ARCHIVES OF METALLURGY AND MATERIALS
Volume 52 2007 Issue 1

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THE ROLE OF ALUMINUM OXIDATION IN THE WETTING-BONDING RELATIONSHIP OF Al/OXIDE COUPLES

WPŁYW UTLENIANIA ALUMINIUM NA ZWILŻALNOŚĆ I WYTRZYMAŁOŚĆ POŁĄCZENIA Al/TLENEK

In several Al/ceramic systems wetting is known to be strongly affected by the presence of oxide film on Al, which prevents a true contact, leading to large contact angles measured. However, the role the oxide plays in determining the bond quality and the resulting joint strength is not clear. This paper presents new experimental results on the effect of metal oxidation on the *wetting – interface microstructure – interfacial shear strength* relationship in Al/oxide systems exhibiting different reactivity with Al (Al_2O_3, TiO_2, ZrO_2, and SiO_2). The results demonstrate that even a few nanometers thick oxide film covering liquid aluminum significantly affects macro-scale properties of Al/oxide couples such as wetting and shear bond strength.

Keywords: Al/oxide systems; Contact angle; Bonding; Surface oxidation

Znany jest fakt, że obecność powłoki tlenkowej na aluminium ma istotny wpływ na zjawisko zwilżania niektórych materiałów ceramicznych, ponieważ stanowi ona naturalną barierę w tworzeniu autentycznego kontaktu, przyczyniając się tym samym do wysokich wartości mierzonych kątów zwilżania. Nie jest natomiast wyjaśniona rola powłoki tlenkowej w kształtowaniu połączenia metalowo-ceramicznego, zwłaszcza jej wpływ na wytrzymałość mechaniczną. W niniejszej publikacji na przykładzie badań kilku tlenków metali różniących się reaktywnością w kontakcie z ciekłym aluminium (Al_2O_3, TiO_2, ZrO_2, and SiO_2) po raz pierwszy zademonstrowano, że w układach typu Al/ceramika utlenianie aluminium jest czynnikiem decydującym o charakterze wzajemnej korelacji pomiędzy zwilżalnością, strukturą granic rozdziału oraz wytrzymałością połączenia. Stwierdzono, że obecność na aluminium powłoki tlenkowej o grubości nawet kilku nanometrów ma istotny wpływ na zjawiska i właściwości w skali makro, np. zwilżalność tlenków przez ciekłe aluminium oraz wytrzymałość na ścinanie połączenia Al/tlenek.

1. Introduction

It is well known that oxygen strongly affects the wetting behavior of metals on ceramics at elevated temperatures. For example, metal/oxide couples with very low levels of dissolved O in the liquid (from the dissolution of the oxide substrate) exhibit large contact angles, θ, and weak bonding [1]. For non-reactive couples with more dissolved oxygen, Me-O clusters are adsorbed at the interface, and yield low θ values. The lowest θ values are achieved in reactive Me/oxide couples that form wettable reaction products having partial metallic character. In addition, residual oxygen in the furnace atmosphere can form a continuous and tenacious oxide skin on the liquid metal, and inhibit its spreading on the substrate. While thin oxide films offer less resistance to spreading than thick films, both hinder true ceramic-to-metal contact, and lead to poor wetting and large scatter in the experimental contact angle data, well documented for the Al/alumina system in references [2-13] using different test methods. Literature data also show that above a critical temperature, T^{w} (~ 1273 K), a transition from non-wetting to wetting occurs in Al/ceramic systems, which is due to oxide removal by a variety of physicochemical and mass transport processes. The role of oxygen transport processes at the solid/liquid interface has been discussed by Eustathopoulos et al. [1], Saiz et al. [9], Ratto et al. [14], and Levi and Kaplan [15]. Saiz et al. [9] demonstrated the effect of oxide film covering an Al drop on the atomic scale structure of the Al/alumina interface produced in wettability tests.

Oxygen-free Al has higher surface tension σ_{lv} than oxygen-saturated Al [16-21]. In addition, oxygen-free Al

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forms a lower contact angle, θ, on different ceramics [1, 3, 5, 10, 22-24]. In view of this, the work of adhesion, W_a (where, $W_a = \sigma_{lv}(1 + \cos\theta)$), that characterizes the bonding properties of metal/ceramic couples, should be larger for oxygen-free Al than for oxygen-saturated Al. In other words, a strong effect of Al oxidation on mechanical properties of Al/ceramic joints is expected [1, 2]. However, a clear and demonstrable experimental evidence of the effect of Al oxidation on interface properties is lacking, with a few exceptions such as refs. [10, 15]. In addition, the role played by surface oxide on Al in chemical interactions in highly reactive Al/ceramic systems is unclear, and only a few works [22-27] discuss this problem in the reactive Al/carbon system, which indicate that oxide-free drops form much lower contact angles than oxidized drops.

In this paper, the effect of surface oxide film on the wetting and bonding properties of Al/oxide couples exhibiting varying degree of reactivity is examined. A sessile drop test with different heating procedures to control the extent of Al oxidation is used for contact angle measurements, and an improved droplet push-off shear test is used to characterize the interface strength.

2. Experimental

Sessile-Drop Test: The contact angle was measured using the sessile-drop method [1]. The test was carried out in a dynamic vacuum of 0.2-0.4 mPa for different contact times and temperatures. Two sample heating procedures were employed to examine the effect of oxide films: 1) contact heating (CH) (~8 K.min^{-1}) was achieved when the couple was first placed in the furnace and then heated to the test temperature; and 2) capillary purification (CP) in which the substrate and the metal were heated simultaneously but separately under vacuum (~8 K.min^{-1}), the metal being in a graphite syringe [24, 25]. At the test temperature, a droplet of the metal was mechanically extruded out of the graphite syringe and brought in contact with the preheated ceramic. The extrusion action in CP erodes the surface oxides thus yielding an oxide-free droplet, and separate heating of metal and substrate eliminates the substrate/metal interactions during contact heating prior to the test. The test variables were temperature, time, substrate type (Al_2O_3, TiO_2, ZrO_2 and SiO_2), and droplet composition (99.9999% pure Al, AlSi11, and AlTi6 alloys). The ceramic substrates were polished with diamond paste up to an average roughness of R_a = 100-120 nm. Directly before the wettability test, the initial surface oxide from each metal sample was mechanically removed and both metal and substrate samples were ultrasonically cleaned in acetone.

Improved Droplet Push-Off Test: In the conventional droplet push-off shear test to measure the bond strength, a shear stress is applied parallel to the substrate to debond the solidified drop. The test is limited to droplets with $\theta > 90°$ due to the practical difficulty of shearing droplets with small θ. A recently developed *improved push-off shear test* overcomes this problem by applying a load at a constant rate (1 mm.min^{-1}) to the flat side of one half of a bisected Al/ceramic couple [11]. The shear stress (τ) versus displacement (l) data are recorded until shear failure occurs. By permitting θ and $\tau_{\max}$ (i.e., maximum shear stress or shear bond strength) to be measured on each test specimen, the improved push-off test allows characterization of the wetting, bonding, microstructure, and chemistry of the interface in the *same* test coupon. The push-off test was done on CP and CH samples of Al/Al_2O_3, $AlSi11/Al_2O_3$, $AlTi6/Al_2O_3$, Al/TiO_2 and Al/ZrO_2.

3. Results and discussion

Al/Al_2O_3

The experimental values of initial contact angle, θ_o, and the values θ_t after a specified time t, as well as corresponding $\tau_{\max}$ values are collected in Table 1. The shear strength values correspond to debonded samples in which fracture occurred at the interface rather than through the ceramic or the metal as confirmed by optical microscopy and discussed in [11]. Measurements of θ as a function of time showed that at 953 K and 1023 K, θ for CH decreased gradually with time, stabilizing at 130° and 128°, respectively [11]. The poor wetting is caused due to copious oxidation of Al drop by the residual oxygen in the furnace at 953 K and 1023 K, temperatures that are less than the wettability transition temperature, T^w, of ~1273 K. In contrast, the θ in CP Al/Al_2O_3 at 973 K shows a significant decrease (immediately upon contact), and attains a low value of 94° [10]. Such a low θ is not achieved for similar test conditions when CH is employed, which suggests that CP removes the surface oxide and yields a clean, oxide-free solid/liquid interface. Extremely short times (< 1 min) are needed to achieve an equilibrium θ by CP even at 973 K; in CH [12], this is possible only at temperatures near T^w (which, incidentally, shows a rather wide dispersion, 1083-1373 K, depending on vacuum level and test procedure used).

TABLE 1

Effect of temperature, alloying and testing procedure on $\theta - \tau_{\max}$ relationship (the composition of Al alloys is in wt.%)

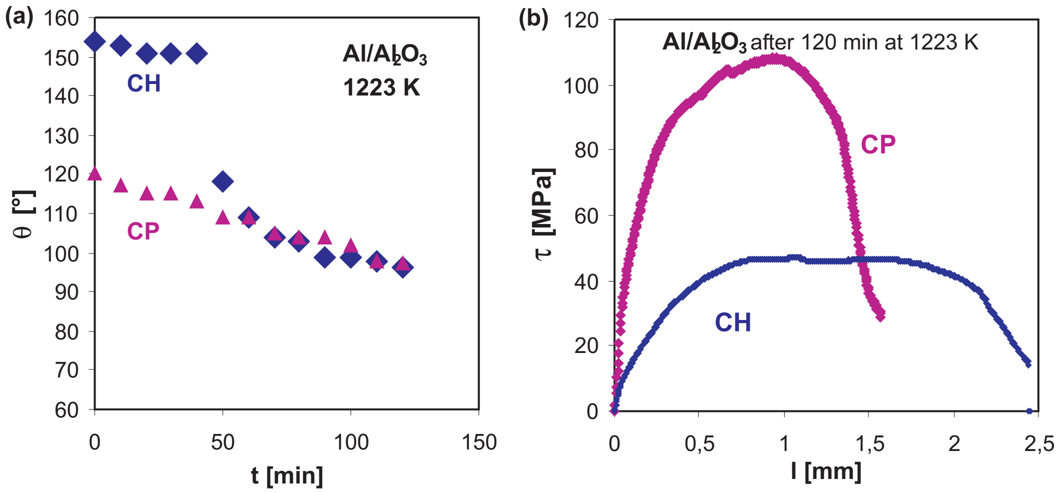
Metal	Conditions for CH procedure	$\theta[°]$		$\tau_{\max}$ [MPa]	Conditions for CP procedure	$\theta[°]$		$\tau_{\max}$ [MPa]
		θ_0	θ_t			θ_0	θ_t	
Al	953 K, 30 min, 0.2 mPa [11]	128	126*	19.1*	973 K, 15 min, 0.3 mPa [10]	101	94*	42.1*
	1023 K, 30 min, 0.2 mPa [11]	127	121*	29.5*				
	1123 K, 30 min, 0.2 mPa [11]	127	96*	35.0*				
	1223 K, 30 min, 0.2 mPa [11]	107	79*	46.6*				
	1323 K, 30 min, 0.2 mPa [11]	87	74*	47.9*				
	1223 K, 120 min, 6.7-1 mPa**	154	96	47.1	1223 K, 120 min, 2.4-0.8 mPa**	120	97	108.1
	1023 K, 15 min, 0.4 mPa	132	130	5.6				
	953 K, 60 min, 0.3 mPa	135	132	47.9				
AlSi11					973 K, 15 min, 0.3 mPa	89	98 [12]	66.5 [12]
	1073 K, 30 min, 0.4 mPa	135	125	58.1				
	1273 K, 30 min, 0.5 mPa	95	84 [12]	66.2 [12]				
	1123 K, 15 min, 0.4 mPa	137	123	18.2				
	1123 K, 30 min, 0.2 mPa	130	122	—				
AlTi6	1073 K, 30 min, 0.3 mPa	138	134	—	1073 K, 15 min, 0.4 mPa	94	91 [12]	5.0 [12]
	1273 K, 30 min, 0.5 mPa	137	103 [12]	17.8 [12]				
	1123 K, 15 min, 0.4 mPa	122	118	—				

* data used for calculation W_a in Fig. 2; ** data shown in Fig. 1.

As expected, the shear strength, $\tau_{\max}$, increases with increasing temperature and for CP it is greater than for CH at $T \leqslant 1123$ K. This shows that the same factors that affect the wetting properties also affect the interface strength. However, measurements of $\tau_{\max}$ are even more sensitive to test conditions compared to the θ values (Table 1).

In order to confirm that beneficial effects of CP indeed originate in the mechanical removal of surface oxide, two additional tests were done under poor vacuum. These tests showed that despite identical thermal histories and furnace conditions prior to the test, a significant difference in the effect of testing procedure on θ and $\tau_{\max}$ occurred. Figure 1a shows that θ values in CH and CP at 1223 K become comparable after ~50 min, being equal to 96° in the 120^{th} min. However, a relatively high θ_o in CH is due to insufficient drop de-oxidation during CH heating to the test temperature while a rather high θ_t in CP is due to oxidation of the initially oxide-free drop during its heating under "poor" vacuum. The room-temperature shear stress (τ) versus displacement (l) curves (Fig. 1b) show that despite the same values of θ_t, the difference between $\tau_{\max}$ values for CH and CP is large and that additional factors may have adversely affected the mechanical bonding in such couples. In CP procedure, a better vacuum was attained (see history of the samples in Fig. 1) and *in-situ* chemical analysis of residual gas in the test chamber using quadrupole mass spectrometer (Prisma QMS200, Pfeiffer Vacuum Inc.) has shown that the atmosphere was "cleaner"(e.g., the oxygen partial pressure, P_{O_2}, was an order of magnitude lower) compared to CH. The improved interface strength of CP Al/Al_2O_3 may be related to the role of graphite capillary as an oxygen getter. Graphite is known to reduce the P_{O_2} via its reaction with oxidizing gases (H_2O and O_2), which forms gaseous products CO and CO_2, easily removed by pumping [28]. Graphite also improves the wettability in yttria-stabilized-zirconia (YSZ)/Ni-Ti [29, 30]. YSZ is not wetted by Ni-Ti alloys ($\theta > 90°$) when a Mo susceptor is used because even minute quantities of O in the furnace atmosphere oxidize the Ti in the Ni-Ti alloy, and render it ineffective in promoting wetting via reactions even at 1773 K in a purified $Ar + H_2$ atmosphere. This agrees with the fact that stable oxides of Ti form even at as low an oxygen partial pressure as $P_{O_2} \sim 10^{-28}$ atm. However, when the Mo susceptor is replaced with a graphite susceptor, the carbothermic reduction of Ti_xO_y can free Ti to react with YSZ and decrease the contact angle, θ [30].

Our results on the beneficial effects of CP agree with the literature reports according to which direct mechanical removal of surface oxide on the Al sample before its placing in vacuum chamber is not effective and oxide monolayer forms almost instantaneously. Oxide growth may occur also in vacuum during pumping and heating, as demonstrated by Csanady et al. [31] who carried out *in-situ* observations in a transmission electron microscope on the oxidation of initially oxygen-free solid



Couple history in vacuum chamber	Pressure, mPa	
	CH	CP
293 K, before heating of a couple	0.22	0.15
993 K (just before squeezing drop in CP)	3.8	1.15
1223 K, t=0 min – beginning of wettability test	6.69	2.42
1223 K, t=120 min – end of wettability test	1.15	0.83

Fig. 1. Effects of wettability tests conditions on (a) wetting and (b) shear behavior in Al/Al_2O_3 at 1223 K

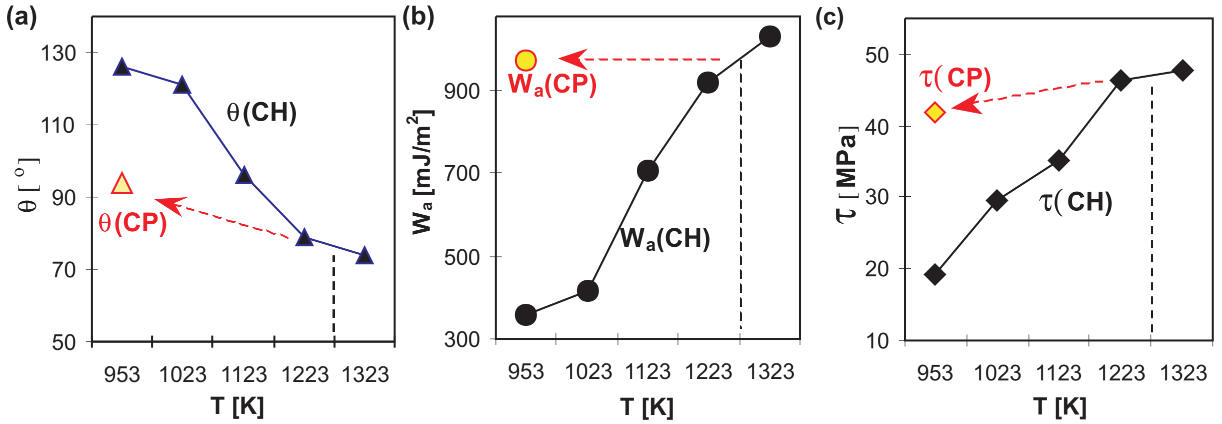


Fig. 2. Effect of temperature and testing procedure (CH, CP) on $\theta - W_a - \tau$ relationship in Al/Al_2O_3. The W_a values were calculated using experimental data of θ and τ from [11] (marked in Table 1 with *), temperature dependence of surface tension of pure Al (σ_{ls}) from [16], and the mean value of σ_{ls} = 1050 mN/m from works [17-21] for oxide-free Al in CP.

aluminum at 573-773 K under various oxygen partial pressures (10^{-3}–10^{0} Pa). These observations suggest that in wettability studies as well as in most technological processes the oxidation of aluminum is generally unavoidable, caused by extremely low equilibrium oxygen partial pressure, P_{O_2} (in the Al-Al_2O_3 system, P_{O_2} calculated for the reaction, $2Al_2O_{3(solid)} = 4Al_{(liquid)} + 3O_{2(gas)}$, over 1000-1375 K is in the range ~10^{-40} 10^{-27} Pa [32, 33]). However, for CH at $T > T^{w}$, the destruction of the oxide film on molten Al droplet and consequent lowering of θ are possible under vacuum due to 1) the formation of volatile sub-oxide Al_2O by the reaction: $4Al_{(l)} + Al_2O_{3(s)} \rightarrow 3Al_2O_{(g)}$, and 2) dissolution of Al_2O_3 skin in molten Al [6]. The calculated equilibrium partial pressure of gaseous sub-oxide Al_2O (P_{Al_2O}) in the above reaction over the same temperature range is $\sim 10^{-7}$ to $\sim 10^{-2}$ Pa [32]. This reaction is favored at the higher temperature and $P_{Al_2O} = 10^{-3}$ Pa is a critical pressure at 1273 K to remove the alumina film of the Al droplet [32, 33]. Following Ratto et al. [14], under dynamic conditions the formation of oxide vapors leaving the liquid metal surface can affect also the oxygen availability in the vicinity of a drop/substrate and contribute to the effective oxygen pressure that may be many orders of magnitude greater than the calculated equilibrium value P_{O_2}. In contrast, in sessile drop wettability tests when the primary oxide skin of a few nanometer thickness is removed from the droplet surface directly in vacuum chamber prior to test via CP [1] or when the oxide layer is effectively destroyed during the test by electromagnetic vibration [3], acute values of $\theta \leqslant 90°$ are obtained even at low temperatures ($< T^w$).

The results obtained suggest that different shear behavior of solidified sessile drop Al/Al_2O_3 couples after subsequent thermal cycling (TC) reported in [11] is also related to the effect of oxide film on Al drop. Moreover, under certain conditions, its presence may play a beneficial role in thermal fatigue resistance of such couples because the TC couples (200 cycles at 300-673 K) produced at low-wettability test temperatures (1023 K and 1123 K, 30 min CH in vacuum 0.2 mPa) had higher $\tau_{\max}$ than non-TC samples. But in high-temperature couples (CH, 1223 K, 30 min), the TC samples exhibited lower shear strength than non-TC couples. At low temperatures of wettability tests ($T < T^w$), the solid/liquid interface in CH is contaminated with the oxide, and further thermal cycling of sessile drop couples fractures and redistributes the fine oxide particles in a thin metal zone at the droplet-side interface, thus effectively strengthening the joint region as in a composite material. In contrast, after 30 min at 1223 K ($\sim T^w$) and under the same furnace conditions, the original S/L interface is relatively clean and devoid of oxide which could have caused strengthening. Therefore, during further TC such an interface is less resistant to the differential expansion and contraction, which induces cracks and interface weakening; thus the $\tau_{\max}$ of TC couples is lower compared to non-TC couples.

Weirauch [5] has shown by CH measurements of θ and oxide thickness in quenched sessile drops (tested under varying oxygen partial pressures, P_{O_2}) that at its melting temperature, liquid Al should form on alumina substrate the true θ of $\sim 78°$ (obtained from data extrapolation to zero oxide thickness). Using this value of θ and σ_{lv} = 1050 mN/m for oxide-free Al, a large value of W_a(~1342.5 mN/m) is obtained, which suggests that a strong mechanical bond should form in CP Al/Al_2O_3, as is actually observed in our tests. Moreover, Figure 3 shows that measured values of θ and $\tau_{\max}$ as well as the calculated values of W_a exhibit similar changes with temperature in CH, while oxide removal by CP leads to $\theta, \tau_{\max}$ and W_a values that are comparable to those of CH at $T \geqslant T^w$ at which oxide is destroyed *in-situ* in vacuum. The correlation, however, is experimental rather than fundamental as it does not consider the role played by the metal plasticity, interfacial defects, and thermal stresses due to expansion mismatch, all of which affect the joint strength to varying degree in different ceramic/metal systems.

Al/TiO_2 and Al/ZrO_2

Compared to "non-reactive" Al/Al_2O_3, both Al/ZrO_2 and Al/TiO_2 are moderately reactive. Since ZrO_2 is less reactive to Al than TiO_2 (Table 2), Al/ZrO_2 exhibits inferior wetting compared to Al/TiO_2. For Al/TiO_2, the θ values for CP at 1173 K and for CH at 1273 K are identical and below 90° (Fig. 4a). This confirms that CP values represent the true θ with an oxide-free droplet in contact with the TiO_2. Such a low θ is obtained by CH only at ~1273 K or above when oxide removal permits direct physical contact. Because kinetics of oxide removal reactions (e.g., dissociation, dissolution) is involved, the θ for CH at 1273 K exhibits pronounced time dependence, especially in the first 20 min of contact in contrast to CP at 1173 K, which is insensitive to time because the droplet is oxide-free from the inception of contact with $\theta = \theta_o$, and the kinetics of oxide removal reactions are of secondary importance in the initial stages. With CH, the θ decreases with increasing temperature, and at 1373 K, an angle of 64° is obtained. Note also that the same values of θ_o for CH at 1373 K and for CP at 1173 K are obtained because in both cases, the droplet is oxide-free from the inception of the contact.

TiO_2 is an ionic transition metal oxide with a large exothermic heat of formation, and a negative Gibb's free energy of formation (Table 2). Its reaction with liquid Al forms titanium aluminide according to: $TiO_2 + Al \rightarrow Al_2O_3 + Al_xTi_y$, where the type of aluminide (Ti_3Al, TiAl, $TiAl_3$) formed depends upon the ratio of TiO_2 to Al. Thus improvement in wetting in Al/TiO_2 is attributed to a favorable interface chemistry resulting from chemical reactions.

The microstructure of Al/TiO_2 interfaces shows [34] that at 1173 K, new Al_2O_3 crystals form at the interface surrounded by Ti-containing Al. At 1373 K, a continuous layer of inhomogeneous structure and thickness forms at the interface. On the drop-side of the interface in Al/TiO_2, large Al_2O_3 crystals grow into the

TABLE 2

The Gibb's free energy change of reactions (ΔG [kJ]) calculated using the software HSC Chem (ver 4.1), Outokumpu Res Oy, Pori (Finland)

Reaction	ΔG_{973}	ΔG_{1173}	ΔG_{1273}	ΔG_{1373}
$2Al + 1.5TiO_2 \rightarrow Al_2O_3 + 1.5Ti$ (1)	-218.6	-205	-205	-192.4
$2Al + 1.5ZrO_2 \rightarrow Al_2O_3 + 1.5Zr$ (2)	-0.43	11.2	16.6	22.2
$2Al + 1.5SiO_2 \rightarrow Al_2O_3 + 1.5Si$ (3)	-267.2	-252.8	-245.4	-163.3

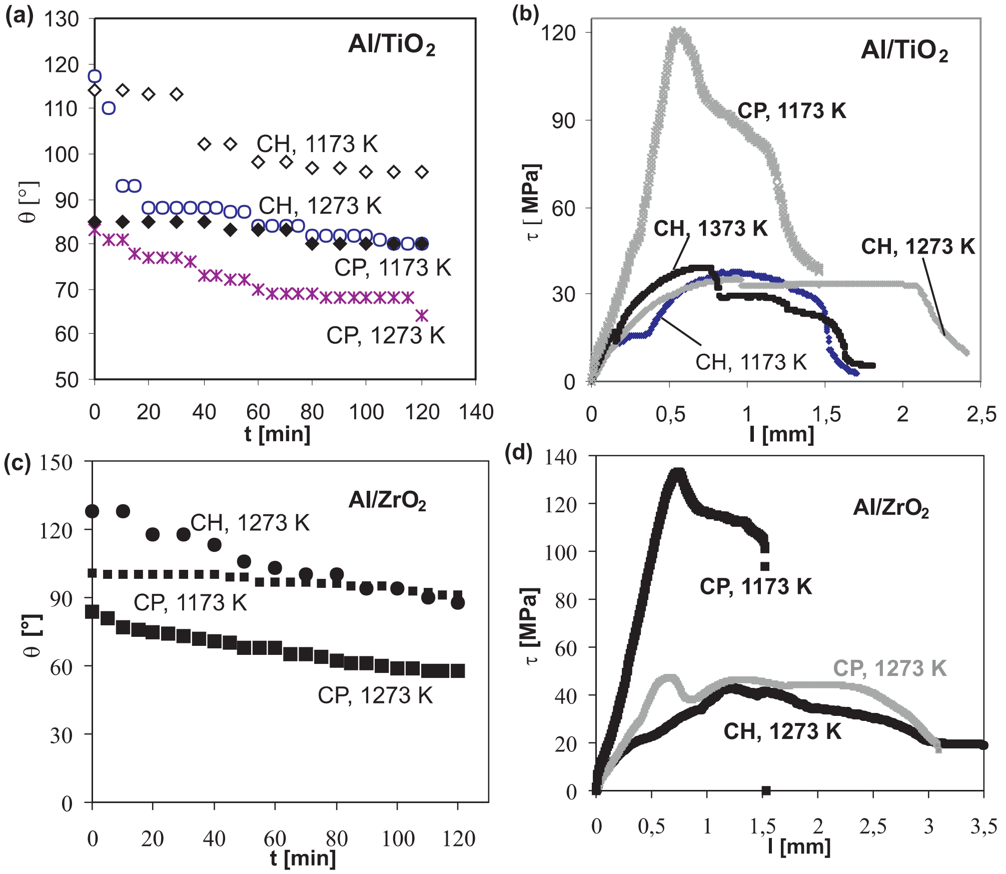


Fig. 3. Wettability (a,c) and shear behavior (b,d) in Al/TiO_2 (a,b) and Al/ZrO_2 (c,d)

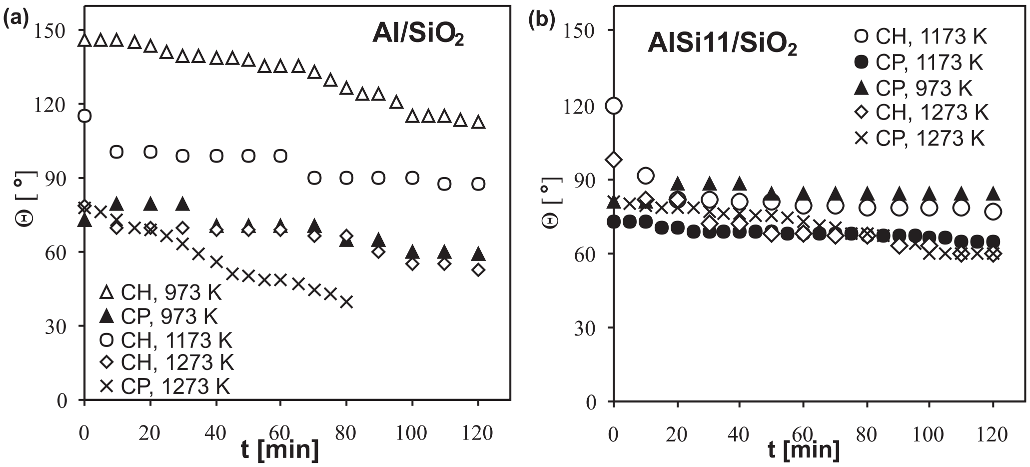


Fig. 4. Effect of testing conditions on wettability kinetics in Al/SiO_2 (a) and $AlSi11/SiO_2$ (b)

droplet; these crystals presumably form by a dissolution-precipitation process. On the substrate-side of the interface, very fine Al_2O_3 crystals, surrounded by an Al impregnated region, form. This gives rise to a continuous network of fine Al_2O_3 crystals interpenetrated by Al.

Figure 4b shows the shear behavior of Al/TiO_2 joints formed at the wettability test temperatures of 1173, 1273, and 1373 K by CH, and of 1173 K by CP. The $\tau_{\max}$ values for CH decreased from 45 MPa to 35 MPa when the temperature increased from 1173 K to 1273 K; the θ values at these temperatures are 96° and 80°, respectively. The effect of CP on $\tau_{\max}$ is pronounced, and a $\tau_{\max}$ of 121 MPa at 1173 K is attained, indicating that oxide removal strongly improves the shear strength. At 1173 K, θ decreased only moderately (from 97° to 80°) when the test procedure was changed from CH to CP; however, a sharp increase in $\tau_{\max}$ occurred at 1173 K when CP was done in place of CH. This suggests that joint strength is more sensitive to interfacial changes at the S/L interface than θ, which is sensitive to the physicochemical processes at the triple line.

In Al/TiO_2, even though both CH at 1273 K and CP at 1173 K yield the same equilibrium θ (Fig. 4a), their $\tau_{\max}$ values (Fig. 4b) are very different. Because of the time needed for the deoxidation reactions, the actual time (out of a total of 120 min contact) available for titanium aluminide formation is limited in CH, and $\tau_{\max}$ is only 35 MPa. On the other hand, the CP drop at 1173 K is oxide-free even for θ_o, and aluminide formation can start immediately upon contact, resulting in a larger quantity of the hard and strong aluminide phase, and a correspondingly high shear strength of 121 MPa. Even though the Al/TiO_2 reaction kinetics will be sluggish at 1173 K than at 1273 K, it does not follow that the deoxidation kinetics at 1273 K will necessarily be faster than the Al/TiO_2 reaction kinetics at the lower temperature. In any case, the extent of Al deoxidation needed to obtain a contact angle drop $\Delta\theta$ may not be the same as the extent of titanium aluminide formation needed to obtain a correspondingly similar increase of $\tau_{\max}$. Moreover, compared to CH, the presence of graphite near a substrate in CP might be an additional factor contributing to better wetting of the TiO_2 and ZrO_2 substrates by Al and caused from beneficial changes of substrate surface chemistry as a result of partial reduction of these oxides.

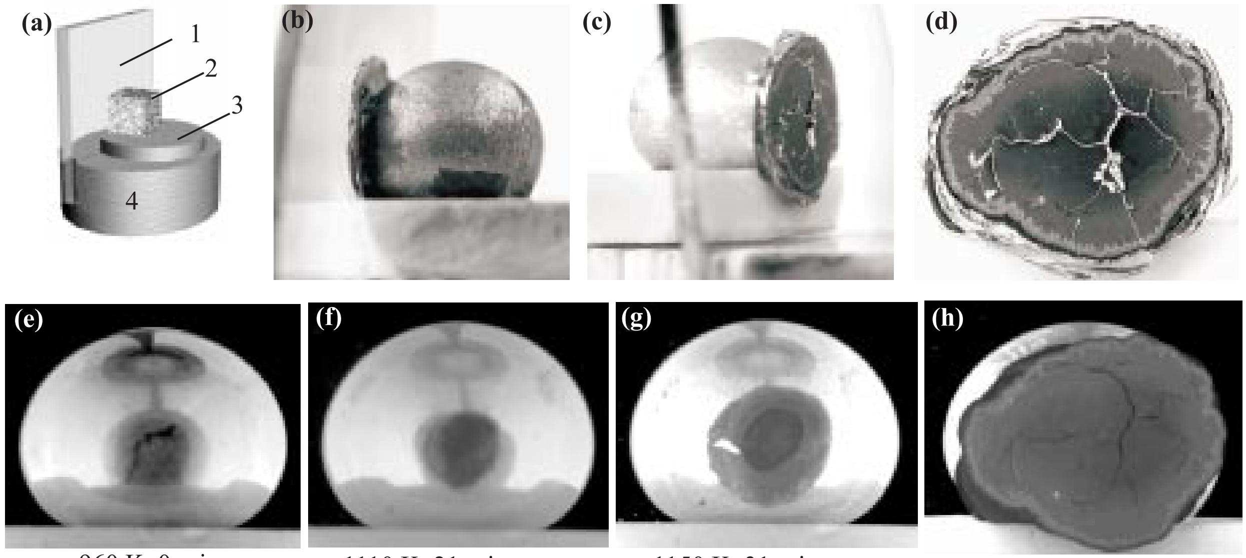
It is also very important to note that the reaction products have both a beneficial and deleterious effects on the shear strength; the critical factor, as demonstrated in numerous studies on ceramic/metal composites, is the thickness of the reaction layer. Indeed, very thin reaction layers provide inadequate strengthening because of their diminished ability to transfer the applied load from the matrix to the reinforcing fiber. In contrast, very thick reaction layers are also detrimental to composite strength because of the brittle nature of the interphase and increased probability of finding strength-limiting structural defects within a thick brittle layer. An optimum thickness (i.e., quantity) of the product phase permits maximum strengthening. The situation becomes more complicated when interaction in a system leads to the formation of heterogeneous reaction product region (RPR) composed of two or more phases. This is also borne out by our structural observations of Al/TiO_2 [34-36] showing that for both CH and CP at 1117-1273 K, the reactivity in the system is weak, particularly at 1117 K while the separate Al_2O_3 crystals noted at the interface are formed rather by dissolution-precipitation (DP) than due to direct reduction of TiO_2 by Al. Similar DP mechanism, leading to reinforcing of the drop-side interface with freshly formed Al_2O_3 crystals, takes place also in the Al/Al_2O_3 system, as described in [12]. At higher temperature, oxy-redox reaction becomes dominant, leading to the reactive metal penetration along grain boundaries and to the formation of relatively thick heterogeneous RPR, composed of Al_2O_3, Al_3Ti and Al-Ti phases. Although CH at 1373 K yields an oxide-free interface at $t \geqslant 0$ min, shear strength is lower (40 MPa) than for CP 1173 K. This is because of faster kinetics of aluminide forming reactions at high temperatures, which lead to extensive formation of brittle aluminides at 1373 K. Moreover, our studies [11, 12] demonstrated that the Al-Ti/Al_2O_3 interface is much weaker than Al/Al_2O_3 (see also Table 1) due to unfavorable structure of a drop-side interface, as explained in detail in [12]. This negative effect of alloying Al with Ti seems to be similar in the Al/TiO_2 couples, when increasing temperature results in higher amount of Ti in the drop and weaker newly formed Al-Ti/Al_2O_3 interfacess. Thus, greatest improvements in the wettability (lowest θ, 64°) are obtained at the expense of the joint strength in CH 1373 K Al/TiO_2 couple.

For CH Al/ZrO_2 at 1273 K (Fig. 4c), θ is initially large, but drops to 90° in 120 min. However, for CP Al/ZrO_2 at 1273 K, $\theta < 90°$ even at $t = 0$, and it gradually decreases to 60° after 120 min. Since Al/ZrO_2 is less reactive than Al/TiO_2 (Table 2), the lowering of the θ by CP is due primarily to oxide erosion rather than chemical reactions. After 60 min, the θ for CP at 1173 K becomes similar to θ for CH at 1273 K. Note that unlike Al/Al_2O_3 couples, the $\theta - t$ curves of Al/ZrO_2 show 30° difference between CH and CP even at the high temperature of 1273 K ($\sim T^w$). This is an effect of incomplete deoxidation of Al droplet under vacuum in CH on the kinetics of chemical interaction. From structural characterization [35] the DP mechanism seems to be a leading one for the interaction between molten Al and zirconia at 1117-1273 K but the amount of the Al_2O_3 crystals at the interface is much smaller than that in more reactive Al/TiO_2 system. Similar to Al/TiO_2, shear tests on the Al/ZrO_2 (Fig. 4d) indicate a beneficial effect of oxide removal by CP on interface strength at 1173 K. However, for CP at 1273 K, this effect is negligible. Most probably, an increase in temperature, and the resulting increased reactivity, leads to unfavorable interfacial changes, similar to those noted in the Al/TiO_2 and $Al\text{-}Ti/Al_2O_3$ couples at high temperatures [12], that mask the effect of oxide on bond strength.

Al/SiO$_2$

The wetting in Al/SiO_2 is reactive, promoted by freshly formed Al_2O_3 from reaction (3) in Table 2. Despite the fact that numerous studies [37-45] have confirmed the formation of a thick reaction product region (RPR) in Al/SiO_2 even at low temperatures, and freshly formed Al_2O_3 should be wettable by liquid Al, there is some uncertainty regarding low-temperature wetting in Al/SiO_2. Laurent et al. [37] suggest that this uncertainty is related to the presence of oxide film on Al, which hinders spreading, while Zhou and Hosson [38] propose that formation of surface cavities ahead of the triple line (TL) hampers the spreading. These cavities may form due to 38% volume mismatch between the reactants and the products in reaction (3) of Table 2.

Our results from CH and CP procedures demonstrate that the wettability kinetics in Al/SiO_2 is different and strongly depends on testing procedure. The $\theta - t$ data for Al/SiO_2 are shown in Figure 4 at different temperatures together with the effect of Si alloying of Al droplet. Similar to the literature data [37-45] for CH at low temperatures (973 and 1173 K), our results show that θ remains obtuse ($\theta > 90°$), indicating poor wetting at $T < T^w$. But for CP Al/SiO_2 at 973 K,$\theta > 90°$, which is similar to CH couples at 1273 K (Fig. 4a). Moreover, at high temperature the reactivity of Al/SiO_2 is very high and wetting occurs for a decreasing droplet volume. This may cause anomalously low θ (because they are receding contact angles, not advancing ones), particularly well noticeable for oxide-free droplet in CP at 1273 K. For the same temperature range, alloying Al with Si inhibits the Al/SiO_2 reaction and leads to higher θ and less difference in the CH and CP values (Fig. 4b). At high temperature 1273 K, the $Al\text{-}Si/SiO_2$ couples demonstrate the same contact angles for both CH and CP because, contrary to Al/SiO_2, the reactivity is strongly reduced thus it does not cause a decrease in the droplet volume.



960 K, 0 min

1110 K, 21 min

1150 K, 31 min

1173 K, 50 min

Fig. 5. (a) Initial configuration of the Al/SiO_2 couple for investigation of interaction with vertical SiO_2 plate (1- SiO_2 plate, 2- Al sample, 3- alumina support, 4- alumina holder); (b-d) different views of the couple after test at 1173 K for 60 min, (e-h) images of Al drop recorded through transparent SiO_2 plate: view (e) shows the first moment of melting accompanyied by cracking of the oxide film covering Al drop; view (f) illustrates drop oxidation (resulting in its matte image) and the formation of a small dark area of reaction products region in the center of the drop image, corresponding to the location of a crack in the oxide film, reordered in view (e); views (g, h) show increasing the reaction area with time accompanyied with cracking of SiO_2 plate

The structural examination of cross-sectioned Al/SiO_2 couples does not show any remarkable cavities at the TL, although numerous cracks are noted in the SiO_2 substrates and a few cracks are in the RPR. Moreover, the heterogeneous RPR, composed of fine alumina particles surrounded with Si and Al-Si phases, propagates even over TL. In such a case the wettability of the system is controlled by the wettability of RPR (i.e., mainly aluminum oxide) and not by the wettability of SiO_2.

In order to demonstrate that the oxide film on Al, which hinders spreading, as explained by Laurent et al. [37], is the more likely cause of inferior low-temperature wetting in Al/SiO_2 than pinning of TL at surface cavities resulting from the volumetric expansion accompanying SiO_2 to Al_2O_3 phase transformation, we performed two tests shown in Figures 5 and 6. The behavior of the Al drop and the formation of the RPR in SiO_2 were easily observed through transparent SiO_2 plates contacting Al samples. These *in-situ* observations evidenced that during heating at the test temperature a few small cracks are formed just inside the RPR while significant cracking takes place only during cooling, particularly at the RPR/SiO_2 interface and much less at the TL. Since these cavities are formed after the wettability test they do not play an essential role in pinning of TL, as suggested by Zhou and Hosson [38]. Moreover, after a few minutes at $T < T^w$ the Al drop becomes matte that presents an experimental evidence of additional oxidation of free surface of Al drop in vacuum chamber. This effect is well distinguished at the 1098 K test as shown in Figs. 6e-g. The formation of thick and continuous oxide film on the Al drop hinders its spreading and wetting on the SiO_2 plates as well as with the Al_2O_3 support (both contacting the Al sample, Fig. 5). Consequently, infiltration of molten Al between vertical SiO_2 plates is also blocked (Fig. 6). In the same time, molten Al has a true contact with Al_2O_3 particles, freshly formed at the Al/SiO_2 interface due to oxy-redox reaction. Since at 1098 K the oxide-free Al wets alumina, liquid metal penetrates between Al_2O_3 particles. Finally, it contributes to the development of a thick RPR growing over the TL inside SiO_2 plates.

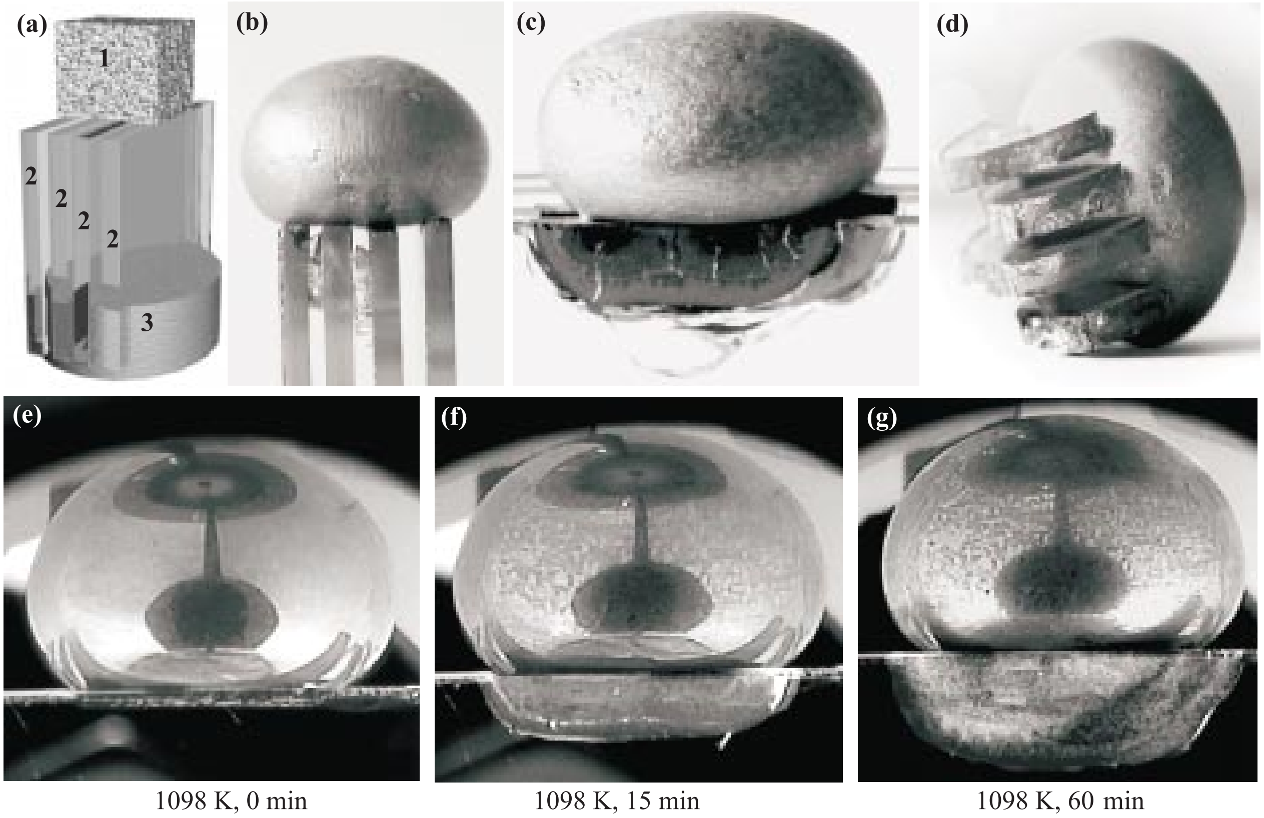


Fig. 6. (a) Initial configuration of the Al/SiO_2 couple for investigation of interaction with a few vertical SiO_2 plates (1- Al sample, 2- SiO_2 plates, 3- alumina holder); (b-d) different views of the couple after test at 1098 K for 60 min, (e-g) images of Al drop and RPR under the drop recorded through transparent SiO_2 plates: view (e) shows the first moment of melting and shiny drop; views (f,g) illustrate drop oxidation (resulting in its matte images) and the formation of thick RPR under the drop.

It is noteworthy, however, that in the case of highly reactive Al/CoO [36] and Al/NiO [46] systems, the presence of oxide film on Al drop does not play a crucial role and under similar testing conditions the wetting phenomenon ($\theta < 90°$) takes place even at $T \ll T^w$.

4. Conclusions

Oxygen in the furnace atmosphere plays an important role in interactions between molten Al and oxide ceramics. The presence of even a few nanometers thick but continuous and tenacious oxide film on the liquid Al droplet, formed either before introduction of the sample into a vacuum chamber or due to Al reacting with the residual oxygen in the furnace atmosphere during wettability tests, may significantly affect macro-scale properties of Al/oxide couples such as wetting and shear bond strength. The effect of aluminum oxide on wetting behavior and wetting-bonding relationship depends upon the reactivity of Al/oxide system.

Acknowledgements

The work has been supported by the Ministry of Science and Information Technology of Poland under Project PBZ/KBN/114/T08/2004. Additional support was provided by the U.S. National Academy of Sciences under the COBASE program supported by Contract No. INT 0002341 from the U.S. National Science Foundation. The authors thank Prof. B. Mikulowski for execution of shear tests.

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Received: 10 July 2006.