chemical affinity for oxygen (noble metals for example) interface (in atomic treatment) remains between terminal layer of metal phase atoms and solid oxides (weak ionic or only van-der Waals bonds will take place).

ii. If metal of liquid phase is of high chemical affinity for oxygen, strength ionic bond will be formed between terminal metal atoms and oxygen of solid oxides. That will result in significant weakening of bond of terminal layer of liquid metal phase to other metal atoms in the depths of melt due to excluding of a part of walent electrons from metal-metal bonds. Displacement of an interface will occur from initial   position of first metal layer/oxide surface to position of first/second metal layer of liquid phase.

Such a hypothesis, formulated early (1980—81) [5, 25], is confirmed by "ab initio" calculations for contact systems metal—oxide [26, 27]. In this sense Finnis works are especially interested. For Nb—Al_2O_3 system Finnis [27] shows that bond of terminate Nb atoms monolayer to oxygen layer on Al_2O_3 surface (ionic bonds), is strong, stronger than Nb—Nb and Nb—Al bonds. In the atomic chain

$$\mathbf{O^{..} — Nb_{terminate} — Nb_{volume} — Nb_{volume}}$$

the most weak link is

$$\mathbf{Nb_{terminate} — Nb_{volume}} \text{ bond.}$$

It is beneficial for good adhesion when only part of valent electrons are excluded from metal—metal bond, i. e. boundary atoms of metal phase (now — are ions!) must be in the state of intermediate valency. <u>The stable state of intermediate valency is characteristic of transition metals.</u>

Transition elements — element with partly occupied d-electron orbitals are characterized by easily moveable electronic structure, an ability to form the different electronic configurations with close energy (hybrid Sd and Spd — orbitals) or in chemical language — ability to form a number of stable compounds with different intermediate valency or in many cases with significant deviation from stochiometry, arising of vacancies in crystallographic lattice and even wide enough area of homogenety in constitutional diagrams of alloys[*].

Taking all that into account let us consider some experimental data including received in the last time for thermodynamic stable oxides (like Al_2O_3, SiO_2, MgO) wettability by liquid metals. As liquid phases alloys containing transition metals — Ti, V, Zr, Cr, Sc will be considered. And for comparing nontransition metals Al, Si, Mg and its alloys will be considered as well. All listed metals possess significant (although somewhat different) affinity to oxygen.

The wettability process for transition metals

Pure Al, Si, Mg wet (but moderately) oxide surface, contact angles are 70—80° (see Table 3).

The addition of these metals (silicon, aluminium, magnesium) to inactive metals, viz metals with very low energy of oxide formation, like Cu, Au, Sn, Pd and others at concentration 5—10% leads to contact

---

[*] As it is said in [31] "Transition elements manifest the much more variety of chemical bond types than any element of the main subgroups of the periodical system. They can exist in many different oxidation states". The same is in [56] "For all transition elements a great number of their oxidation states is characteristic of …".

angles dropping from 120—130° to 60—80° [5, 19, 29, 52] (Fig. 3), viz $\Delta\theta$ ~50—60°.

According to [19] wetting action of Mg in liquid Pd (system Pd—Mg—Al_2O_3, 1565 °C) is as follows: at Mg concentration ~4—10% (at.) contact angle drops from $117 \pm 5°$ (pure Pd) to 84°; $\Delta\theta$ ~40°.

So one can say that reactive (nonequilibrium) wetting action is significant, but some restricted, for systems considered.

The wetting of Ti, V, Zr is much more strong. At more lower concentration of these metals — 2—15% wettability of Al_2O_3 by alloys on base of Cu, Sn, Au and others is high; contact angles are 10—30°, very high of adhesion activity is observed for Sc as well (see Fig. 3 and Fig. 6).

T a b l e 3. **Wetting of oxides by pure nontransition metals**

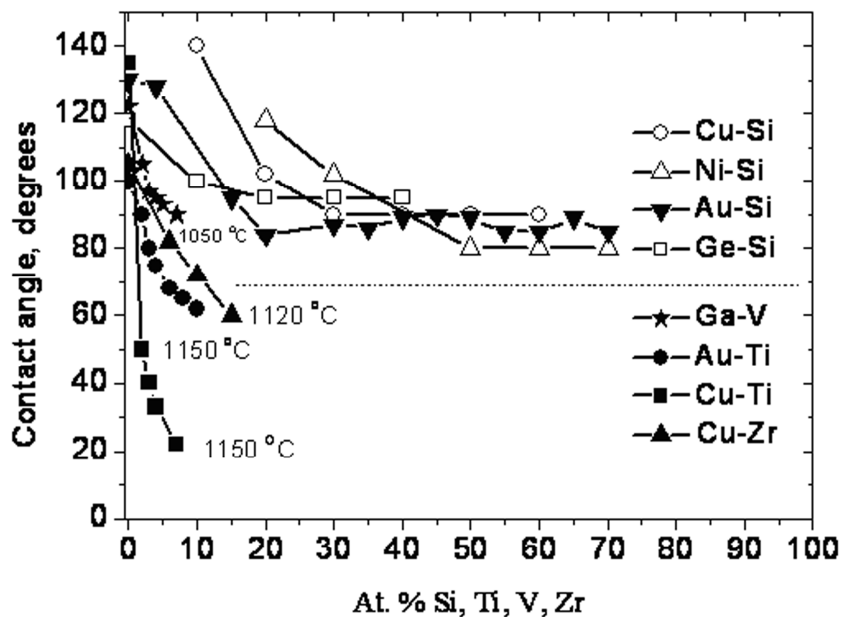| Systems	T, °C	$\theta°$	Refer.
Al_2O_3—Si	1450	82	[44]
Al_2O_3—Si	1417	80	[40]
MgO—Si	1450	101	[44]
BeO—Si	1450	76	[44]
Al_2O_3—Al	1600	61—70	[50]
Al_2O_3—Mg	720	78	[46]
Al_2O_3—Mg	700	65—70	[47]

Fig. 3. Comparative data for wettabilitty of Al_2O_3 by alloys Cu, Au, Ge, Ga with nontransition metal (Si, 1150—1200 ^oC) and transition metals Ti, V, Zr [28, 30, 48]. (The data for Au—Si alloys are presented more exactly on Fig. 8)
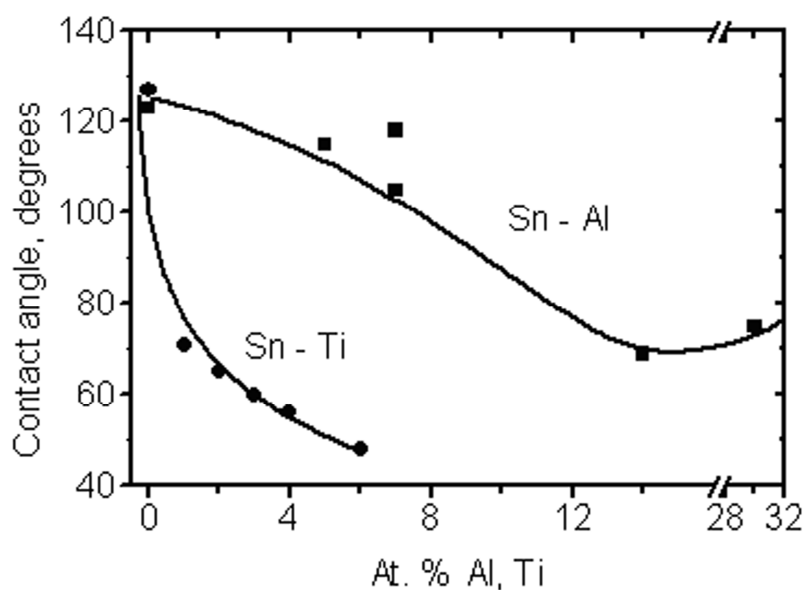

Fig. 4. Comparative data for wetting activity of Al [29] and Ti [30], dissolved in Sn at contact to Al_2O_3, $T = 1000$ ^oC

The same one can see at comparing of a weak wetting activity of Al and strong activity of Ti, dissolved in liquid Sn (Fig. 4). So transition elements possess much more adhesioactivity, than nontransition elements.

The main reason for it according to mentioned above is as follows: transition metal atoms (in difference from nontransition ones) can participate <u>simultaneously</u> in interatomic bonds of different kinds — metal, ionic, covalents; strict valent relations of components are not so importent in this case.

So, if terminate atomic layer of liquid metal and formed by him of mono- or several atomic dimentions layer of a new interface compound (oxide in this case) to consider as a link, bonding liquid metal and solid ionic substrate, it is necessary to allow that metal atoms of this layer take part in bonds of different type – ionic and metallic. Both bonds — ionic and metallic have to be of high strong in order to wettability would be high enough. The transition metals mitt these conditions on the whole. But it is necessary to define this rule with more accuracy end explain it on atomic — electron level.

To understand the nature and reasons for arising of metal type bonding in a ionic substrates, electronic structure of an intermediate oxides of low valency at the interface in relation to wetting processes have to be considered. <u>Ligand field theory</u> [31—33] can be propose to use for it.

Ligand field theory as it is known was firstly developed for complex compounds of transition elements and then enlarged on various refractory compounds by american works (Morin [34] and especially Gudinough [35]) and by russians (Geld-Shveikin works [36—38]) particularly for transition metals oxides.

The essence of this theory (for oxides particularly) is as follows:

- In monoxides (MeO) of Sc, Ti, V, Nb, Zr, Hf with NaCl structure;
- In oxides (Me_2O_3) with corundum structure;
- In bioxides (MeO_2) with rutile   structure;

transition metal cation   is in an octahedral (or distorted octahedral) interstice of an oxygen anion sublattice. The electrostatic   interaction[*] between negative oxygen ions (Ligands) and positive transition metal ions causes a splitting of energy of d-cation electron level (initialy five multiple degenerated)   to a more stable triply   degenerated t_{2g} level (three-d_{xy}, d_{yz}, d_{xy} atomic orbitals) directed away from   neighboring oxygen anions, and a less stable double degenerative e_g level (two-d_{z2}, d_{x2-y2} orbitals) directed towards neighboring   anions (Fig. 5). In all above mention oxides the splitting Δ (difference between energy of t_{2g} and e_g levels) is smaller than the intra-atomic electron exchange energy E_{ex}; viz $\Delta < E_{ex}$ (Fig. 5, *a*). So d-electrons, at least if n≤5 in according to Hund's rule, will in a high-spin state and will   "ready" to coupling and bonding neighboring cations (Fig. 5, *b*); (n is number of d-electrons in cation).

The   direct   cation—cation   interaction   via   overlapping   cation   d-electron wave functions of neiboring   cations will take place and intercations bonds (including metal—like ones!) can arise if distance between cations is lower than some critical value.

It means that lower oxides of transition elements, situated at the left part of periods of periodic system (n < 5) can possess metallic properties.

Especially favourable case is when d-electrons number in transition metal cation n ≤ 3; the electrons occupy only t_{2g} levels, and cation-cation

_____

[*] Really covalent interaction due to overlapping of p-orbitals of oxygen and d-orbitals of metal and electron-spin interaction (exchange interaction) take place; in our case we neglect these effects (for simplicity). So that theory of "crystal field" in essence is under consideration.
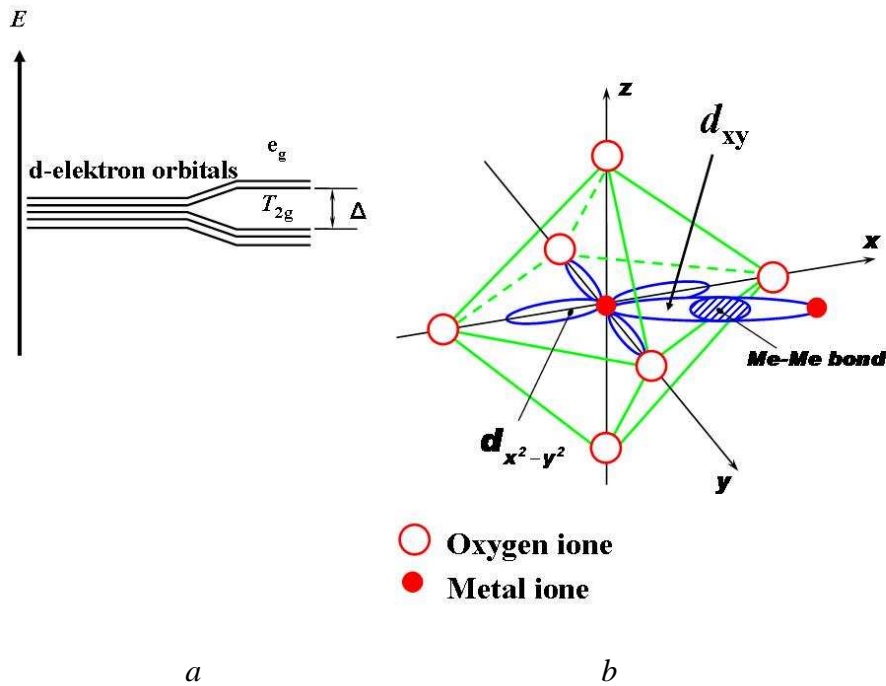
Fig. 5. Spliting of energy of d-cation electron level (initialy five multiple degenerated) on more stable triply degenerated T_{2g} level (three d_{xy}, d_{xz}, d_{yz} orbitals) and less stable double degenerated e_g level (two d_{z^2}, $d_{x^2-y^2}$ orbitals) — *a*, and metal bond formation between neighboring metal iones (*b*)

interaction is very strong (stronger than the cation-anion-cation interaction). Point is that: e_g-orbitals directed towards neighboring anions (Ligands) and electron on these orbitals cause a repulsion colomb[*] forces, increasing parameter of crystal lattice of compound and cation-cation distance, and overlapping of its orbitales decreases. An absence of e_g electrons allows a minimal separation between neighboring cations and maximal overlapping of t_{2g} electron wave functions, and if cations have half—or—less—filled cation orbitals viz partly—filled electroconductive zone, such compounds have to possess really the metal properties: electroconductivity of metallic type, weak Pauli paramagnetizm, metal luster.

---

[*] Really repulsion can be caused by exchanged energy of electrons as well.

Metalic preperties of intermediate phase are very beneficial for good wetting in contact systems with liquid metals.

Quantitative numerical parameter determining intensity of cation-cation interaction is integral of overlapping of cation-d-electron wave functions $\int \psi_i \psi_j dv$, where ψ_I and ψ_j are wave functions (d_{xy}, d_{xz}, d_{zy} in our case) for neighboring cations dv—element of volume, which was calculated by Shveikin and coauthors [36—38]   for various oxides of d-transition elements.

The overlapping integral $\int \psi_i \psi_j dv$ characterizes strength of cation-cation metal bonds in ionic compound of transition metals and can be consider as electronic criterium of metalicity of ionic substrates. In our case we are talking about compound (intermediate oxide), arised at the interface of metal melt, containing transition metal—solid oxide as a result of chemical interaction between metal melt and base solid oxide. So in adhesion and wetting in system metal/oxide this parameter can be of key factor (of course beside chemical thermodynamic factor—affinity of metal of liquid phase for oxygen (Gibbs potential change ΔG when the chemical reaction metal—oxide occurs).

As above mentioned in our earlier works [30] more high wettability degree was revealed for systems in which at the interfaces lower TiO oxide arises comparing to systems where Ti_2O_3 was identified (see Table 2). This fact has been explained on the simple phenomenogical   consideration: TiO is more metallike compound than Ti_2O_3.

The Ligand field theory allows to give the more deep theoretical treatment of these phenomena. On the Table 4 electronic properties of titanium oxides put in conformity to wetting behavior of titanium in different alloys which are in the contact to Al_2O_3, MgO, SiO_2.

For TiO interaction cation—cation is strong and metal type bonds are provided by two d-electrons (d_E electrons), overlapping integral is 0,02 (it is not so little value). The wettability in systems with TiO at the interface is as follows: contact angle drops from 129—133° for pure Cu as liquid phase to 14—16° for alloy Cu—8% (at.) Ti. In oxide Ti_2O_3 cation has only one d-electron; there is moderate cation-cation interaction; overlapping integral is lesser, namely 0,012; Ti_2O_3 — is semiconductor with narrow energy gap, metal type conductivity is observed only at high temperature. The wettability in systems where Ti_2O_3 arises at the interface is less intensive; Contact angle drops at the same concentrations of Ti — 8% (at.) to 65—80°. Meanwhile in both type systems (with TiO and Ti_2O_3 at the interface) nonequilibrium (reactive) and equilibrium contributions to adhesion work act in the same favorable direction increasing the wettability.

The work of adhesion for the first case ("TiO case") is much more than that for "Ti_2O_3 case". (These data were presented in Table 2).

TiO_2 — dielectric, insulator; d-electrons for cation—cation interaction bonding are absent; overlapping integral is O; Bonds between cations is realized only through anion oxygen viz Ti^{+4} — O_2^{--} — Ti^{+4}.

For such a material only nonequilibrium reactive contribution can act (first term of equation 2).

The experimental data for wettability by Ti — containing melt for case of TiO_2 as intermediate phase formed are absent. But there are data [39] for systems where the intermediate phase Ti_5O_9 is formed (closed by composition to TiO_2). For such system ($Ni55Pd45$—Ti/Al_2O_3) Ti_5O_9 was identified at the interface, and contact angle drops from 112 to 92° only.

T a b l e 4. **Wettability in systems titanium containing alloy/oxides in relation to chemical composition and electronic structure of new intermediate phase at liquid—solid boundary**

Composition of intermediate oxide	Crystal structure of new oxide	Metal-metal distance in intermediate oxide, A°	d-electron number in metal-metal bound	Overlapping integral of d_π-electron wave functions $\int \psi_i \psi_j\, dv$	Capillary properties: contact angle dropping when Ti – concentration increases		Temperature, additional remarks
					System	$\theta_{(\gamma Ti=0)} \rightarrow \theta_{(\gamma Ti=8)}$	
TiO (metallic properties)	NaCl — type	2,956	2	0,02 strong cation-cation interaction Ti^{2+}-Ti^{2+} ($Ti3d^2$-$Ti3d^2$)	CuTi/Al2O3 CuTi/MgO CuTi/SiO2	129°→14° 133°→16° 128°→22°	T=1150 °C
Ti2O3 (intrinsic semiconductor with narrow energy gep. Metallic conductiving at high temperature)	Corundum – type	2,99	1	0,012 moderate cation-cation interaction Ti^{3+}-Ti^{3+} ($Ti3d^1$-$Ti3d^1$)	AuTi/ Al2O3 NiTi/ Al2O3 (Ni58Mo42)Ti/Al2O3 SnTi/ Al2O3	135°→65° 110°→83° 114°→64° 131-127°→68-38°	1150 °C 1500 °C 1500 °C 900-1150°C
TiO2 (dielectric insulator)	Rutile – type	2,96	0	0 interaction cation-anion-cation Ti^{4+}-O^2-Ti^{4+}	(Ni55Pd45) Ti/ Al2O3	112°→92°	T=1250 °C Intermediate phase Ti5O9*

* Data [39].

Thus on the whole there is correlation between electronic structure of intermediate phase formed at the liquid/solid boundary and wettability in system.

The decrease of the value $\int \psi_i \psi_j dv$ causes decrease of metallic bounds in compound. For oxides of various valence for one and the same transition metal, metallic properties are the greatest for lower oxides and decrease down to those which inherent insulator substances (with maximum valence of metal).

In distinction from data of Table 4, where relation of wetting activity for one and the same metal (Ti) in different valence state, electronic structure and overlapping integral for d-electron wave functions is considered, we can try to ascertain how much the wetting activity of different transition metals (at least for the same period) in the same oxidation state Me^{++} (monoxides) relates to electronic properties of interfacial oxides and corresponding overlapping integrals.

(Geld-Shveikin [36—38] calculated overlapping integral values for monooxides MeO, where Me—transition metals in 3d, 4d and 5d periods of periodic systems; Table 5).

The experimental data-namely concentration dependences of the wettability in the systems with 3d elements — Sc, Ti, V, Cr (as additions to nontransition metals) at contact to oxides are available and fitted to compare [41, 42]. Let us consider these data.

Sn—Sc/Al_2O_3, In—Sc/Al_2O_3 systems can be compared with the same systems with titanium. The wetting activity of Ti in Ga-melts contacted Al_2O_3 and SiO_2 can be also compared with that of vanadium and chromium (Fig. 6, 7, Table 6).

Scandium being dissolved in indium and tin was shown to decrease sharply the contact angle in contact systems with Al_2O_3 and SiO_2 (see Fig. 6 *a*, *b*). Wetting action of scandium is stronger comparing to the

T a b l e 5. **Electronic structure of monoxids (MeO) of 3d-transition metals—overlapping integrals of d-electronic wave functions** $\int \psi_i \psi_j dv$. **(Geld's—Shveikin's calculation). For comparing the data for 4d- and 5d- transition metals are presented**

3d-metals						
Metal	Sc	Ti	V	Cr	Mn	…….Fe
$\int \psi_1 \psi_2 dv$	—	0,02	0,008	—	—	0,0004
4d-metals						
Metal	—	Zr	Nb	……………………………..		
$\int \psi_1 \psi_2 dv$	—	0,077	0,057	……………………………..		
5d-metals						
Metal	—	Hf	Ta	……………………………..		
$\int \psi_1 \psi_2 dv$	—	0,128*	0,108*	……………………………..		

* The values for hypothetic monooxides.

T a b l e 6. **The wettability (contact angles, deg) of Al_2O_3 and SiO_2 (solids) by In—melts containing additions of Sc and Ti**

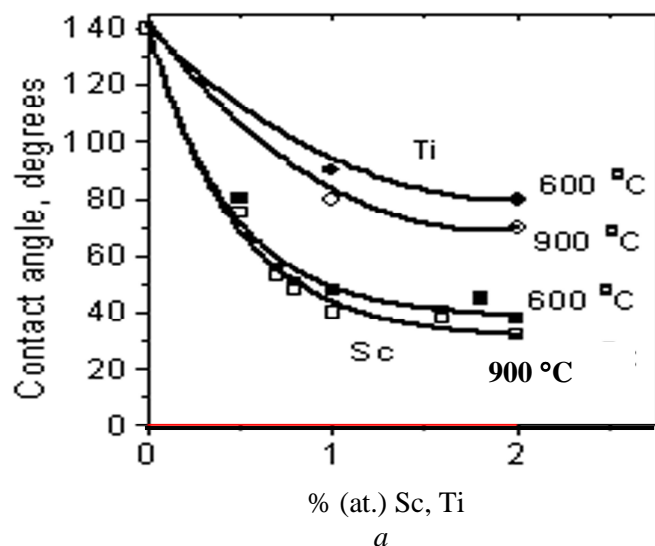| Melt composition, % (at.)	T, °C	Solid substrates	
		Al_2O_3	SiO_2
In—2% Ti	600	52	—
	700	48	64
In—2% Sc	600	35	35
	700	10	12
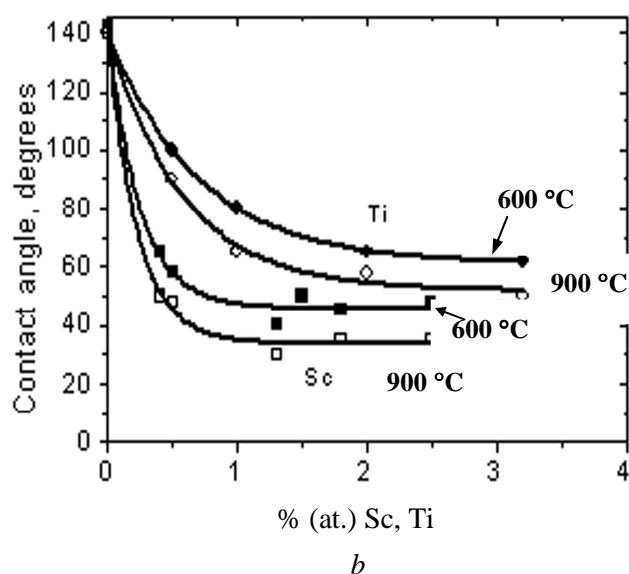
Fig. 6. Wetting of Al_2O_3 (*a*) and SiO_2 (*b*) by Sn—Sc, and Sn—Ti melts [41]

action of titanium. There are data [60] showing that ScO is of cubic structure (NaCl type $a = 4{,}54 \overset{\circ}{A}$) and possesses metallic properties— metallic electroconductivity evidently similar to TiO[*]. Integral of

---

[*] The question about existence of two-valence Sc compounds is under discussion. In [48 (1964)] one believes that only Sc''' valence compounds exist, but in more later works [60 (1974)]Sc'' valence compounds (ScO) was declared to obtaine; its crystallographic structure and some properties were identified. Evidently we can follow to these later work.
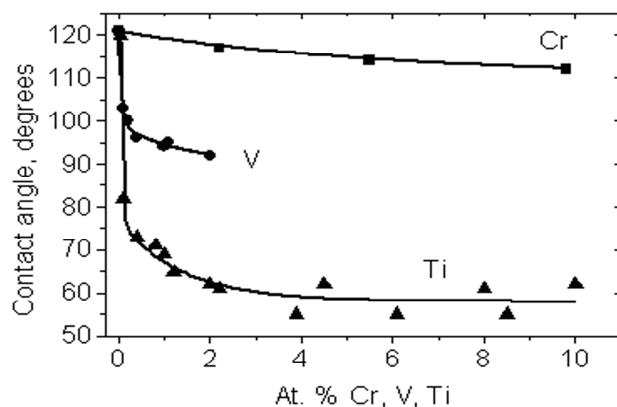
Fig. 7. Al_2O_3 wettability by Ga base melts, $T = 1050\ °C$ [48]

overlapping of wave d-electron functions is not know for ScO. But we can suggest that this integral would be higher than that for TiO in accordance with the general tendency considered earlier. That can explain more higher Sc wetting activity.

Ti promotes wettability much more than V (Fig. 7). The contact angle decrease $\Delta\theta$ for Ga—Ti melt/Al_2O_3 at 1050 °C is near 60° when Ti concentration is ~2% (at.); in the same time $\Delta\theta$ ~30° for Ga—V melt at the same conditions. This is in accordance with much higher value for the overlapping integral of $3d_\varepsilon$-electronic orbitals for Ti^{++}-iones in TiO oxide (0,02); the such value for vanadium oxide (VO) is equal 0,008. Thus the electronic structure of VO is less beneficial for the wettability than the structure of TiO. The difference in wetting activity of Ti and V is also conditioned by different affinity of these metals for oxygen (ΔH_{298} for TiO and VO equal 124 $^{kcal}/_{mol}$ and 98 $^{kcal}/_{mol}$ respectively). This difference is not so significant and it is probably not enough to explain the markable difference in the wetting behavior of Ti- and V- containing alloys (taking also into account that thermodynamic activity of Ti in Ga-melt must be much lower than that for V. This can be deduced from corresponding constitutional diagrams Ga—Ti and Ga—V alloys). At

least we can consider that the change of the overlapping degree of $3d_\varepsilon$ - electron orbitals does not contradict to the change in wettability. So value of $\int \psi_i \psi_j dv$ is important factor for characteristic of metallic interatomic bonds formation and metallic properties of lower oxides of transition elements. Higher value $\int \psi_i \psi_j dv$ is favourable for the good wettability of solids oxides by liquid metals.

Adhesion activity of chromium is low (Fig. 7). Contact angle decreases only by ~5—7° for the system Ga—Cr/Al_2O_3 at Cr-concentration 10% (at.) and at temperature 1050 °C.[*] At the same conditions contact angle for the systems with vanadium decreases by ~30°. It is hard to explain such data only by lesser affinity of chromium for oxygen (1/3 ΔH_{298} for $Cr_2 O_3$ is 90 $^{kcal}/_{g.\ atom\ O2}$; this value for vanadium oxide ΔH_{298} for VO is 98 $^{kcal}/_{mol}$). Reason for such weak wettability of chromium containing melts must be in the peculiarity of electronic structure of chromium and its lower oxides, which can formed at the interface.

Analysis of Geld's-Shveikin's calculation data, concerning to the overlapping integrals for the wave d-electron functions for the oxides of 3d (and 4d and 5d metals), Table 5, shows that the overlapping integrals are the greatest for the elements in the beginning of a period and decrease with increase of the element atomic number along the period. In other words there is a tendency for the overlapping integral to decrease from the left part to the right one of the period of periodic system. (Unfortunately we cannot say that such dependence is strongly

---

[*] Some more chromium wetting activity was found in [43]. For alloy Ni—19,3Fe—20,7Cr (% (at.)) which was in contact to Al_2O_3 at temperature 1470 °C contact angle decreases from 112° for Ni—Fe alloy without cromium to 90° for alloy with cromium. It contradicts mentioned above but can be conditioned by very high temperature and significant greater chromium concentration.

monotonous; extremal points are possible for middle of period — when d- cation electrons number are in range n ≥ 5).

As it has been pointed out above wetting activity depends also on the thermodynamic factors, first of all on the chemical affinity of liquid metals for oxygen. The affinity of metal to oxygen is also changed along the period from the left to the right part of the row of elements. The greatest most values ΔH, ΔG for oxide formation inherent for elements which are disposed at the beginning of period, decreasing to the right part of period. We have to accent, that "affinity factor" produces the nonequilibrium, reactive part of adhesion (first term in the equation (1); In prolonging discussion about Cr—adhesioactivity it should note an electron—valent state of chromium compound.

Many two-valence chromium (Cr″) compounds are known [48, 59]. The lower chromium oxide CrO exists (black chromium suboxide [59]) and is characterized as chemically inert compound at temperature ≤ 700 °C. Compound CrO at heating to T > 700 °C in vacuum conditions is transformed to Cr_2O_3. But if we consider interface of chromium containing melts/Al_2O_3 in conditions of oxiden lack (due to high thermodynamic stability of Al_2O_3 and strong Al—O bonds) we can suggest that chromium suboxide (CrO) can exist at the interface at the more high temperature. In this case we can discuss electronic properties of CrO.

CrO crystallographic structure is not known. We can believe that it is cubic structure of NaCl type, like TiO and VO structure. But in any case for all (almost) compounds of Cr(II) (two valence chromium), chromium cationes are in a octahedral (or partly distorted octahedral) interstice of anion sublattice — O^{--} ligands [48, page 232]. Coordination number for the cation is 6. According to magnetic measurements for almost all Cr (II) compounds high spin electronic state takes place. Therefore electronic configuration of Cr^{++} cation must be $T_{2\,g}^{3}\,e_{g}^{1}$ (but not T_{2g}^{4}).

That means that one of d-electrons will fill the higher d_γ level (e_g). So distance between the cations must increase due to repulsion forces between electrons on the e_g level orbitals directed to ligands O^{--} and the overlapping d- electronic orbitals must be small. Unfortunately the overlapping integral for CrO is not known now. According to the general tendency and mention above considerations, we can expect that the overlapping integral for chromium cations electronic orbitals must be small and lesser then that for vanadium (and titanium) monoxide and metallic properties of CrO should be express faintly. That can explain poor wetting activity of chromium.

As to mechanism of bonding of terminal atoms of liquid phase containing transition metal (Ti for example) with the layer of intermediate (lower) oxide formed at the interface, we can allow possibility formation besides ionic bonds with anion of oxide also metal-bonds with cations in this oxide. As usual this last interaction is weak or absent for nontransition metal oxides due to   particularly dimensional reasons – great anion radius (O^{-2}) comparatively to the cation radius. For Al_2O_3 e. g. value

$$\frac{r_{cation}}{r_{anion}} \sim \frac{0,5\overset{o}{A}}{1,32\overset{o}{A}} \sim 0,37.$$

For oxides of the transition metals (TiO) this relation is more favorably by factor ~2

$$\frac{r_{cation}}{r_{anion}} \cong \frac{0,8\overset{o}{A}}{1,32\overset{o}{A}} \sim 0,61.$$

So bond between positive metal ion of Me^+ in oxide and neutral metal atom in liquid phase can exist. We consider interatomic transition metal bonds on the same concept — splitting   the d-level on t_{2g} and e_g sublevels, high spin state of electronic systems and overlapping of the d-

electron wave function with creation of the bonds between transition metal atoms.

The structure of d-electron orbitals and their role in an interatomic bond for the transition metals is under discussion during many years. Perhaps beginning with Pauling (and not withstanding by Mott) "atomic" treating of d-orbital electrons as localized near atom framework (Heitler-London approaching) is declared. Such orbitals are positioned inside atomic sphere and almost not overlapped with d-orbitals of neighboring atoms. Friedel [57] argued it and presented a number of facts which confirm d-d-interaction between the nearest atoms. Many of these facts are evident: contribution of d-electrons to electruconductivity and electronic heat capacity at low temperature; known correlation between degree of occupation of d-orbitals by electrons and bonding energy, with the maximum of bonds value when d-electrons number equaled 5 and others. F. Cotton and G. Wilkinson emphasize that …"d-orbitals is placed in space, extending far away on periphery of atoms or ions" [48, page 11]. According to Biltz [49] d-electrons of Me-Me bonds particularly in lower titanium compounds of such a tipe, provide the greatest long-range interaction between ions and determin electroconductivity and magnetic properties of substances.

The sum inference can be formulated as follows: the wettability in the most contrast (as to nature of interatomic bonds) contact systems metal melt/solid substrate with predominate ionic bonds will be the most high when melts containe transition metals with electronic structure d^1-d^5, and these metals are of high chemical affinity for electronegative elements— oxygen, sulfur, fluorides or complex anion like $SO_4^{..}$, $PO_3^{...}$ and others.

The wettability process for nontransition metals

Below the contact systems nontransition melt/ionic or ionocovalent solid substrate (for example typical oxide like Al_2O_3) will be considered.

If chemical affinity of metal for oxygen (or other electronegative element) is high enough, chemical interface reaction occurs and new phase — compound at contact boundary is formed. New interatomic bonds arise and their energy — chemical reaction energy — gives the nonequilibrium part of adhesion $W_{A\ nonequil}$ (equation 2).

As pure nontransition metals Si, Al, Mg are considered, for which wettability data are available and which are of high enough chemical affinity for oxygen to interact with oxide of solid phase.

These pure metals wet (moderately!) thermodynamically stable oxides — Al_2O_3, MgO, BeO. The data are presented in the table 3. As one can see the contact angles are 70—80° — sometime 100°.

The contact angles (for Si, Al, Mg) don't attain essentially low values (say 20—25°) as much as new phases arising at the liquid metal—solid boundary (oxides, spinels) are not possessed metallic properties, it means that $W_{A\ equilibr}$ term in equation (2) is almost not "working" in this case. The such behavior is observed in system Pd—Mg alloys contacted Al_2O_3 [19]: Mg additions ~10—12% (at.) to Pd—melt at 1565 °C allow to decrease the contact angles from value ~110—120° (pure Pd) to ~85° only, although the chemical affinity of Mg for oxygen is very high.

The data in detail were obtained in our works for binary alloys containing nontransition metals (mainly silicon) as additions to base metals (Cu, Au, Ge, Ni e. c.) contacted oxides (Al2O3, SiO2). Systems investigated are of: Al_2O_3/Me—Si, Me—Au, Cu, Ge, Pd, Ni; SiO_2/Me—

Si, Me—Au, Ni, Pd[*] [52, 53]. Alloys Al—Ni contacted Al_2O_3 were studied as well [50].

In literature there are data for Si-adhesioactivity in Al_2O_3/Au—Si system [66], separate single data for Au—31% (at.) Si alloy [68] and Ni—63% (at.) Si [69] contacted Al_2O_3. In all cases final contact angles were in the range 70—85°.

So general assertion can be done as follows.

The adhesioactivity of metals investigated (nontransition metals Si, Al, Mg) is significantly lower than that for transition metals, say titanium whose chemical affinity for oxygen is not so greater than that for silicon and close to chemical affinity for oxygen of Al and Mg.

Interesting peculiarity observed at systematic investigations of Si-, Al- containing alloys in our works [52, 53] and still earlier in one work [66] for Si—Au alloys contacted Al_2O_3.

At heating such alloys and after total melting (closed to liquidus line) there is no wetting, θ ~120—130°. Then at further heating contact angles decrease and at 1100—1150 °C its values are ~65—75°. For systems: Au—Si, Pd—Si, Ni—Si contacted Al_2O_3 or SiO_2 contact angles after primary decreasing and after some time holding at constant temperature attain minimal value ($θ_{min}$) and then begin increase by circa 15—20° viz <u>dewetting phenomenon occurs.</u>

The wettability data for systems in which anomalous phenomena — dewetting processes are exhibited in Fig. 8—11. It is important that at increase of wetting angle the reduction in liquid—solid contact square ("retreat" of the melt) occurs but drop volume remain constant. The process of "retreat" of melt is shown on the photo (Fig. 11) for Au—Si.

---

[*] Pd, Ni are transition metals, but with almost completely full d-electronic orbitals and low (or very low) chemical affinity for oxygen.
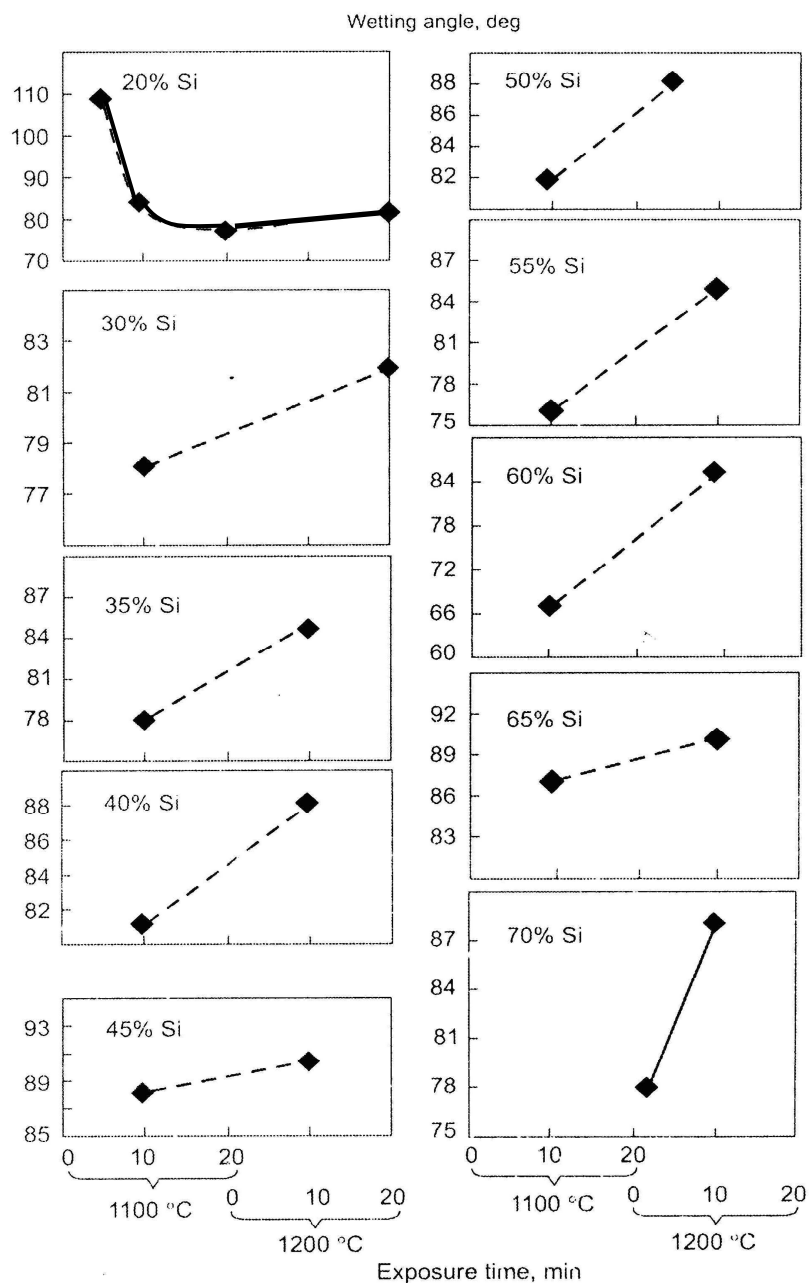
Fig. 8. Temperature-time dependence for wetting angle in the system (Au—Si) — Al_2O_3. (The solid line is the change in wetting angle with time at constant temperature (1100 °C); the broken line is the temperature-time dependence of contact angle. Initial contact angle at T <1000—1100 °C is more than 90°; these data are not presented excluding first above left picture)

It should noted that C. Marumo and J. Pask [67] in investigation of Al_2O_3 (monocrystal) by alloy Au—31% (at.)Si (only one composition was studied) in vacuum and at continious heating (800—1200 °C) found only contact angle dropping (from 150 to 78°) when temperature increases.

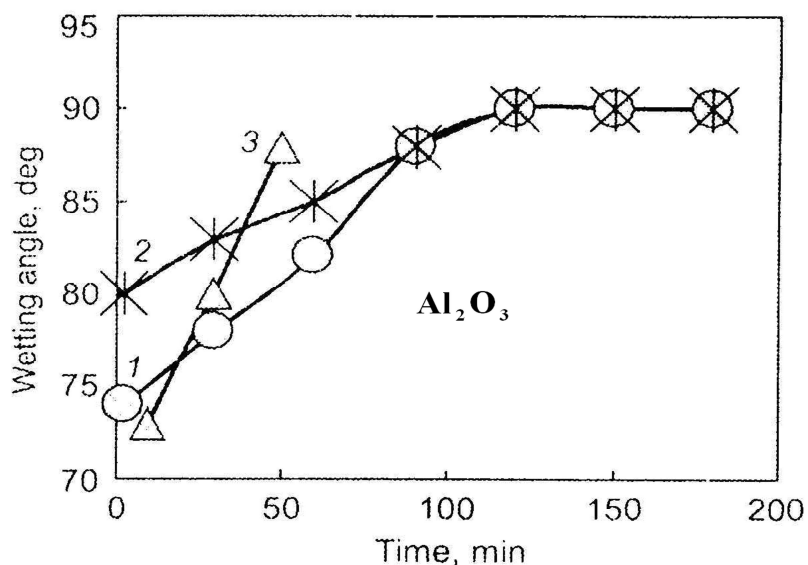Treatment and explanation of all these processes can be done as follows.[*]

Fig. 9. Time dependence of dewetting process for an Al_2O_3 surface with melts of Au—30% (at.) Si (1) and Au—60% (at.) Si (2) at 1150 °C and Pd—58% (at.) Si (3) at 1200 °C

---

[*] In some cases an evaporation of liquid phase (decrease of volume of liquid drop on solid substrate surface) and pinning of the liquid phase perimeter on a triple line can simulate wetting — dewetting processes: at drop evaporation visible decreasing contact angle is observed ("wetting" increases) and then an equilibrium shape of drop is restored contact angle increases (pseudo-dewetting behaviour). Such "geometrical" process we don't consider, but chemical processes at the solid—liquid interface resulted in wetting change are under study.
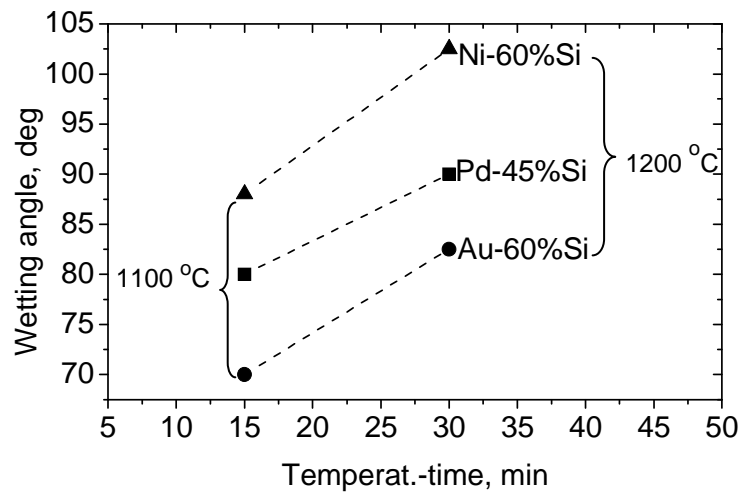
Fig. 10. Time-temperature dependence for wetting angle in systems Ni—60%Si — SiO$_2$, Pd—45%Si — SiO$_2$, Au—60%Si — SiO$_2$
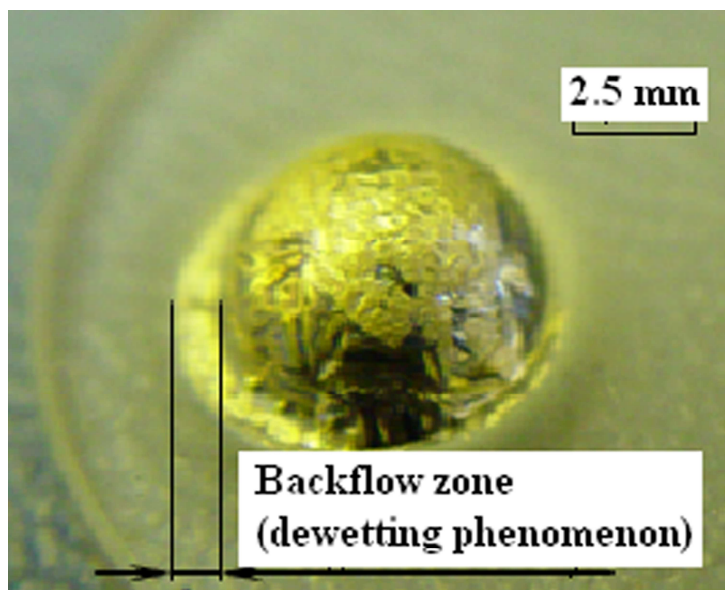

Fig. 11. Photograph of a Au—Si drop solidified on Al$_2$O$_3$ surface. Concentration of Si is 60% (at.), T = 1150—1200 °C

As pointed above for high wettability of iono – or ionocovalent substrates (oxides) is favorable when metal in a new compound arised at the interface is in the state of intermediate valence, lower than group valence in period system. Such ionic compounds are frequently (but not always!) lightly evaporated (sublimated).

J. A. Chempion et al. [70] which at first performed experimental investigations of contact system liquid aluminium/ aluminium oxide (Al_2O_3 monocrystal) observed reaction rings formation around the Al drop at temperature 1350 °C in vacuum. The reaction rings arise periodically on the solid surface and periodically contact angles are jumplike changed.

Increase in the contact angle occurs by strong jumps from 55—60° up to ~80°. This process cannot be called as ”dewetting“ in the sense mentioned before, nevertheless it can be beneficial to consider this process for understanding in the whole speciality of interface interaction of nontransistion metals Al, Si contacted solid oxides.

J. A. Chempion et al. [70] believe (postulate) that the volatile oxide of aluminum, Al_2O is formed at the contact region Al—Al_2O_3 (reference to Brewer and Searcy work [71] (1951)) and progressive decrease in drop volume of aluminum melt contacted Al_2O_3 occurs due to intensive evaporation of both Al_2O and Al. But the more later works M. Hoch and Jonston [72] (1954), Cochran [73] (1955), A. E. Vol [74] (1959)showed that Al_2O oxide dose not evaporate in vacuum <1 Pa (10^{-2} tor) up to temperature 1700 °C. So at interaction of Al with Al_2O_3 at high temperature (1350 °C) only Al is evaporated very intensive. The volume of the drop Al decreases by more then 0,6 of initial value (1,0) when holding time was 60 min.

Thus for Al and at the conditions of high temperature (1350 °C) and intensive Al evaporation the observation of dewetting phenomena is hard or impossible.

Nevertheless in special work [50] for Al—Ni alloys (not for Al pure) contacted Al_2O_3 the very process of dewetting can be reproduced and investigated. The Al—Ni alloys (15% (at.) Ni and 30% (at.) Ni contacted Al_2O_3 were used. The temperature was 1600—1700 °C, gas media: purified argon, P ~1 atm was used.

After holding time ~30—60 min the contact angles from minimal values ~60—65° increase: 64→76°; 66→78° (30% (at.) Ni) and 68→76°(15% (at.) Ni).

Strong Ni—Al bonds and low thermodynamic activity of components in Ni—Aluminid compounds prevent evaporation of aluminium and drop volume of alloys are practically no changed, in spite of changes in contact angles and drop diameter occur periodically. All these phenomena we can consider as dewetting processes.

The main question is: what is the reason for and physicochemical nature of dewetting processes?

Let us consider once more the literature data mentioned above concerning wetting of oxides by silicon and aluminium melts in view point of question formulated.

B. Drevet, D. Chatain, N. Eustathopoulos [66] observed increase in the contact angle by ~20° (dewetting) in Au—Si/ Al_2O_3 systems at Si-concentration $X_{Si} \cong 0,13; 0,25; 0,3; 0,5$ at almost constant temperature ~1000—1100 °C at holding time 60—120 min.

Contact angles were as follows:

at $X_{Si} = 0,13$; $\theta_{min} = 80°$; $\theta_{final} = 94°$;

at $X_{Si} = 0,30$; $\theta_{min} = ~65°$; $\theta_{final} = ~85°$;

at $X_{Si} = 0,50$; $\theta_{min} = ~63°$; $\theta_{final} = 83°$;

According to authors opinion … "a likely explanation of this processes lies in a variation in the concentration of a trace elements (impurity) probably oxygen". Oxygen is really active element influencing on liquid—gas and liquid—solid boundary, but mechanism of the very dewetting process stay not clear. C. Marumo and J. Pask [68] which investigated wettability of alumina by alloy Au—31% (at.) Si at continions heating (800—1200 °C) observed only contact angles dropping — from 150 to 78°.

According B. Drevet and N. Eustathopoulos [69] for system Al_2O_3/alloy Ni—63% (at.) Si at temperature 1200 °C contact angle decreases from 112 °C ($t = 0$ sec) to 95° ($t \sim 20$ sec) and then exhibits "small oscillations" around this later value. Amplitude of the oscillation was of 2—3° with the period 5—10—20 sec.

An oscillation of contact angle was explained by special topography of alumina surface contacted Si—Ni alloy. This phenomenon evidently does not relate to dewetting processes. Note, authors of this work-review, published in 2012 don't refer to their more earlier paper (1990, [66]), in which increase in the contact angle (dewetting) was observed and discussed.

So in this contradictious situation and the question mentioned above other approach to solve the problem can be proposed.

Point is: there is another factor influenced up on the wettability and contact properties in metal—oxide systems. Namely, the ionic compounds of intermediate valence are inclined to reaction of disproportionation, at which the compound of the highest valence (higher oxides) and metal of zero valence are formed.

For system Al—Al_2O_3 when liquid Al interacts with Al_2O_3 at high enough temperature ($\sim$1200—1300 °C) low aluminium oxide Al_2O (and AlO as well) is formed.

Al_2O is formed by reaction: $4Al_{(liq)} + Al_2O_{3(solid)} \leftrightarrow 3Al_2O$.
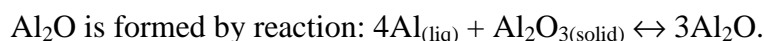
This oxide at the definite temperature — time conditions (~1000 °C) is under went by reaction of disproportionation:

$$3Al_2^+ O^{--} \rightarrow 4Al^o + Al_2^{+++} O_3^{--}.$$

This reaction will occure, when Al_2O will be accumulated at the interface and the equilibrium of the reaction ( ) will be displaced from right to left side.

It is especially important that at this process zerovalence aluminium is formed, therefore some part of aluminium atoms will be bound to Al_2O_3 by week not chemical van der Waals forces; that leads up to adhesion decrease, contact angle increase and <u>dewetting phenomena will occure.</u>

The phenomenon of reaction of disproportionation should consider as a guide factor in the treatment of wetting/deweting processes, and it allows to explain many peculiarities of contact, capillary, adhesion behavior in systems with nontransition metals.[*]

About Al_2O oxide and its properties mentioned above. When silicon (liquid or solid) reacts to SiO_2 oxide at temperature ~1150—1250 °C in vacuum, chemical reaction occurs [67]

$$Si + SiO_2 \leftrightarrow 2SiO$$
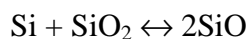
The same tipe reaction for systems Si—Al_2O_3 oxide must be as follows:

$$2Si + Al_2O_3 \leftrightarrow 2SiO + Al_2O$$

That is at such interaction low valence oxides are formed.

---

[*] The conception of reaction of dispropotionation is used in many areas of chemistry, including transformation in ionic or ionocovalent structures, particularly, explains nonstability of monogalogenides of the alkaline earth metals (see e. g. [54, 55]). It should be noted that the main reason for nonstability of the lower ionic (ionocovalent) compounds of nontransition metals is a low energy of the crystall latice of compound (thermodynamic general considiration), which in its turn conditioned by abcence in a compound of the direct bonds between metal atoms (cations): intercation bonds accomlished only trough anions in distinction from transition metal compounds of lower valence, where strong enough direct metal bonds between cations exist (atomic level consideration).

SiO is stable compound in gaseous state at T ≥ 1000 °C. At some lower temperature crystals of SiO were obtained: cubic structure, a = 5,16 $\overset{\circ}{\text{A}}$, density is 2,13 g/cm^3. (This later assertion is sometimes under discussion). When temperature decrease up to ~700 °C SiO undergo by intensive reaction of dispproportionation:

$$2Si^{++}O^{--} \rightarrow Si^o + Si^{++++}O_2,$$
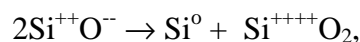
and zero valence $Si(Si^o)$ is formed like as it was declared for Al containing alloys. For SiO investigation in detail was performed by P. Held and M. Kochnev [51], which suppose that SiO is real chemical compound, but to keep it in solid state according [59] very rapid cooling is necessary.

The situation related to state, stability of SiO, or its inclination to reaction of disproportionation can be some other, when not pure Si but Si-alloys contacted any oxides are under experimental study, especially for alloys where thermodynamic activity of Si is low [75] and there are strong bonds Si/base metal. Just these cases were realized in system Si—Au alloys and Al—Ni alloys considered and discussed above. In these cases we can believe that interface reactions (including reaction of disproportionation) must be retarded.

The reaction of disproportianation can hinder to optimal (in view point of high adhesion in system metal/ionic compound) distribution of the valent electrons of metal, at which optimal part of the valent electrons are accepted by electronegative element (oxygen for oxide as solid phase).

Summarizing all data, we can consider that the dewetting processes in oxide/nontransition metal systems can be determined in significant degree by reaction of disproportionation.

Nevertheless chemical composition of Al-or Si-alloys contacted Al_2O_3 or SiO_2 at high temperature should control after dewetting process occured possible changing in concentration of

elements (Al, Si) due to its evaporation, or evaporation of its lower oxides.

In our experiments chemical analysis was performed for Pd—Si melts contacted Al_2O_3. Two alloys with initial concentration of silicon 45% (at.) and 58% (at.) (18% (mass.) and 27% (mass.) Si accordingly) were used.
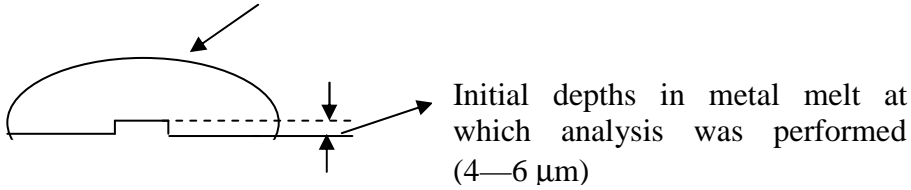
Analysis was performed after initial wetting process occurred (θ decreases from ~120° to ~75°) and then θ increases to ~85—90° (dewetting). The results of analysis are presented on Table 7. The data received showed an increase (not decrease!) of Si content in melt (in zone closed to interface): from 18% (mass.) to 32,56% (mass.) Si, and for other alloy from 27% (mass.) to 36,0% Si. Evaporation of SiO if it really took place could be resulted in decreasing Si-content in melt. Aluminum concentration in Pd—Si melts (45% (at.) and 58% (at.) Si) being initially zero, after contact processes of melt with Al_2O_3 becomes 4,75 and 6,42% (mass.) accordingly. These data (related to Al) denote the partial dissolution of alumina in Pd—Si melt (chemical interface interaction).

The process of "retreat" of the melt is shown on the photo (Fig. 11) for Au—Si drop on the Al_2O_3 surface. The same picture is observed for Pd—Si drop on Al_2O_3 surface.

Profilographic investigations of Al_2O_3 surface after removal of Pd—Si drop show that same very small (~1—1,5 μm) Pd—Si alloy goes deep in to Al_2O_3 substrate.

So it is possible that increase of Si-content in Pd—Si alloy observed in experiments can be conditioned by some segregation of silicon at the interface Pd—Si alloy/Al_2O_3 (polymolecular adsorption, aluminum silicate layer formation). Part of this can be near to zone of action of instrument VG-900 (see figure in the table No. 7).

T a b l e   7. **Results of mass-spectrometric analysis (instrument VG-9000) of chemical composition of Pd—Si drops which contacted Al$_2$O$_3$ during 60 min at *T* = 1200 °C**

Content of element	(Pd—45% (at.) Si)/(Pd—58% (at.) Si)
C, ppm	17,998/0,126
O, ppm	41,597/12,316
Mg, ppm	752,530/854,650
Al, % (mass.)	4,75/6,424
Si, % (mass.)	32,562/35,998
Fe, ppm	3284,800/4036,900
Ni, ppm	1160,900/1328,700
Mo, ppm	4499,800/11196,000
Pd, % (mass.)	60,966/53,117
W, ppm	5087,200/18971,000

1 ppm = 10^{-4} % (mass.)

The scheme of mass-spectrometer analysis

Pd—Si drop, separated from sapphire

Initial depths in metal melt at which analysis was performed (4—6 μm)

Bottom surface of a metal drop (separation was purely adhesive).

The base of a drops after separation from the Al$_2$O$_3$ was analyzed in a mass spectrometer in a glow discharge (instrument VG-9000) at the depth ~4—6 μm.

So most facts and theirs discussion bear the witness that main reason for dewetting processes observed in systems ionic substrates (oxides)/metal melts containing nontransition elements (Si, Al) is the reaction of disproportionation — disintegration of low (intermediate) nonstable compounds arised at the interface solid—liquid and formation of zero valence metal and high (group) valence oxide.

On the whole nontransition metals (pure or as additions) even with high enough affinity for anion of solid ionic or ionocovalent compounds can provide only moderate wetting degree.

The practical recommendations related to wetting process control and regulation in systems liquid—metal/ceramic materials

The wettability degree is key factor in many technological operations-joining of dissimilar materials, composite materials manufacture, deposition of metal coating on ceramics et. c.

The considerations of the physico-chemical nature of contact processes at the boundary liquid metals/solid nonmetal substrates allow to formulate the methods in order to govern and change a wettability degree in direction we need. In the most cases the high enough wettability and adhesion must be reached.

We will talk about the most contrast systems related to chemical nature and interatomic bonds in contact pair viz metal/ionic or ionocovalent ceramic materials.

Typical interface interaction at the liquid—solid boundary are as follows:

1. Dissolution of solids in liquid melt.
2. Diffusion of liquid phase atoms in solid substrate.
3. New interface compound formation.

This last process should be considered as the most perspective for wettability regulation and it will be discussed below.

In this case wettability degree will depend in the whole on agregate state of a new phase — solid, liquid, gas. For solid state of a new phase wettability will depend on chemical nature (type of interatomic bonds in interface compound and its properties — ionic, covalent, metalic substrates).

General requirement for high wettability is faivourable combination of great nonequilibrium part in adhesion work and significant equilibrium contribution to adhesion liquid/solid boundary, viz both terms of equation (1) must be high enough. It means that an intensive chemical interface interaction mast be occurred with great ΔG — Gibbs potential change, high chemical affinity of liquid metal for solid substrate (oxygen for oxides) that will result in formation at the interface intermediate oxide. It is very favourable if this oxide will possess metallike properties.

The Ligand field theory explanes the possibility of existence metalic interatomic bonds in ionic structures (oxides). As mentioned above significant d-electronic orbitals overlapping of neibouring cations, high value of overlapping integral $\int \psi_i \psi_j dv$ have to lead up to strong direct cation$_i$— cation$_j$ bonds of metalic nature between atoms (cations) and metalic properties in new oxide at the interface.

Such a situation is realised if interfacial oxides are formed by transition elements of 3d, 4d, 5d periods of periodic system and such elements are placed at the left part of periods of periodic systems viz number of $d_{electrons}$ have to be n $\leq$ 5 (preferably n $\leq$ 3). These elements are: Sc, V, Zr, Hf, Nb and some others. These elements are as a rule used as adhesioactive additions to nontransition metals like: Sn, Cu, Ag, Au and others.

By other words for high wettability of stable oxides of type Al_2O_3, BeO, MgO, SiO_2 by liquid metals favourable combinations of thermodynamic ΔG—Gibbs potential changing, when reaction occures

and electronic ($\int \psi_i \psi_j dv$) factors for contact system are necessary. Such a combination is possible for transition metals.

The nontransition metals in pure state or as additions even with high affinity to oxygen allow to get only low or moderate wettability of above mentioned oxides.

The fulfillment of given instructions results in high enough "chemical" stength of liquid metal/solid ceramic interface (high adhesion and wettability values).

High wettability (contact angle value must be ~10—30°) determins very possibility of formation of brazing joint or composites processing by liquid phase sintering or infiltration.

For practice we need to get high enough mecanical contact strength as well. It is special questions, which demands separate detale consideration. Now we can say that high chemical interface strength is nesessary (but not enough) condition to reach high mecanical strength, nevertheless one can say, that at least at abidance of the elementary technological conditions, for example, if the coefficients of thermal expantion of dissimilar materials to be joined would be different not so significantly, correlation between mechanical and chemical strength of brazing joint will be take place.

Another point. For ceramic/metal joining by brazing process brazing alloys have to containe adhesioactive elements — Ti, Zr, Nb and others. These metals are caracteristic of high chemical affinity for oxygen, nitrogen, sulfur and other nonmetal atoms. So technological process must be performed in high vacuum (10^{-3}—10^{-4} Pa) or in gas media — helium, argon of high purity.

Conclusion

The review concerning to high temperature wetting processes in ceramics-liquid metal systems including analysis of the new data received in the last time are presented. New theoretical conceptions are proposed to treat wettability phenomena.

In the whole case for nonequilibrium contact systems and when chemical interaction at the interface occures, work of adhesion can be written down by equation

$$W_A = W_{A\,equilibr.} + W_{A\,nonequilibr.} \qquad (3)$$

Where W_A terms are of equilibrium and nonequilibrium parts of total work of adhesion.

$W_{A\,nonequilibr.}$ – is direct contribution of chemical interface reaction to wetting. As this assertion in some works up to now is denyed or is debateble, special consideration of this key question has been performed for various contact systems. It has been shown that really free energy of chemical interface reaction is identically equal to the energy of chemical interface bonds established and gives direct contribution to liquid/solid adhesion.

The consideration of atomic mechanism of interface bonds formation especially for the most contrasted as to nature of interatomic bonds in substrates contacted – metal melt/ionic or ionocovalent compounds (oxides first of all, like Al_2O_3, MgO, SiO_2, BeO) allows to drow conclusion as follows: for high enough wettability terminate atomic layer of liquid metal atoms must participate simultaneously in interatomic bonds of different types – metallic bonds with deeply placed metal atoms and ionic bonds with solid substrate (oxide in this case). Transition elements – elements with partly occupied d-electron orbitals are characterized by easily moveable electronic structere, ability to form the different electronic configurations and to be in the stable state of intermediate valency mitt these requirements.

The both bonds—ionic and metallic have to be of high strength in order to adhesion and wettability would be high enough. So at the interface liquid metal/solid oxide intermediate low valency oxide of metal of liquid phase is formed. It is especially favourably when such oxides are possessed of metallike properties. All these processes are considered on atomic-electron level. Ligand field theory was proposed to use for it. Quantitative numerical parameter determining intensity of cation—cation interection and stregth of metal interaction bonds is integral of overlapping of cation-d-electron wave functions $\int \psi_i \psi_j dv$, where Ψ_i an Ψ_j are wave functions of electrons for neiboring cations.

The chemical compounds of intermediate valency (low then group one) for nontransition metals are as the rule nonstable substrates, inclined to reaction of disproportionation (metal of zerovalency and compound of the highest valency are formed). The dewetting process occures, contact angle increases, and wettability degree in this case is low or moderate.

Bassed on all above mention regularities practical recommendations to control and govern wettability can be used in various technological procedures.

РЕЗЮМЕ. Сделан обзор и представлены некоторые общие комментарии, касающиеся научных проблем высокотемпературной смачиваемости и адгезии в системах жидкие металлы—твердые керамические материалы, включая анализ полученных в последнее время данных. Разработаны теоретическая трактовка процессов высокотемпературной смачиваемости и механизм, основанный на традиционных термодинамических представлениях, и новый подход на атомном и атомно-электронном уровне. В первую очередь в качестве керамики рассмотрены различные субстраты, а именно, субстраты с преобладающими ионными межатомными связями

(например, оксиды), которые обычно плохо смачиваются жидкими металлами.

Рассмотрен и проанализирован вклад в процесс смачивания неравновесной и равновесной составляющих адгезии.

"Активные" металлы, а именно, металлы с достаточно высоким химическим сродством к атомам твердой фазы или ионам разделены на переходные металлы (d-электронные орбитали частично заполнены электронами) и непереходные металлы (d-орбитали не заполнены или полностью заполнены электронами).

Смачиваемость в первом случае (переходные металлы) намного интенсивнее, чем для непереходных металлов, несмотря на термодинамические факторы (химическое сродство металлов к атомам твердой фазы близко). Множество экспериментальных данных иллюстрирует эту закономерность.

Для объяснения и трактовки на электронном уровне превосходства переходных металлов в плане адгезионной активности предложена теория поля лигандов.

Адгезионная активность непереходных металлов к твердым субстратам (оксидам) намного ниже или является умеренной, и в этом случае часто наблюдаются явления десмачивания. Эта характерная особенность объясняется образованием на поверхности раздела нестабильных соединений промежуточной валентности, которые могут подвергаться реакции диспропорционирования.

Даны некоторые практические рекомендации, касающиеся регулирования и управления процессами смачивания в различных технологических процедурах.

Ключевые слова: высокотемпературное смачивание, адгезия, керамика, переходные и непереходные металлы, d-электронные орбитали и теория поля лигандов, десмачивание, реакция диспропорционирования.

Reference

1. *Young T.* An essay on the cohesion of fluids. Phil. Trans. Roy. Soc., London, 1805, I, 65—87 (read at sess. Brit. Roy. Soc. Decemder 20, 1804).

2. *Gibbs DW.* The scientific papers of J. W. Gibbs. V. 1. Thermodynamics, Dower publications, inc. 1961;**4** (Originally published by Langmans, Green and Company, 1906).

3. *Rideal EK.* An Jntroduction to surface chemistry. Cambridge, 1930.

4. *Adam NK.* The Physics and Chemistry of surfaces. Third ed. 1941.

5. *Naidich Y.* The wettability of solids by liquid metals. *In: Progress in surface and membrane sci.* 1981;**14:**353—484.

6. *Stoneham A, Duffy D, Harding J.* Understanding wetting and spreading:non-reactive metals on oxides and similar systems. Proc. Intern. conf. "High temperature capillarity", Bratislava, Reproprint, 1995:1—10.

7. *Magaud L, Pasturel A. A* First principles theory of metal—ceramic of interfaces. Proceedings of "High temper. Capillarity" Internat. conf, HTC-97. Foundry Res. Inst., Cracow, Poland, 1998:3—11.

8. *Eustathopoulos N, Drevet B.* Interactions at non-reactive metal/iono-covatent oxides interfaces: Physical or chemical, Ibid. 1998:35—44.

9. *Levin A.* Sbornik trudov Dnepropetrovskogo metallurgicheskogo Instit. Dnepropetrovsk, 1952; **28:**89 (Russ).

10. *Kukjian C., Kingery W.* Surface tension at elevated temperature. III. Effect of Cr, In, Sn, Ti on liquid nickel surface tension and interfacial energy with Al_2O_3. *J. Phys. Chem.* 1956;**60(7**):61—63.

11. *Eremenko V, Naidich Y.* Liquid metal wettability of solid surfaces of refractory oxides. *J Phys Chem (USSR)* 1959;**37**(6):1239.

12. *Naidich Y.* About surface energies and contact angles of wetting of solids by liquid in equlibrium and nonequilibrium systems (Russ). *J Phys Chem (USSR)* 1968;**42**(8):1946.

13. *Jordane D, Lane I.* Diffusion and reaction influence on wetting in systems metal—metal. J. *Austral. Inst. Metals.* 1962;**7**(1):27—33.

14. *Juhovizki I, Grigorian V, Mihalik E.* Surface effect of chemical process. DAN USSR. 1964;**155(**2):392.

15. *Ono S, Kondo S.* Molecular theory of surface tension in liquids. Hanbuch der physik Herausgegeben vons. S. Flugge band X, Springer-verlag. 1960.

16. *Aksay J., Hoge C., Pask J.* Wetting under Equilibrium and Nonequilibrium Conditions. *J Phys Chem.*1974;**78(**12):1179—1183.

17. *Eustathopoulos N.* Influence of interfacial reaction on wettability and bonding in metal/oxides systems. Proceedings of High Temp. capillarity Int. conference, Smolenice Castle, Bratislava, Slovakia. 1994; 11—17.

18. *Espie L, Drevet B, Eustathopoulos N.* Experimental studies of the influence of interfacial energies and reactivity on wetting in metal/oxide systems. *Metallurg and Mater Trans* 1994;**A 25**(3):599—605.

19. *Guesdon J, Saint-Antonin F, Hodai F, Goudurier L, Eustathopoulos N.* Interfacial reaction and wetting in Pd—Mg/Al_2O_3 system: Experimental facts and mechanisms. Trans. of JWRI (High Temper. Capillarity). — 2000, Kurashiki, Japan. *Joining and Welding Reserch Jnst* 2001;(**30):**33—38.

20. *Madelung E.* The atomic constitution of a crystal surface, Physikalische Zeitschrift. 1919; **20:** 494—496.

21. *Dent B.* The effect of boundary distortion on the surface energy of a crystal. J Phil Mag 1929;**8**(51):530—539.

22. *Weyl W. A.* Atomistic interpretation of mechanism of solid state reaction and sintering. Ceramic Age 1952;**60**(5):28.

23. *Kiselev V, Kozlov A, Zoteev A.* Osnovi physiki poverchnosti tverdogo tela. (Physical bases of solid surface). M. MGU. 1999. (Russ).

24. *Luth K.* Surface and Interfaces of Solids. Springler-Verlag, Berlin-Heidelberg. 1993.

25. *Naidich Y., Perevertailo V., Lavrinenko I., Kolesnichenko G., Zhuravlev V.* The surface properties of melts and solids and theirs use in material science. (Russ.). Edit. Y. Naidich, Kiev, Naukova Dumka, 1991, chapter 5, p. 62—64, 67.

26. *Nath K, Anderson A.* Oxidative bonding of (0001) α-Al_2O_3 to close-packed surface of the first transition-metal series, Sc through Cu. Physical Review "B". 1989;**39**(2):1013—1019.

27. *Finnis M.* The theory of metal—ceramic interfaces. Phys. Condens. Matter. 1996;**8**:5811—5835.

28. *Batirev J., Alavi A., Finnis M., Deutsch T.* First—principles calculations of idial cleavage energy of bulk niobium/α-Al_2O_3 (0001) interfaces. Physical Rev. Letters. 1999; **82(7)**:1510—1514.

29. *Li J., Chatain D., Coudurier L., Eustathapoulos N.* Wettability of sapphire by Sn-Al alloys. J. Mater Sci Letters 1988;**7**(9):961—963.

30. *Naidich Y, Zhuravlev V.* Adhesion, wettability and interaction of Ti-containing alloys with refractory oxides (Russ). *Ogneupori.* 1974;**1**:50—55.

31. *Murrell J, Kettle S, Tedder J.* The chemical bond, John Willy Sons, Chichester N. Y., Brisbane, Toronto, 1978.

32. *Coulson C.* Valence, (second edition) Oxford University. press, 1961.

33. *Figgis N, Hitchman M.* Ligand Field theory and its application, Wiley-VCH. 2000.

34. *Morin F.* Oxides which show a metal-to-insulator transition at the Neel temperature. Phys Rev Letters. 1959;**3:**34—37.

35. *Goodenough J.* Direct Cation — Cation Interaction in Sevaral Oxides. Phys. Review, 1960;**117**(6).

36. *Geld P, Xhai B.* Some questions of crystal—chemistry of cubic oxides and carbide of Ti, V, Nb, In. Trudi postoyanogo mejinstitut

colocvium po tverdim fazam peremenogo sostava. P. 2. L. Isdatelstvo L. im. V. Ulianova-Lenina Universitet (Russion). 1962;**2**.

37. *Xhai B, Geld P.* Influence of screening and overlapping d-orbitals on some properties of evquiatomic oxides and carbides Ti, V, and Nb. J of Structure Chemistry (Russian) 1964;**5**(2):275—280.

38. *Geld P, Xhai B, Shveikin G, Alamovski S.* Effect of screening Me—Me bonds and structure peculiarities of lower oxides of transition metals of IVa and Va subgrup of periodic system. Physical Chemistry of oxides. M., "Nauka" (Russ.). 1971:167—178.

39. *Kritsalis R., Theasis Ph. D.* Technical Univ. of Athens Greec, 1990, in N. Eustathopouls, B. Drevet, Mecanism of wetting in reactive metal/oxide systems. Mat Res Symp. Proced. Joining and Adhesion Advance of Inorg. Mat. 1993;**313:**20.

40. *Drevet B, Chatain D, Eustathopoulos N.* Wettability and three-phase equilibria in the (Au—Si)/Al$_2$O$_3$ system. Chim Phys 1990;**87:**117—126.

41. *Zhuravlev V, Krasovskaya N, Sudavtsova V, Naidich Y.* Wetting of nonmetal materials by Sc-containing melts based on In, Sn, Cu. In Proceedings of Intern. Conf. High temperature capillarity, Crakow, Poland. 1998;158—163.

42. *Naidich Y., Chuvashov Y.* Wettability and contact interaction of gallium-containing melts with non-metallic solids. J. Material Science. 1983;18:2071—2080.

43. *Wan C, Kritsalis P, Drevet B, Eustathopoulos N.* Optimization of wettability and adhesion in reactive nickel—based alloys/alumina systems by thermodynamic approach J Mater Sci and Engineering. 1996;**A 207**:181—187.

44. *Humenik M, Kingery W.* Metal—ceramic interactions: III Surface tension and wettability of metal—ceramic systems. J Am Ceram Soc 1954;**37**(1):18—23.

45. *Kingery W. D.* Metal—ceramic interactions: IV Absolide measurement of metal—ceramic interfacial energy and the interfacial adsorption of silicon from iron—silicon alloys. J Am Ceram Soc. 1954;**37(2**):42—45.

46. *Wen Shi, Makoto Kubashi, Takao Chon.* Wettability of solid substrates by molten magnesium. Third international conf. Abstract, "HTC-2000"; Kurashiki, Japan. 2000:108.

47. *Nijenko V, Naidich Y.* Wettability of Al_2O_3 by liquid Mg (unpublished data). Institute for material sci. problem. National Acad. of Sci. of Ukraine.2000.

48. *Cotton F, Wilkinson G.* Advanced inorganic chemistry. Second Ed. Part 3. Interscient publ. J Wiley and Sons. N-Y, London, Sydney, 1966.

49. *Bilz H.* Uber Elektronenz Ustande von Hartstuffen mit Natriumechloridstruktur, Zeitshrift fur physic A. 1958;**153**(3)**:**338—358.

50. *Grigorenko N., Zhuravlev V., Poluyanskaya V., Naidich Y. V., Eustathopoulos N., Silvain J. I,* Wettability of α-Al_2O_3 single crystals by Ni—Al melt. In Proceeding of High temperature capillarity international conference HTC-97, 1997, Poland. Foundry Research Institute, Cracow, Poland. 1998;133.

51. *Geld P. V., Kochnev M. J.* Equilibrium of systems, containing silicon oxide. J Prikladnoi Himii (Russ). 1948;**21**(12):

52. *Naidich Y., Poluyanskaya V., Puszikov J., Danko A.* Interaction of silicon-containing melts with single crystal aluminium oxide. Powder metallurgy and metal ceramic. 2006;**45**(9/10):468—497.

53. *Naidich Y., Poluyanskaya V.* The date unpublished earlicr.

54. *Bewer L., Mastick D.* Theoretical calculation of the stability of solid and gaseous alkali and alkaline earth oxides. J Am Ceram Soc. 1951;**73:**2045—2050.

55. *Barnard A. K.* Theoretical bases of inorganic chemistry. MoGraw-Hill Pablishing Comp. Limited NY.- London - Toronto 1965;82—85.

56. *Brewer L.* Thermodynamic stability and nature of bond independence on electronic and crystal structure. In "Electronic structure and alloy chemistry of the transition elements". (Based on a symposium held in New York, February 22, Ed. P. Beck. Interscience Publ. 1962;218.

57. *Friedel J.* The transition metals. Electronic structure of d-zones and its role in crystal and magnetic properties. In "The physics of metals. Electrons." Ed. J. Ziman, Cambrige, the University press, 1969;373—444.

58. *Grigorenko N., Poluyanskay V., Eustathopoulus N., Naidich Y.* Wettability and spreading kinetics of Ni and Ni—Pd melts over silicon carbide and vitrous carbon surfaces. High temperature capillarity conference, HTC-97, Foundry Res. Ins. Poland, 1998;27—34.

59. *Necrasov B.* Osnovi obshey himii (the bases of general chemistry) Russ., Moskva, Himiya. 1973;**1**:380.

60. *Tretiakov Y. D.* "Chimiya nestechiometricheskih okislov". (Chemistry of nonstoihiometric oxides), Russ, Moskow university publishing house. 1974;113.

61. *Levi G., Kaplan W.* Aluminium—alumina morphology and thermodynamics from dewetting experiments. Acta Materialia. 2003;**51**:2793—2802.

62. *Fukuda A., Yoshikawa T., Tanaka T.* Measurement of solid—liquid interfacial energies in alloys.6th International conference High Temperature Capillarity, Athens Abstracts. 2009;119.

63. *Nakae H., Goto A.* Reactive and nonreactive wetting. In Proceed. High Temperature Capillarity, HTC-97, Cracov, Poland. 1998;12—17.

64. *Rabkin E., Chatain D., Bernardini J., Monchou X. J.* Grain boundary wetting by liquid metals — the role of interface faceting. Trans. Of JWRJ, HTC-2000, Special Issue. 2001;**30**:1—9.

65. *Wynblatt P., Takashima M.* An emperical model of grain boundary energy and its application to grain boundary wetting. Ibid. 2001;**30**:11—20.

66. *Drevet B., Chatain D., Eustathopoulus N.* Wettability and three-phase equilibria in the (Au—Si) Al_2O_3 systems /J. Chim. Phys., 1990; 87:117—126.

67. *Wagner C.* Passivity during the oxidation of silicon et elevated temperature / J. Appl. Phys., 1958; 29:1295.

68. *Marumo C.*, *Pask J.* Reactions and wetting behaviour in the system AuSi alloy — $2Al_2O_3$ /J. Amer. Ceram. Soc., discussion and notes, 1977; **60**(5, 6): 276—277.

69. *Drevet B., Eustathopoulus N.* Wetting of ceramics by molten silicon and silicon alloys: a review/ J. Mater. Sci., 2012; 47:8247—8260 (HTC 2012).

70. *Champion J. A., Keen B. J., Sillwod J. M.* Wetting of aluminium oxide by molten aluminium and other metals/ J. Mater. Sci., 1969; 4:39—49.

71. *Brever L., Searcy A. W.* / J. Amer. Ceram. Soc.,1951; 73(11):5308.

72. *Hoch M., Johnston H. /* J. Amer. Ceram. Soc., 1954; 74(9):2560.

73. *Cochran C. /* J. Amer. Ceram. Soc., 1955; 77(8):2190.

74. *Wol A. E.* Structure and properties of binary metallic systems, Moscow, 1959; 1:247—252 (Russ.).

75. *Kubashewski O., Alcook G.* Metallyrgical thermochemistry, Ed. Pergamon, 1979.

НАЙДІЧ Ю. В.

ПРОГРЕС У ТЕОРІЇ ЗМОЧУВАННЯ У СИСТЕМАХ КЕРАМІКА/РІДКИЙ МЕТАЛ. ОСОБЛИВІСТЬ КОНТАКТНИХ ПРОЦЕСІВ ДЛЯ ПЕРЕХІДНИХ ТА НЕПЕРЕХІДНИХ МЕТАЛІВ

Зроблено огляд та подані деякі загальні коментарі, що стосуються наукових проблем високотемпературного змочування та адгезії у системах рідкі метали—тверді керамічні матеріали, включаючи аналіз одержаних останнім часом даних. Розроблені теоретична трактовка процесів високотемпературного змочування та механізм, що базується на традиційних термодинамічних уявленнях, і також новий підхід на атомному та атомно-електронному рівні. У першу чергу як кераміка розглянуті різні субстрати, а саме, субстрати, де переважають іонні міжатомні зв'язки (наприклад, оксиди), котрі звичайно погано змочуються рідкими металами.

Розглянуто й проаналізовано внесок у процес змочування нерівноважної та рівноважної складових адгезії.

"Активні" метали, а саме, метали з досить високою хімічною спорідненістю до атомів твердої фази або іонів розділені на перехідні метали (d-електронні орбіталі частково заповнені електронами) та неперехідні метали (d-орбіталі не заповнені або цілком заповнені електронами).

Змочування у першому випадку (перехідні метали) набагато інтенсивніше, аніж для неперехідних металів, попри термодинамічні чинники (хімічна спорідненість металів до атомів твердої фази близька). Багато експериментальних даних ілюструють цю закономірність.

Для пояснення та надання трактовки на електронному рівні переваги перехідних металів у плані адгезійної активності запропоновано теорію поля лігандів.

Адгезійна активність неперехідних металів до твердих субстратів (оксидів) набагато нижча або помірна, і в цьому випадку часто спостерігаються явища дезмочування. Ця характерна особливість пояснюється утворенням на поверхні розділу нестабільних сполук проміжної валентності, котрі можуть піддаватись реакції диспропорціонування.

Подані деякі практичні рекомендації щодо регулювання та керування процесами змочування у різних технологічних процедурах.

Ключові слова: *високотемпературне змочування, адгезія, кераміка, перехідні та неперехідні метали, d-електронні орбіталі та теорія поля лігандів, дезмочування, реакція диспропорціонування.*