

The mystery of molten metal

*Natalia Sobczak¹, Jerzy Sobczak¹, Rajiv Asthana² and Robert Purgert³

(1. Foundry Research Institute, 30-418 Cracow, Poland; 2. Department of Engineering & Technology, University of Wisconsin-Stout, Menomonie, WI 54751, USA; 3. Energy Industries of Ohio, Cleveland, OH 44131, USA)

Abstract: Recent advances in scientific understanding of high-temperature materials processing using novel experimental methodologies have shed light on the complex role of surface and interface phenomena. New in-situ studies on molten metal/solid ceramic interactions using a unique experimental complex at the Foundry Research Institute, Krakow, have revealed a number of unusual observations in materials processing at high temperatures. We present some such unusual observations and their explanation with reference to liquid metal processing of Al, Ni, and Ti, and their alloys in contact with oxide ceramics. In particular, we focus on the following aspects: primary oxidation of Al from residual water vapor or oxygen, capillary purification to remove surface oxide, substrate protection by CVD carbon, roughening due to spinel whisker formation, inclusions in castings due to mechanical detachment, floatation due to buoyancy forces, and segregation due to directional solidification, modification of the solid surface morphology by metal vapor ahead of the liquid, and the complication due to multi-component alloys melted in crucibles made from complex oxide-based ceramics. In the case of Ti, rapid reactions with oxides result in undesirable volumetric changes that create difficulty in casting high-quality Ti parts, particularly by investment casting. Nanoscale (e.g., colloidal) coatings based on Y_2O_3 protect crucibles and hold ladles against such attack. Practical insights and recommendations for materials processing emerging from the fundamental studies on high-temperature interfacial phenomena have been described.

Key words: molten metal; high-temperature phenomena; in-situ observation; casting defects

CLC number: TG146

Document code: A

Article ID: 1672-6421(2010)04-425-13

1 Introduction

Many important techniques of materials processing require the contact between molten metals and refractory materials (i.e., casting processes, liquid metal handling, brazing ceramics, and fabrication of metal-ceramic composite materials). For such techniques, the resulting properties of final products are closely related to high-temperature properties of a liquid metal and, particularly, high-temperature surface and interfacial phenomena. Thus the interaction between a liquid metal and a solid material and the nature of interfaces formed play a key role in selecting suitable material or processing parameters.

*Natalia Sobczak

Female, born in 1956, Prof., DSc, PhD, Pl. Specialist in the field of high temperature liquid state materials science, composite synthesis and joining dissimilar materials by liquid-assisted processes, casting of advanced and specialty materials. Head of the Center for High Temperature Studies at the Foundry Research Institute (Cracow) and Scientific Adviser at the Motor Transport Institute (Warsaw). She received her MSc and PhD degrees from St Petersburg State Polytechnic University and DSci from the Polish Academy of Sciences. Visiting professor at University of Wisconsin-Milwaukee (1994-1996), Hokkaido University (2000), Osaka University (2000-2001), University of Wisconsin-Stout (2002), Institute for Energetics and Interphases IENI-CNR in Genova (2007, 2008, 2009). Head of Section 8.1. Cast Composites of World Foundry Organization (since 2001). Member of Polish Foundrymen Association, Polish Society of Composite Materials, Polish Society for Materials Science, ASM. Winner of numerous national and international awards including Gold Medal Award of Polish Foundrymen's Association, Third Prize at Int. Metall. Contest, IMS & ASM, First Prize Award of Polish Agency for Enterprise Development in the category "Polish Product of the Future", Award of Polish Academy of Sciences for young scientists, Awards from Polish Ministry of Industry for Innovative products, Silver Medal at Salon Int. des Inventions in Geneva, Gold and Bronze Medals of the Belgian Chamber for Innovation, Brussels Expo. Autor and co-author of 4 books, more than 200 papers and 14 patents.

E-mail: natalie@iod.krakow.pl

Received: 2010-07-13; Accepted: 2010-08-20

Since at high temperatures everything reacts with everything, such interactions can be accompanied by a number of complex chemical reactions at liquid metal/atmosphere and liquid metal/solid interfaces, leading to significant changes in interface structure and chemistry thus affecting the properties of final products. Therefore, it is highly desirable to develop experimental techniques and equipment that allow in-situ observation and analysis of high-temperature behavior of liquid and semi-liquid alloys. This could be accomplished in a unique experimental complex developed by the Center for High Temperature Studies at the Foundry Research Institute (Poland).

In this paper, methodological, scientific and practical aspects of high-temperature studies using the above experimental complex are discussed from viewpoints of production of advanced cast materials with special attention to high-temperature phenomena affecting quality of castings due to formation of different casting defects.

2 Experimental complex for high-temperature characterization of liquid materials

Among methods for examination of properties of liquid metals and alloys as well as accompanying high temperature phenomena, the sessile drop method is widely used because of its relative simplicity coupled with opportunity to extract fundamental information of practical importance. In the

classical sessile drop procedure, the metal/substrate couple is contact heated to the experimental temperature while the recorded images of liquid drops are used for measurements of surface tension (σ_{lv}), density of the liquid, characterization of its wetting and spreading properties by measurements of the contact angle (θ) and work of adhesion [$W_a = \sigma_{lv} (1 + \cos\theta)$] between the liquid and the solid substrate. Despite the small quantity of liquid metal used in the sessile drop method, the observations of wetting and spreading behavior are useful in various liquid-assisted manufacturing processes [1]. Moreover, visualization accompanying the sessile drop method may be utilized for observation of metal behavior during melting, heating or cooling as well as experimental estimation of metal expansion during heating or metal shrinkage during cooling. These thermophysical properties are particularly important for computer simulation and modeling of liquid-assisted processes.

Figure 1 illustrates two examples using the sessile drop test for observation of critical phenomena that are common in foundry practice and significantly affect the structure and properties of castings. Figure 1(a) shows a high-temperature interaction between a liquid alloy and a ceramic substrate accompanied by the formation of gaseous reaction products that

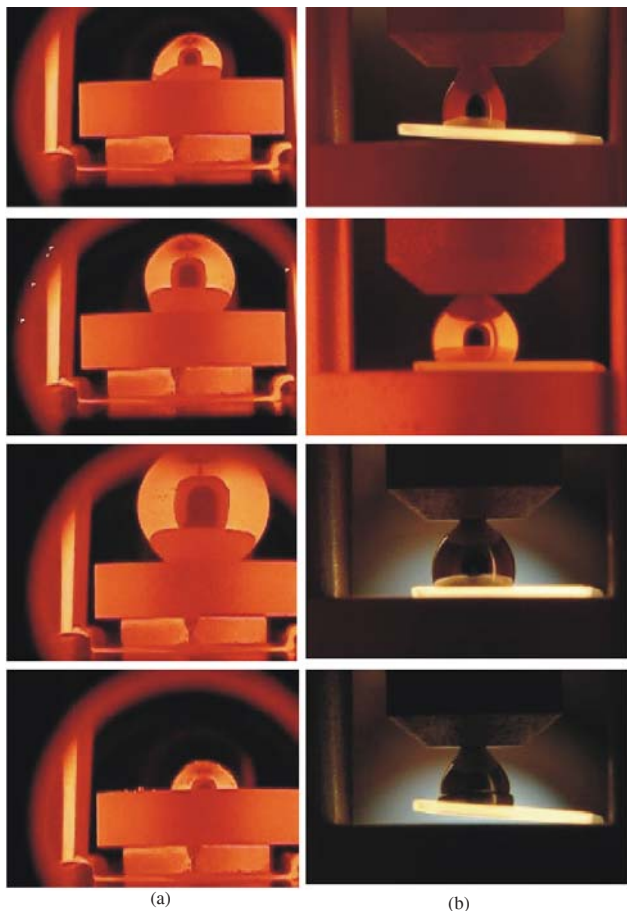


Fig. 1: Visualization of high-temperature phenomena in a sessile drop test: (a) interaction between a liquid alloy and ceramic substrate accompanying with the formation of gaseous and solid products responsible for structural defects in ready castings (porosity and non-metallic inclusions); (b) liquid Al shrinkage and expansion during subsequent cooling and heating resulting in the movement of the MgO plate contacting with the Al drop produced by squeezing the metal from a capillary situated above the MgO plate.

are evidenced by periodic increases of the drop volume and solid precipitates floating on the surface of the liquid drop. Obviously, this ceramic material is not suitable for melting or casting this particular alloy since the reactively formed porosity and non-metallic inclusions are unavoidable. Figure 1(b) presents the behavior of a liquid Al drop contacting a MgO single crystal plate during periodic cooling and heating. In this test, the Al drop was produced by squeezing the liquid metal melted in a ceramic capillary situated above the MgO plate at a constant distance. During interaction, strong adhesion between the Al drop and the MgO plate was established while during cooling and heating, metal shrinkage and expansion resulted in movement of the MgO plate vertically either upward or downward.

The significant methodological and practical issues in wettability measurements at elevated temperatures by the sessile drop method have been discussed in references [1–3] while some useful recommendations for its application have been summarized in references [4, 5]. In order to fulfill all requirements, an experimental complex (Fig. 2) with unique operating capabilities was developed [6]. Its design in Fig. 3(a, b) permits multiple complex functions to be performed including, among others, ‘pushing’, ‘smearing’ and ‘rubbing’ a spreading drop, thus making it possible to mimic the behavior of liquid or semi-solid alloys in real technological processes. For this propose, special manipulators were developed and utilized for an up and down movement of both a ceramic support and a ceramic capillary filled with molten metal; a rotation or side movement of the support; and a drop movement or removal by either pushing or sucking. As a result, besides classical sessile drop and large drop procedures, new testing procedures and methods can be realized simultaneously or independently as shown in Fig. 3(c,d). The tests of different materials (metals, alloys, ceramics, glass, fluxes, dross) can be done at a temperature of up to 2,100°C under vacuum of up to 10^{-7} hPa or in protective atmosphere (static or flowing gas with controlled rate at required level of pressure).

The experimental complex with its unique design, as shown in Fig. 3 (a, b), was built on the concept of LEGO blocks. It integrates several apparatuses having unique possibilities for complex materials characterization at high temperatures by different testing methods and various procedures for simultaneous estimation of different characteristics in one test under high vacuum or flowing inert gas. Its central part employs a chamber for the transfer of the samples between different apparatuses without opening and dehermetization, so that there is no contact with air.

Vacuum of 10^{-7} – 10^{-10} mbar is produced by turbomolecular and ionic pumps. The chamber for sample treatment and surface characterization (chemistry, impurities, and oxidation) is equipped with an Auger spectrometer and an ion gun (for surface cleaning or for neutralization of electrical charges at the surfaces of ceramic samples).

The main part of the complex is a high-temperature chamber (up to 2,100°C), working under high vacuum or flowing inert gas. It is equipped with a quadrupole residual gas analyzer (for characterization of gases formed during materials heating),

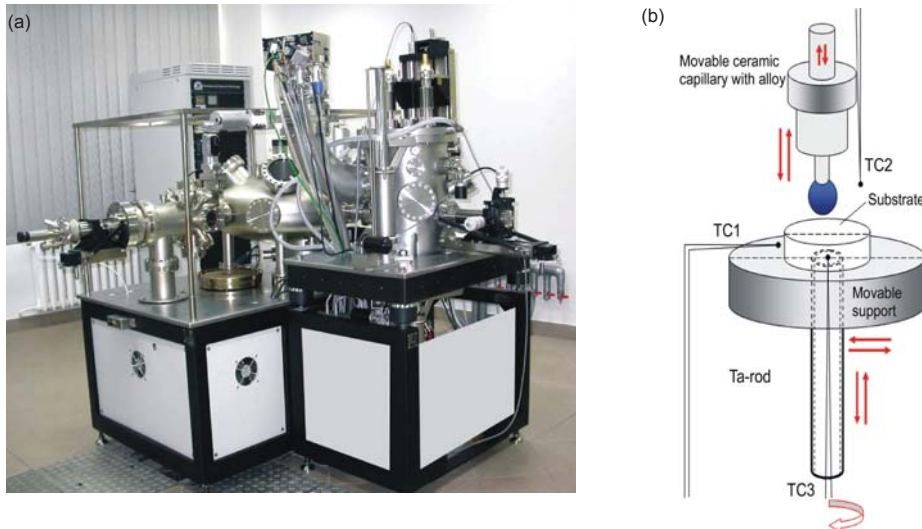


Fig. 2: Experimental complex for high temperature studies (a) and scheme of its movable elements allowing examination by different testing methods and procedures (b)

a manipulator for the movement of the experimental table in an XY plane or its rotation up to 270°, a manipulator for loading, removal and transfer of the samples between different chambers and apparatuses, a manipulator located above the drop in order to transfer from the top an additional substrate or capillary with liquid metal, which can also permit squeezing of a metal through a capillary in order to realize the in-situ drop cleaning from an initial oxide film by the capillary purification procedure or dispensed drop method. This chamber has four windows and it is operated with a high speed CD camera (up to

2,000 frames per second), and it is used for direct visualization of behavior of liquid metals and alloys at high temperatures

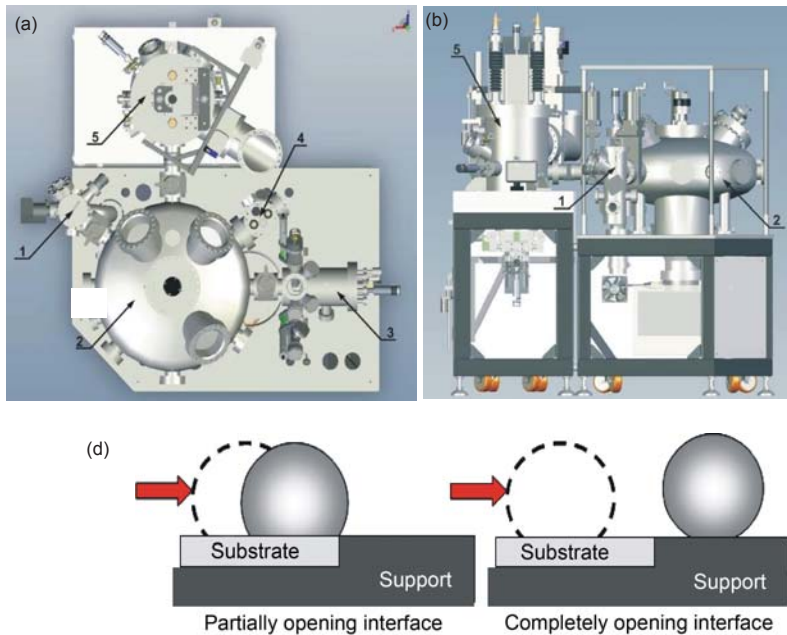


Fig. 3: Schemes of experimental complex design (a, b) and methods and procedures that can be applied in a new complex (c) [6], including recently developed procedure for interface “opening” by the drop replacement using a special design of ceramic support (d) [17].

- (1) Vacuum chamber for the first stage of sample preparation by preheating in vacuum up to 200°C in order to remove adsorbed gases;
- (2) Chamber for transferring the samples between the chambers using a manipulator that allows to bring the samples of different sizes and various shapes;
- (3) Analytical chamber containing Auger spectroscopy for surface characterization of examined materials before and after high temperature treatment, ion beam for etching/cleaning samples and removal of surface films from examined samples;
- (4) Portable chamber (vacuum “traveling-bag”) for storage and collection of specimens after testing under vacuum;
- (5) Experimental chamber for high-temperature studies of materials in solid, semi-solid or molten states, containing experimental table (metallic or ceramic support) with rotation and up-and-down movement, the heater and screens with up-and-down movement, additional windows for observation and recording, quadrupole residual gas analyzer for real time recording of chemical composition of atmosphere in a vacuum chamber, capillary with up-and-down movement (for capillary purification procedure or for removal of a drop after testing directly at high temperature in a vacuum chamber, for example in order to “open” the interface or the reaction products formed at the interface), manipulator, located under a drop/substrate couple, which allows to delivery another substrate (for sandwiched drop procedure) or alloying additions (for in-situ alloying in vacuum chamber), automatic real-time temperature control by 4 thermocouples located in selected positions.

that is particularly helpful for understanding of different mysterious high-temperature phenomena accompanying different liquid-assisted processes.

3 Several examples of high temperature tests

In order to demonstrate the wide testing possibilities of a new experimental complex and applicability of such studies in foundry practices, several examples of high temperature tests with molten Al, Ni and Ti alloys are discussed below.

3.1 Al alloys

Pure aluminum and its alloys are known to be sensitive to oxidation and the presence of even negligibly small amounts of oxygen are sufficient to instantaneously ($\sim 10^{-23}$ s) form a monolayer of aluminum oxide at room temperature. The presence of this primary oxide film on aluminum is the main reason for a large scatter in experimental data on wetting properties in all Al/ceramic systems [7-11]. Consequently, primary oxidation generates many problems for practitioners and engineers since it leads to contradictory recommendations, depending on the data selected as the correct one. It might be illustrated with an example of Al/alumina system shown in Fig. 4. At 700°C, the highest contact angle is $\theta = 162^\circ$ that corresponds to the lowest value of work of adhesion $W_a = 41.6 \text{ kJ}\cdot\text{m}^{-2}$, showing non-wetting and very weak bonding in the system. Thus one may recommend alumina as a suitable material for crucibles, molds and protective coatings. However, if for the same temperature the lowest value of $\theta = 88^\circ$ is taken to be the true contact angle and corresponding highest value of $W_a = 880 \text{ kJ}\cdot\text{m}^{-2}$ were selected, then one may conclude that it is possible to produce well-bonded Al/alumina joints at 700°C and hence this system is a good candidate for low-temperature cast composite synthesis even though alumina is not suitable for foundry appliances.

It is not only oxygen in the furnace atmosphere that plays an important role in interactions between molten Al and refractory ceramics, but also water vapor in the chamber, which is almost unavoidable. In the presence of water vapor,

oxidation of aluminum takes place even under ultra high vacuum at temperatures below $\sim 1,000^\circ\text{C}$ [11]. Figure 5 shows a change in the amounts of residual gases in the vacuum chamber equipped with a gas spectrometer which is operated during the test. When an oxide-free AlSi12 alloy drop was produced at 900°C by squeezing the alloy through graphite capillary, a sudden decrease in amount of water vapor was recorded together with remarkable increase in amount of hydrogen that represents experimental evidence of the liquid/gas reaction: $2\text{Al} + 3\text{H}_2\text{O}(\text{g}) \rightarrow \text{Al}_2\text{O}_3 + 3\text{H}_2(\text{g})$. Subsequently, this reaction results in secondary oxidation of the initially oxide-free aluminum drop (and was confirmed during real-time observation of the drop surface since the drop surface became matte with time) and it is also responsible for the formation of bubbles inside the drop. In foundry practice, the same reaction between molten metals and residual water vapor in the furnace's atmosphere or from foundry appliances presents one of the most common factors responsible for structural defects in castings such as oxide inclusions and gas porosity.

Furthermore, the studies [7-11] showed that even a continuous and tenacious oxide film few nanometers thick covering the liquid aluminum significantly affects macro-scale properties of Al/ceramic couples such as wetting and shear bond strength;

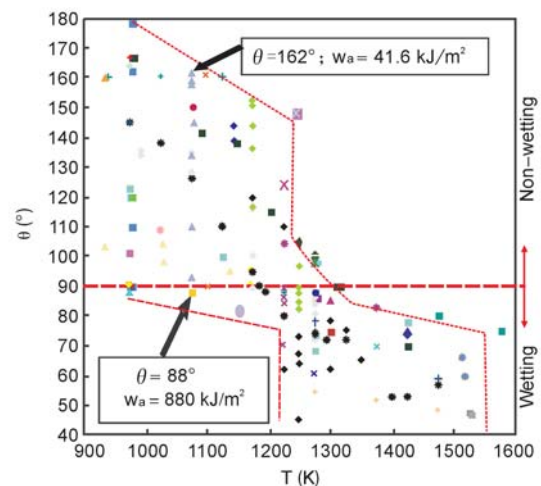


Fig. 4: Literature data on temperature dependence of contact angle values in Al/Al₂O₃ system

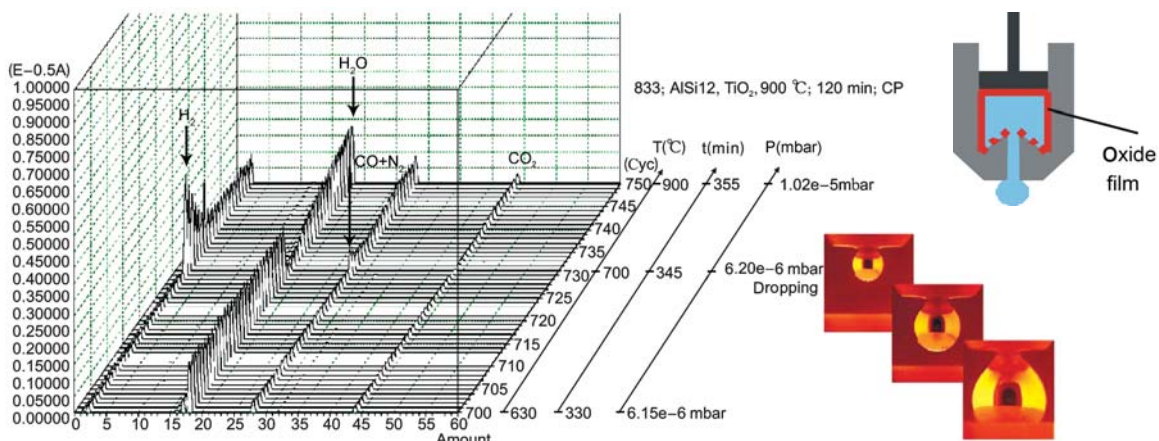


Fig. 5: Change in the amount of residual gases in a vacuum chamber during wettability test of AlSi12/TiO₂ system at 900°C for 120 min by capillary purification procedure; inserts show a design of a graphite capillary and steps of squeezing metal [11]

these properties are particularly important in the practice of metal matrix composite synthesis and joining ceramics. It was demonstrated that compared to the classical contact heating procedure (CH), the removal of the primary oxide film from the aluminum drop in CP procedure results in improvement of both wetting (Fig. 6a) and bonding (Fig. 6b) in Al/Al₂O₃ couples. This effect is used in the practice of cast composite synthesis by the application of different methods to effectively remove primary oxide films from the metal/ceramic interface mechanically (by intensive stirring of metal-ceramic slurry), physically (through application of ultrasounds) or chemically (by the addition of Mg into molten matrix in order to consume the primary oxide by the formation of MgAl₂O₄).

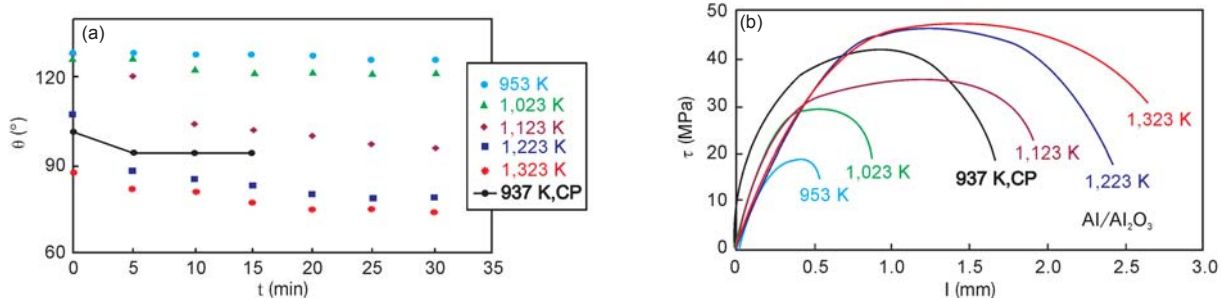


Fig. 6: Effect of testing procedure (CH, CP) and temperature on wettability kinetics (a) and shear behavior (b) of sessile drop Al/Al₂O₃ couple recorded as a change of shear stress $\tau = (F/S)$ with displacement l [7]

formation of a thick reaction product region (RPR) in Al/SiO₂ even at low temperatures, and freshly formed Al₂O₃ should be wettable by liquid Al, there is some uncertainty regarding low-temperature wetting in Al/SiO₂. Laurent et al. [12] suggested that this uncertainty is related to the presence of oxide film on Al, which hinders spreading, while Zhou and Hosson [13] propose that formation of surface cavities ahead of the triple line (TL) hampers the spreading. These cavities may form due to a 38 % volume mismatch between the reactants and the products in the redox reaction mentioned above.

Recent research [11] demonstrated a strong dependence of the wettability kinetics in the Al/SiO₂ testing procedure (CH, CP), as shown in Fig. 7(a) for different temperatures together with the effect of Si alloying of an Al droplet. Similar to the data of the literature [12, 13] for 973K, the couple exhibited a lack of low-temperature wetting for CH ($\theta = 114^\circ > 90^\circ$). However, for the same temperature, it becomes wettable ($\theta < 90^\circ$) for CP, indicating $\theta = 59^\circ$ similar to that recorded with CH at 1,273K (θ

$= 53^\circ$) when the primary oxide film is in-situ removed under vacuum by the formation of gaseous aluminum suboxide Al₂O from the reaction: $4Al + Al_2O_3 = 3Al_2O$ (g).

In additional tests by CP at 1,273K, the oxide-free drop, deposited at 973K and then quickly heated to 1,273K (~ 40 K \cdot min⁻¹), exhibits the highest decrease in contact angle (up to $\sim 40^\circ$) during an 80 min contact (Figs. 7a, 10a).

Alloying Al with Si inhibited the Al/SiO₂ reaction, and led to higher contact angle values (Fig. 7b). The structural examination of cross-sectioned Al/SiO₂ couples did not show any remarkable cavities at the TL, although numerous cracks were noted in the SiO₂ substrates. A few cracks were also in the heterogeneous reaction product region (RPR), composed of fine alumina particles surrounded with Si and Al(Si) phases; such cracks propagated even over the TL. These observations were found as experimental evidence for a key role of primary oxide film on Al drops on contact angle measurements [11]. They prove also the fact that the wettability of the Al/SiO₂

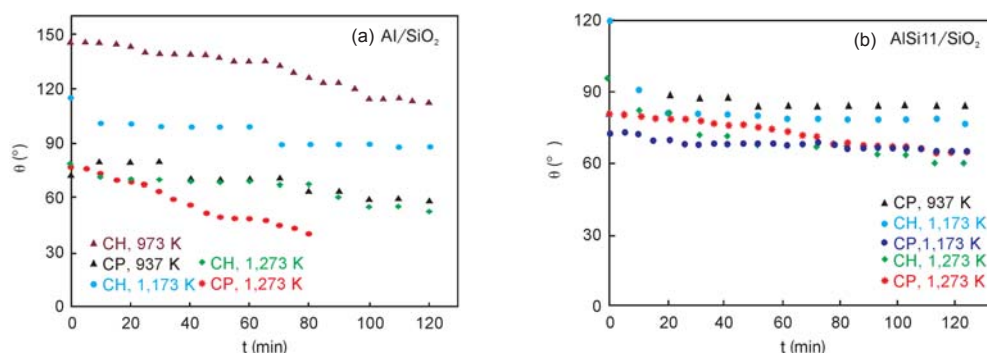


Fig. 7: Effect of testing conditions on wettability kinetics in Al/SiO₂ (a) and AlSi11/SiO₂ (b) [11]

system is controlled by the wettability of RPR (i.e., mainly aluminum oxide) and not by the wettability of SiO_2 while this process is strongly affected by kinetic factors, particularly in an oxidizing environment. This statement is in agreement with foundry practices and confirms that SiO_2 -containing refractories are suitable for short-times or low-temperature contact with molten low-silicon Al alloys in air (e.g. molds). At high temperatures, the lifetime of such materials significantly decreases and thus they should not be used as crucibles.

On the other hand, redox reaction taking place in the Al/ SiO_2 system has been successfully utilized for the in-situ synthesis of interpenetrating composites (IP) of an Al- Al_2O_3 type by

reactive metal penetration of dense SiO_2 -rich ceramics with liquid Al at high temperatures [11]. However, if the starting ceramic has high porosity, liquid Al does not flow inside the porosity channels even at high temperatures when Al exhibits very good wetting. The porosity in the starting ceramic remains unfilled with molten metal because the reaction takes place through the ceramic only (Fig. 8). Consequently, the obtained IP composite is also porous and thus pressure-assisted processes are needed in order to produce a dense IP structure. Similar behavior was observed with many SiO_2 -rich ceramics such as mullite, kaolin, and fly ash.

Another example is the effect of a carbon layer on ceramics

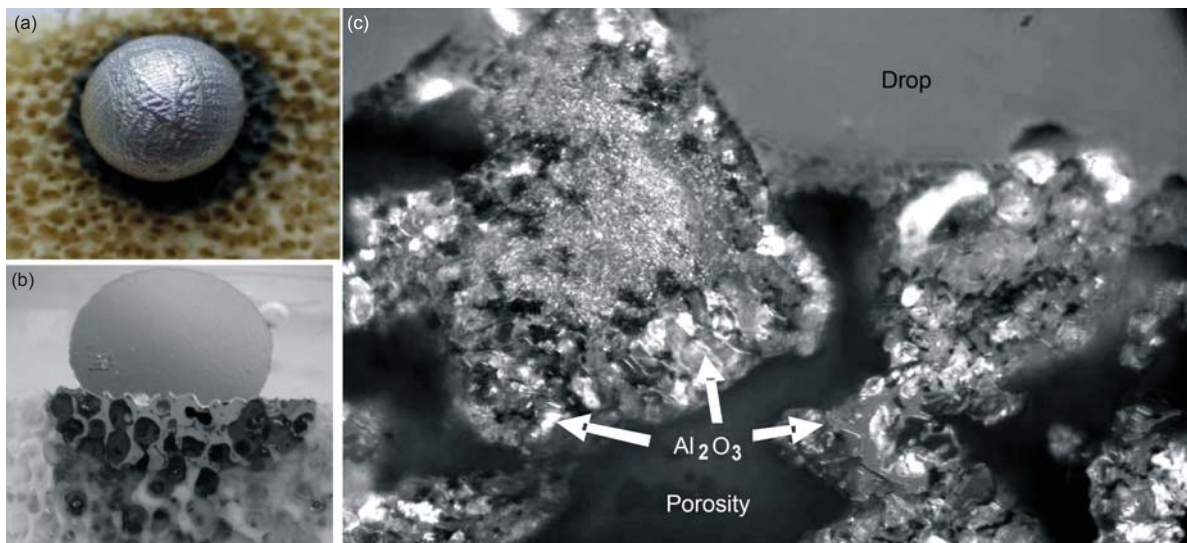


Fig. 8: Pure Al drop after interaction with porous SiO_2 preform (1,000°C, 120 min, vacuum): (a) top-view; (b, c) cross-sections (OM)

when being wetted by Al alloys. As demonstrated in [14], even a very thin carbon film deposited by a CVD method or mechanically using soot or graphite as a paint (e.g. from a pencil) results in better wetting and improved bonding in Al/alumina systems ($\theta^{\text{Al}/\text{Al}_2\text{O}_3} = 96^\circ$ contrary to $\theta^{\text{Al}/\text{C}/\text{Al}_2\text{O}_3} = 79^\circ$). Particularly, it is well-distinguished with Al alloys containing carbon-forming additions, e.g. alloying with 6wt.% Ti results in perfect wetting of carbon-coated alumina ($\theta = 17^\circ$) and more than twice increases in shear strength of AlTi6/C/ Al_2O_3 couple ($\tau = 42.8$ MPa), contrary to non-wetting of an uncoated alumina substrate (for AlTi6/ Al_2O_3 : $\theta = 103^\circ$, $\tau = 17.8$ MPa) [14]. These observations are in sound agreement with the positive effect of alloying Al with Ti on wetting reported for both crystalline (graphite) and amorphous (vitreous carbon) carbon materials [1,10]. The above beneficial effect of a thin carbon coating may be successfully utilized in both composite synthesis or ceramic joining. But on the other hand, it may cause some problems in melting and casting of aluminum alloys containing Ti or other carbon-forming additions when the surface of molds, crucibles or holders are stained with carbon. However, absolutely different behaviors of highly reactive and well wetting AlTi alloys in contact with a carbon material was observed in the test, when under identical testing conditions, the graphite substrate was replaced by carbon nanotubes (CNT) in the form of a paper. As recorded by high-

speed CCD camera (Fig. 10b), after squeezing AlTi6 alloy through alumina capillary at 1,273K (there is no reactivity in AlTi6/ Al_2O_3 system at 1,273K [7,14]), the AlTi6 drop, falling from ~5 mm height, touches the CNT paper and immediately jumps up without wetting and spreading. The drop jumping repeats 4 times and finally the drop settles without any spreading forming a high contact angle of ~140°.

More work is needed in order to understand this ‘mysterious’ behavior of Al-Ti alloy on nanostructured carbon material. However, whatever the reason for the ‘jumping ball’ effect, it suggests that a nanoscience approach might be useful for development of a new generation of refractory materials resistant to aggressive attacks of reactive liquid alloys. This idea has been successfully demonstrated by examples of interactions of Ni-based superalloy IN740 with ZrO_2 -based ceramics using additions of nanoparticles $\text{Y}_2\text{O}_3^{\text{np}}$ or $\text{Zr}_2\text{O}_3^{\text{np}}$ [15] showing that at 1,773K a much worse wetting (the contact angles are 150° and 129°, respectively) along with a lack of bonding between the alloy and such ceramic substrates contrary to ZrO_2 -based ceramic produced by conventional high temperature synthesis using 3% of micro-sized Y_2O_3 powder and characterized by $\theta = 95^\circ$ coupled with certain degrees of reactivity (e.g. the formation of oxygen-rich precipitates at the drop surface as well as at the substrate-side interface was recorded).

Many unusual and apparently difficult to explain phenomena

in foundry practices are caused from roughness of real surfaces, particularly when there is a certain degree of reactivity between the liquid metal and the contacting of solid material. It is illustrated by an example of wetting behavior of AlSi22 alloy on a rough graphite substrate at 1,000°C using the experimental complex described above as shown in Fig. 9. After deposition of an oxide-free drop using a CP procedure and ~30 s contact, the drop does not wet the substrate ($\theta \gg 90^\circ$) and it is easily removed by sucking it into an alumina capillary due to the weak adhesion between the drop and the substrate while the remaining “daughter” droplet exhibits good wetting since it forms the contact angle of $\sim 60^\circ$ (Fig. 9a). Then the

substrate was rotated and the second drop was deposited in a new place, kept 5 min and sucked-up again (Fig. 9b). In this case, a good contact and adhesion were established, accompanied by the formation of SiC due to reaction between Si from the alloy and graphite. Consequently, both drop sucking and detachment were more difficult and a large amount of the alloy remained on the substrate but this second drop did not wet the substrate ($\sim 150^\circ$) despite strong adhesion. In the next step (Fig. 9c), the substrate was rotated once more and the third drop was deposited without detachment from the capillary and sucked after ~30 s. The daughter droplet again formed a small contact angle of $\sim 60^\circ$. The next or fourth drop

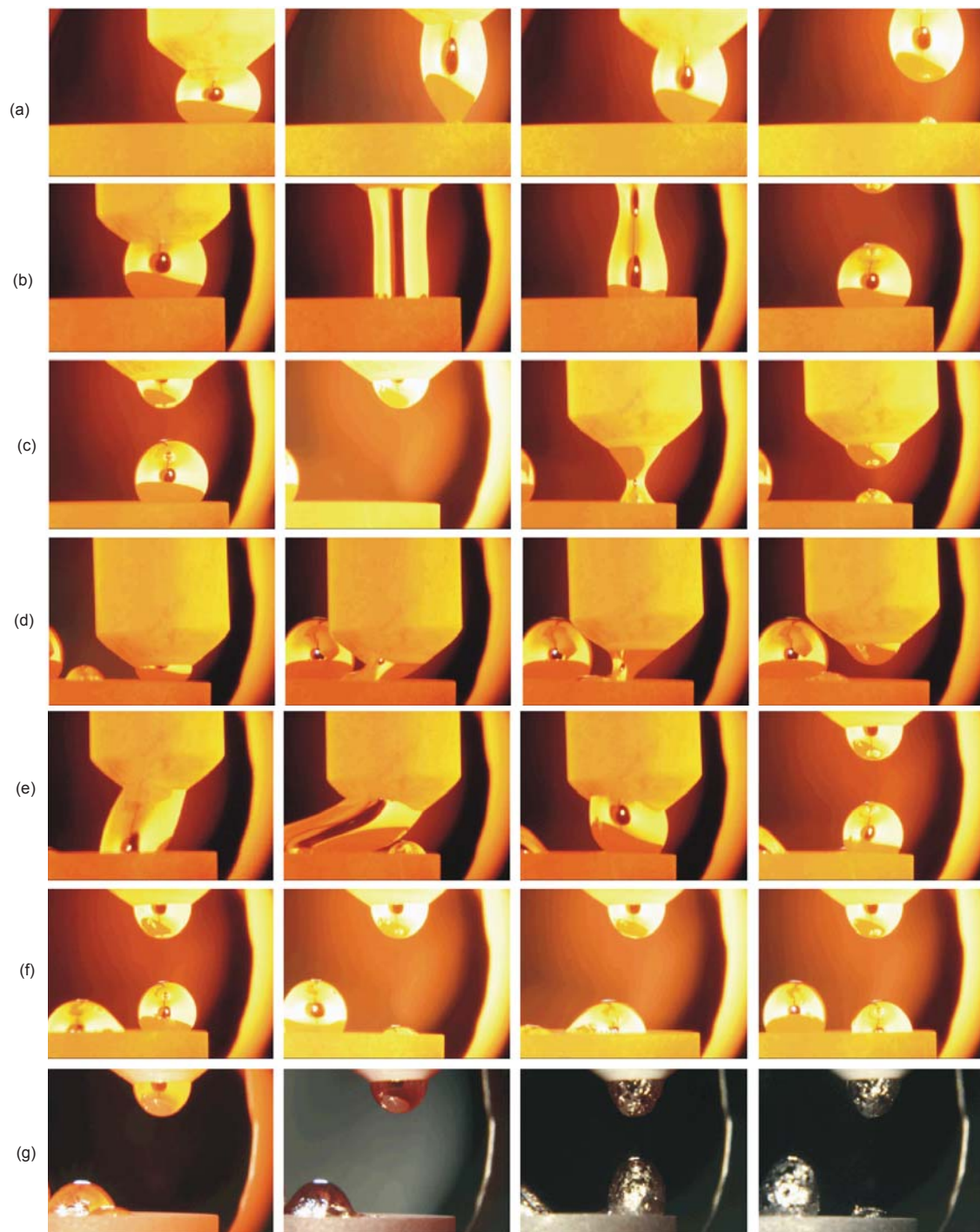


Fig. 9: Visualization of the behavior of AlSi22 drops deposited on rough graphite substrate by squeezing the metal through alumina capillary at 1,273K (a-f) and subsequent cooling (g)

(Fig. 9d) was deposited by low positioning of the capillary and by simultaneously rotating the substrate causing metal smearing along the substrate and resulting in the formation of the lowest contact angle of $\sim 30^\circ$. Then a fifth large drop (Fig. 9e) was deposited by the high positioning of the capillary coupled with substrate rotation in such a way that the freshly produced and smeared drop with an artificially low contact angle touched the second drop. It caused immediate metal breaking into two drops but the situation became reversible, i.e. former fifth drop became non-wetting while former second non-wetting drop became wetting. After a few minutes (Fig. 9f) the drops images were observed by substrate rotation and no significant change in contact angles were recorded.

The question is: “Why does the same alloy on the same substrate and at the same temperature form such different contact angles vary from 150° to 30° and what is the true contact angle?” In this test, all recorded contact angles present apparent values corresponding to receding and advancing

contact angles formed on a rough surface of the graphite substrate used (R_a : $\sim 150 - 400 \mu\text{m}$, depending on location). These observations clearly showed the role of physical heterogeneity of real surfaces on wetting and spreading behavior of liquid metals that resulted in different adhesion and bonding and caused disagreement between practice and experimental literature data that are almost always obtained on perfectly smooth, flat and non-deformable substrates.

There are also at least two other questions that resulted during the last step of the above tests (Fig. 9g) to be answered which is the reason that more fundamental research is needed: (1) “Why during solidification of all AlSi22 drops did they exhibit a noticeable extension in a vertical direction corresponding to the direction of drops’ tension, independently of the values of the contact angles?” (2) “How may we utilize these observations in foundry practice?”

Moreover, the most confusing observations are noted in Al/

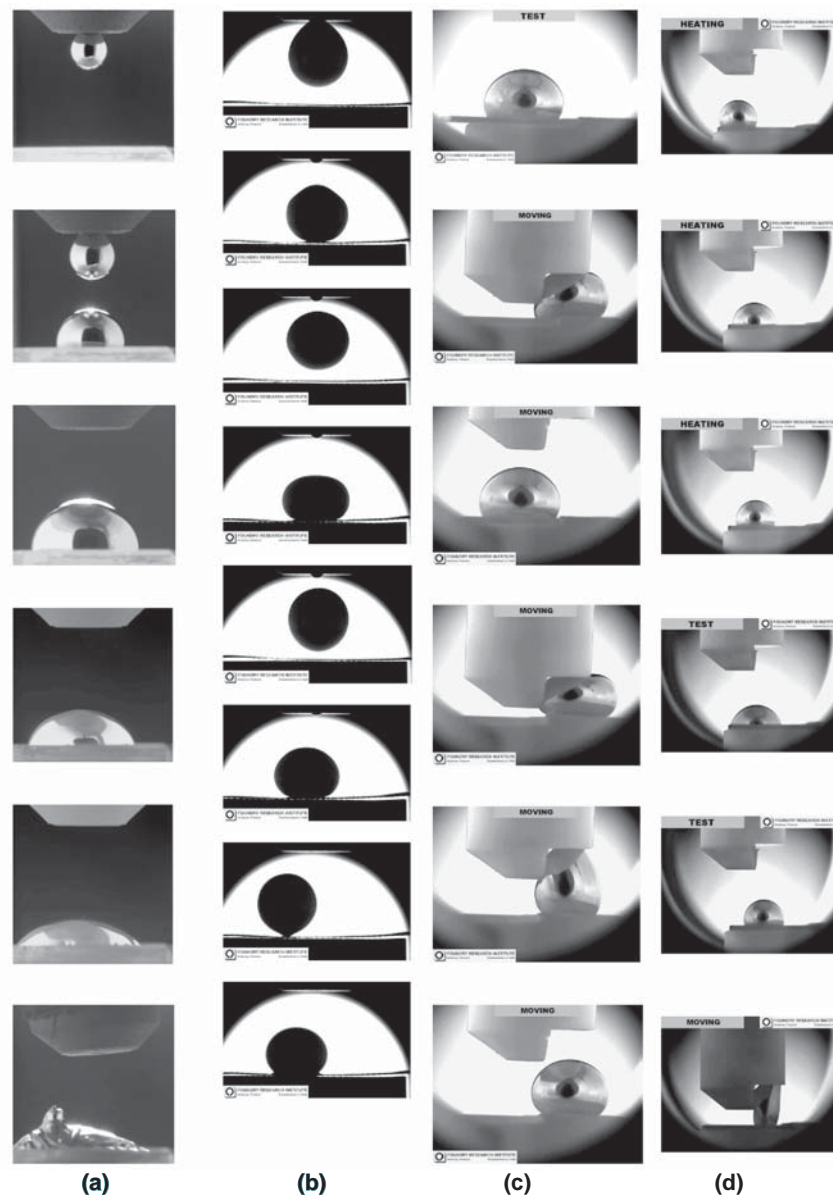


Fig. 10: Visualization of the behavior of different metals on ceramic substrates during wettability test using CP procedure: (a) Al/SiO₂, squeezing at 973K and fast headed to 1,273K, total contact time 80 min; (b) AlTi6/CNT-paper, 1,273K, 5 min, (c) NiW10 and (d) NiCr10 alloys on MgO(100) single crystal at 1,773K, 10 min

ceramic systems of high reactivity on rough ceramics when the effect of physical surface heterogeneity is coupled with the effect of primary oxide films. Such an example is shown in Fig. 11(a-e) that illustrates wetting behavior of liquid Al placed between two vertical yttria plates of different roughness at 1,000°C under high vacuum [16]. On a polished (R_a : ~ 120 μm) surface, the contact angles are 72° and 70°, measured for both a liquid and solidified drop, respectively. On a rough surface (R_a : ~ 400 μm), they are 97° and 77°, correspondingly, and present advancing contact angles caused mainly from physical heterogeneity of the substrate surface. But what is interesting is that despite identical testing conditions the shape of the reaction product region (RPR) formed inside the substrate is different. For rough surface, it has a classical leaf-like shape typical for reactive systems. On the contrary, for polished substrate the RPR is unusually more than twice thinner in the

central part of the drop, compared to its periphery (Fig. 11). As explained in [16], this unusual shape of RPR is related with the effect of the competition between the kinetics of the chemical reaction and the kinetics of deoxidation of liquid Al taking place at high temperatures under a vacuum due to the formation of gaseous aluminum suboxide Al_2O . Consequently, the kinetics of the removal of Al_2O from the drop/substrate interface presents a key factor and it depends on the type of the Al/substrate contact. In the case of polished substrate, this contact is continuous (“hermetic”) and the primary oxide film on Al specimen remains undestroyed thus preventing the formation of a true drop/substrate contact for longer time. In the case of rough substrate, the Al/substrate contact is discontinuous, allowing much easier and faster removal of gaseous product Al_2O from the interface in the contact area.

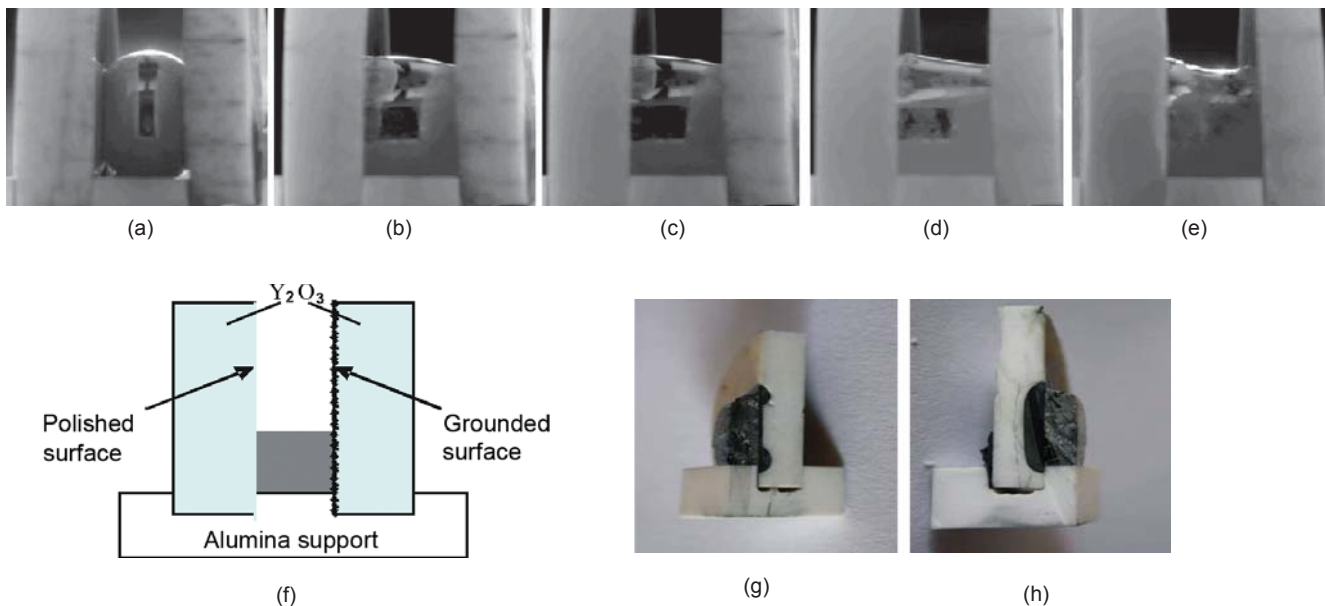


Fig. 11: (a-e) Visualization of the behavior of pure Al placed between two dense yttria plates, during melting (a), heating to (b) and at (c,d) 1,000°C followed by cooling (e); (f) scheme of the examined assembly; (g,h) Cross-sections of assembly showing the formation of regular shape of RPR with polished yttria plate (g), contrary to unusual RPR shape with rough (grounded) yttria plate (h)

3.2 Ni alloys

Liquid pure Ni shows non-wetting and a non-reactive (no new reactively produced phases) character in contact with all oxides used for the manufacture of ceramic products for melting and casting of Ni-alloys. Nevertheless, the high melting temperature of Ni influences its interaction with oxides due to an increased role of ceramic dissolution in liquid Ni. Since the surface tension of liquid Ni strongly depends on the amount of dissolved oxygen [17], one may expect some changes in wetting and spreading behavior of liquid Ni during any long-time contact with a ceramic substrate. Moreover, despite non-wetting and its non-reactive character, pure Ni and some of its alloys show good adhesion to many bulk oxides. In a recent study [18] on a Ni/ Al_2O_3 (sapphire) system the Ni drop was sucked via an overhead alumina capillary (using the procedure shown in Fig. 3c) after 10 min contact at 1,773 K in order to

separate the Ni drop from the sapphire substrate. However, contrary to expectations for most non-reactive and non-wetting systems, during drop sucking, a well-adhered sapphire substrate was picked up along with the drop thus preventing a drop-substrate separation, as shown in Fig. 12. Likewise, it was impossible to reposition the drop to another location using the drop pushing procedure of Fig. 3(c), because the whole drop/sapphire couple, and not just the Ni drop, moved on the alumina support [18]. Strong adhesion and problems with drop de-bonding by either drop pushing or drop sucking procedures were also noted for non-reactive and non-wetting Ni and NiW10 drops with MgO [18], ZrO_2 and Y_2O_3 substrates.

Therefore, for such systems, a special support fixture was designed to separate the oxide substrate from the drop for either partial or complete in-situ opening of the interface at the test temperature as shown in Fig. 3(d). Using this improved

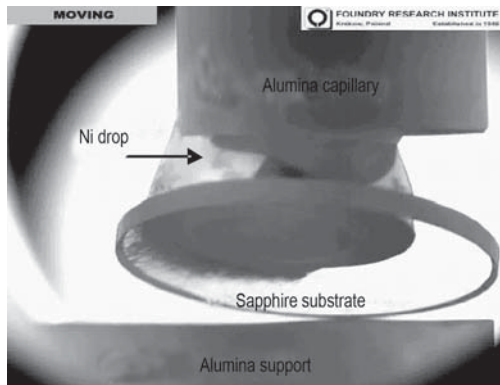


Fig. 12: Visualization of a good adhesion of Ni drop to sapphire substrate (transparent) at 1,773 K resulting in up movement of the substrate during drop sucking into the alumina capillary

drop pushing procedure several interesting observations were made with Ni and NiW10 drops on single crystal MgO(100) substrates described in detail in [18]. Figure 10(c) presents the visualization of the behavior of the NiW10 alloy on a perfectly smooth MgO(100) single crystal substrate (8 \AA roughness) at 1,773K, forming a contact angle of 118° . After a 15 min hold in the 1st position, the NiW10 drop was pushed and partially deposited onto polycrystalline alumina support ($\text{Al}_2\text{O}_3^{\text{PC}}$) in such a way that only $\sim 2/3$ of the drop's bottom surface was "seated" on the support. However, it was observed that the drop returned almost to the same position on the MgO(100) substrate immediately after upward movement of the alumina pusher, despite the fact that only $\sim 1/3$ of the drop base was on the MgO(100). In the second attempt, the drop was pushed again, positioned wholly on the support and kept for 15 min. Since the alumina support surface had a much higher roughness, the difference between the left and the right angles on $\text{Al}_2\text{O}_3^{\text{PC}}$ was noticeable ($\sim 15^\circ$) while average contact angle value was 27° higher compared to reference sapphire substrate ($\theta^{\text{sapphire}} = 112^\circ$, $\theta^{\text{Al}_2\text{O}_3} = 139^\circ$ [18]).

These observations were found to be consistent with the calculations of work of adhesion (Wa) as for NiW10/MgO, Wa is more than twice that for NiW10/ $\text{Al}_2\text{O}_3^{\text{PC}}$. They suggest also the reason for quite common MgO-rich inclusions in Ni-based castings since during processing, small MgO particles could be detached from the surface of foundry appliances made from polycrystalline MgO-rich ceramics which come into contact with the liquid alloy. For such systems, the role of dissolutive character of interaction contributing to establishment of a good bonding between the melt and the ceramic should be taken into consideration in the development of melting and casting processes because it facilitates mechanical detachment of oxide particles from the surface of crucibles, filters and molds, especially if it is accompanied with any movement of the melt during processing (e.g. mixing, flowing, pouring).

Another reason of such inclusions is related with an oxide substrate ridging around small gas bubbles easily formed at the melt/crucible interface. These 'hills' also might be mechanically destroyed and introduced into the melt during conventional pouring. In foundry practice, the non-wetting

behavior in the Ni/MgO system ($\theta = \sim 112^\circ$) coupled with the significant density difference of MgO and Ni cause the enhanced floatation of the MgO particles and their collection to the top of the melt. Therefore, it is reasonable to use a bottom metal pouring instead of pouring by crucible tilting. Furthermore, during solidification the introduced MgO inclusions could be pushed by the non-wetting solidifying alloy and hence directional solidification is the preferred casting process for Ni-base alloys in order to remove these inclusions.

The study [18] also provided evidence for the pristine ceramic surface modification by metal vapor from Ni-base alloys ahead of an advancing triple line (TL). Such surface modifications take place even when metal vapor neither reacts with nor condenses at TL but nevertheless causes significant changes in surface morphology resulting in the formation of numerous cavities that might affect the surface quality of the final cast products. If volatile additions in the alloy react with the oxide ceramic the formation of new oxide crystals at the oxide substrate ahead of an advancing triple line takes place by a mechanism similar to the CVD process. Such an example is shown in Fig. 13(a) for Ni-Al/MgO couple at 1,773 K where Al vapor was responsible for growth of MgAl_2O_4 spinel whiskers around the drop. These results are important in view of possible crucible degradation above the level of molten metal affecting the lifetime of foundry appliances and the formation of non-metallic inclusions, particularly in metal pouring by tilting a crucible.

Interestingly, the formation of the same spinel whiskers was also observed in case of wettability test with Ni-Al alloy on an alumina substrate if the alloy was pre-melted in a crucible made from MgO-based ceramic. In this case, Mg was first introduced into alloy due to redox reaction of MgO with Al. Next in the wettability test, it evaporated and reacted with the alumina substrate to form spinel whiskers around the drop. The growth of whisker-like crystals is possible also directly at the drop surface due to interaction between the drop and the gaseous compounds evacuated from the substrate. An example is shown in Fig. 13(b) for interaction between Al alloys with a rough graphite substrate without prior heat treatment since pre-heating at 1,273K causes the decomposition of residual organic compounds from the substrate.

Another example of an unusual behavior, shown in Fig. 10(d), was recorded during high-temperature wettability tests at the Foundry Research Institute with NiCr10 alloy on MgO(100) single crystal at 1,773K under flowing high-purity Ar. During an isothermal hold at the test temperature, the drop slowly spreads and wets the substrate to form a contact angle of $\sim 70^\circ$. Next, sudden de-wetting takes place and the drop returns to almost its initial shape of a high contact angle of $\sim 140^\circ$. This wetting-de-wetting process repeats periodically 5 times during 15 min contact. In the final step, the drop was pushed into another position by the alumina pusher. However, during picking up of the pusher, unexpectedly, the drop was easily detached from the substrate and moved together with the rising pusher. Based on these observations, one may conclude

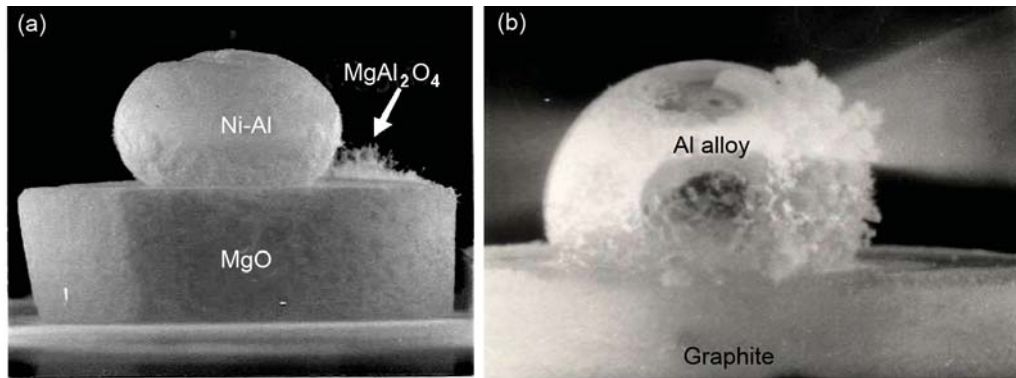


Fig. 13: (a) Ni-Al/MgO couple after wettability test at 1,773K showing the formation of whisker-like $MgAl_2O_4$ crystals at the substrate around the drop. Note similar effect was recorded on alumina substrate with Ni-Al alloy prior melted in MgO crucible; (b) Al alloy on raw graphite material without prior heat treatment with Ni-Al alloy showing the formation of whisker-like crystals at the drop surface due to interaction between the alloy with gaseous products formed due to decomposition of residual organic compounds in the substrate.

that adhesion of NiCr10 alloy with MgO is weaker than that with alumina. But the reason for this is not clear, particularly when taking into account the wetting character in NiCr10/MgO contrary to the non-wetting character in NiCr10/ Al_2O_3 . Presumably, interaction with NiCr10 alloy is strongly affected by the evaporation from the alloy as evidenced by a green color (typical for chromium oxide) on the area under as well as near the drop. Possibly it was formed by the consumption of oxygen from MgO by Cr evaporated and deposited on the substrate surface in the vicinity of the drop. Research is under progress to explain this unusual behavior.

In foundry practice of high-temperature melting of multi-component Ni-base alloys in crucibles made from complex oxide-based ceramics, the situation would become even more complicated because of the confluence of vapors of different compositions and history, and formation of whisker-like crystals of new oxides, usually deposited at cooler parts of the furnace. These observations demonstrate the importance of information on melting history of not only the Ni alloy and the crucible but even the furnace used for its melting in order to understand the reasons for expected structural defects in castings of Ni-base alloys.

3.3 Ti alloys

Pure liquid Ti easily reacts with many oxide-based ceramics by forming different interfacial Ti-rich oxides, depending on the processing conditions. Contrary to most industrially important systems, high reactivity of Ti with these oxides is not accompanied by good wetting ($\theta = 130\text{--}60^\circ$ ^[19]) thus making possible a selection of suitable mold materials for casting Ti. However, one of the main problems in foundry practice of Ti is related with volumetric increase of oxide ceramic during interaction with liquid Ti and caused due to the formation of reaction products inside the ceramic, as reported in [6]. Particularly for investment castings, such dimensional changes generate difficulties in manufacturing final Ti products of high quality. An application of a nano approach in manufacturing of oxide-based ceramics with additions of Y_2O_3 nano-particles was found to reveal beneficial effects, compared

to conventional mold materials^[20].

Among different alloying additions to Ti, Al exhibits the strongest effect on reactivity and wetting behavior of oxides, resulting in nonwetting-to-wetting transition from Ti/oxide to Ti-Al/oxide. Alloying Ti with 50% Al results in perfect and immediate wetting of alumina mold at 1,773K ($\theta\sim 38^\circ$). At the same temperature, it forms $\theta\sim 30^\circ$ on ZrO_2 mold after 2 min and $\theta\sim 50^\circ$ on MgO-containing ZrO_2 after 5 min^[21]. The highest contact angles were reported on Y_2O_3 -containing ZrO_2 ($\theta\sim 75^\circ$ after 25 min) and on pure Y_2O_3 mold ($\theta\sim 85^\circ$ after 23 min)^[21]. These data are consistent with practical recommendations on use of Y_2O_3 -based colloidal (nano approach) protective coating on crucibles or containers in high temperature measurements of thermophysical properties of liquid reactive alloys^[20].

Further alloying of Al-rich titanium alloy with such reactive additions as Nb or Ta (e.g. in alloys suitable for casting of large turbine blades for aero-engines and stationary gas turbines) increases its melting temperature and as consequence, its reactivity^[22]. It creates many difficulties in processing the liquid phase in a crucible. As an example in Fig. 14, the $Ti_{46}Al_{46}Nb_8$ alloy starts to wet the Al_2O_3 substrate even before complete melting of the alloy (drop formation stage) has occurred, and immediately after melting, it forms $\theta\sim 57^\circ$ and $\theta\sim 42^\circ$, at $\sim 1,920K$ and $\sim 2,020K$, respectively. Covering alumina substrate with Y_2O_3 -based colloidal protective coating increases the contact angle of the alloy, showing after 5 min of contact, $\theta\sim 120^\circ$ at 2,008 K. Interestingly, for the same contact time, an increase in the temperature of only $\sim 20K$ results in θ dropping to 77° (2,030K).

These results suggest the possibility to prepare accurate tests for determination of thermophysical properties of liquid TiAlX-based alloys (X: Nb or Ta) by utilizing kinetic factors, i.e. under certain conditions and time, even extremely reactive alloys are 'kinetically' stable thus allowing reliable data on high temperature measurements to be experimentally accessed. This concept was utilized in the study on measurements of surface tension and density of TiAlX-based alloys^[21] using two methodologies in a single test (i.e. the pendant drop and

sessile drop) and an advanced experimental complex described above. In order to make the measurements with pendant drop method highly reliable, special testing conditions were created by reduction of alloy/ceramic true contact through the presence of native primary oxide film on the $Al_{45.5}Ti_{46.5}X_8$ alloys during their melting in an alumina capillary. For the next-step involving sessile drop test on oxide-free droplets produced by squeezing the alloy through the capillary, the yttria-based porous barrier layer on alumina substrate (formed from colloidal yttria spray) was found to have sufficient stability. The results obtained showed a good agreement with those obtained by container-less method.

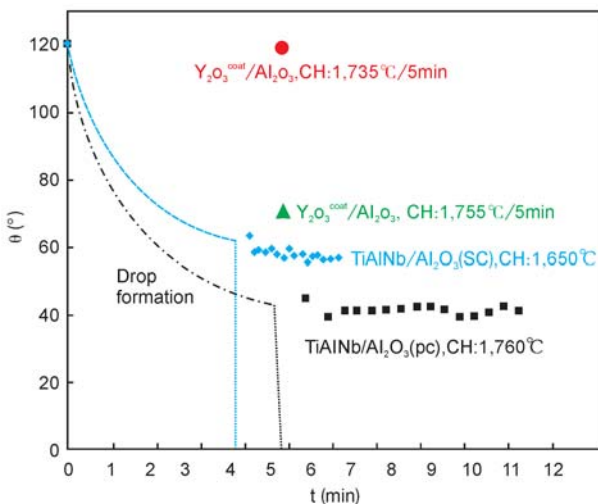


Fig. 14: Wettability kinetics of $Ti_{46}Al_{46}Nb_8$ alloy (mole %) on pure Al_2O_3 substrate (PC-polycrystalline; SC-single crystal) and the values of contact angles formed after 5 min contact on Y_2O_3 -coated alumina at 1,735°C and 1,755°C.

4 Summary and conclusions

The field of high-temperature liquid-state materials science impacts a number of advanced processing and manufacturing technologies such as casting, soldering, brazing, welding, liquid-phase sintering, and cast composites. The production of advanced materials is impacted by wettability, spreading, infiltration, volumetric changes, nonmetallic inclusions, refractory degradation, roughening, whiskering, and metal oxidation. The properties of the final product depend upon these factors and are related to high-temperature properties of liquid metal and, particularly, high-temperature surface and interfacial phenomena. Thus interactions between liquid metals and solids, and the nature of interfaces formed play a key role in selecting suitable materials and processing parameters.

Recent advances in methodological, scientific and technological aspects of high-temperature processing using new, sophisticated experimental techniques have begun to unravel the complex role of fundamental phenomena. A unique experimental complex designed and developed at the Foundry Research Institute, Krakow, allows in-situ studies at high temperatures. Its unique design and multiple features permit complex functions such as 'pushing', 'smearing' and 'rubbing' of sessile drops to be done under stringent test conditions (10^{-7} – 10^{-10}

mbar vacuum, 2,100°C) to mimic the behavior of liquid or semi-solid materials (metals, alloys, ceramics, glass, fluxes, dross) in real technological processes. In this paper, new interfacial studies relevant to the production of advanced cast materials of three groups of alloys: Al, Ni, and Ti were presented.

Aluminum is known to exhibit extreme sensitivity to oxidation and the presence of even minute amounts of oxygen (e.g., water vapor) lead to a primary oxide film on Al and considerable dispersion in wetting properties. Aluminum oxidizes even under ultra high vacuum at temperatures below ~1,000°C. Reaction between molten metals and residual water vapor in a furnace atmosphere or from foundry appliances is the most common factor for structural defects in castings such as oxide inclusions and gas porosity. In addition, even a few nanometers thick tenacious oxide films on liquid Al adversely affects the wetting and joint strength, factors important in cast MMCs. Removal of oxide films via capillary purification improves both wetting and bonding, and this provides the basis for application of oxide removal methods for MMCs, such as intensive stirring, ultrasound, or addition of Mg to Al melts, to transform primary oxides into $MgAl_2O_4$.

Likewise, reactions between molten Al and SiO_2 are particularly important because of extensive use of silica in many refractory ceramics used for melting technology products such as molds, filters, crucibles, etc. Tests show that wettability in the Al/ SiO_2 system is controlled by the wettability of Reaction Product Region (RPR) and not by the wettability of SiO_2 . Thus, SiO_2 -containing refractories are suitable for short-time or low-temperature contact with molten low-silicon Al alloys in air. At high temperatures, the lifetime of such materials significantly decreases and they should not be used in crucibles. In another example, the effect of CVD carbon films (or mechanically smeared soot or graphite paint) results in better wetting and bonding. However, it may cause some problems in melting and casting of Al alloys containing Ti or other carbide-forming solutes when the surface of molds, crucibles or holders is stained with carbon. Many unusual interfacial phenomena are caused by roughness and whiskering, and lead to large dispersion in contact angles on smooth and rough surfaces.

Nickel is non-wetting and non-reactive in contact with oxides used in the manufacture of ceramic products for melting and casting of Ni-alloys; however, Ni dissolves oxides and the surface tension of liquid Ni depends upon dissolved oxygen. Ni alloys show good adhesion to bulk oxides such as MgO ; this leads to the frequent occurrence of MgO -rich inclusions in Ni-base castings that get mechanically detached from the surface of foundry appliances made from polycrystalline MgO -rich ceramics, especially if accompanied by a fluid flow (e.g. mixing, flowing, pouring). Such inclusions could also form because of a detachment of oxide substrate ridges that develop around tiny gas bubbles formed at the melt/crucible interface.

The non-wetting behavior of Ni and MgO coupled with the significant density difference between them causes MgO floatation and segregation at the top thus necessitating bottom pouring during casting. Furthermore, as MgO inclusions

could be pushed by non-wetting solidifying alloys, directional solidification is profitably used to remove such inclusions.

It is well known that pristine ceramic surface morphology gets modified by the metal vapor ahead of an advancing triple line (TL) even when the metal vapor neither reacts with nor condenses at TL. This leads to the formation of numerous fine cavities that affect the surface quality of the cast product. Volatile solutes in alloys react with oxide ceramics to form new oxide and spinel whiskers ahead of the TL thus degrading the crucible even above the level of molten metal and affecting crucible life. For example, spinel whiskers form with Ni-Al alloy on alumina if the alloy is pre-melted in a crucible made from MgO-based ceramic. Whisker growth is also observed at the drop surface due to the interactions of the drop with the compounds out-gassing from the substrate under vacuum.

Some ceramic/metal systems [e.g., NiCr10/MgO(100)^{SC}] exhibit a repetitive wetting-de-wetting process because of evaporation and reaction under and near the liquid with a corresponding fluctuation in the contact angle. Multi-component alloys melted in crucibles made from complex oxide-based ceramics further complicate the situation because of the confluence of vapors of different compositions and history, and formation of whisker-like crystals of new oxides, usually deposited at cooler parts of the furnace. It is, therefore, important to examine melting history of not only the alloy and the crucible but also the furnace used for its melting in order to understand and control the structural defects in castings.

Finally, in the case of Ti, it is well known that pure liquid Ti readily reacts with oxides to form Ti-rich oxides; however, the reactions do not result in wetting. But volumetric increase of oxides following reaction with liquid Ti and the associated dimensional changes create difficulty in casting high-quality Ti products, particularly by investment casting. Y₂O₃-based colloidal coatings protect crucibles and holding ladles from such attacks. Moreover, reactive solutes such as Nb or Ta in Al-Ti alloys increase their melting temperature and reactivity thus creating challenges in processing; however, the contact angle remains obtuse for several minutes. Such a kinetic delay in establishing physical contact via spreading has been profitably used at the Foundry Research Institute to reliably measure high-temperature properties (e.g., surface tension and density) of highly liquid reactive TiAlX-based alloys (X: Nb or Ta).

References

- [1] Sobczak N. Some methodological aspects of high temperature capillarity phenomena investigations – Part I. Transactions of the Foundry Research Institute, Krakow, Poland, 1994, XLIV (4): 221–238.
- [2] Asthana R, Sobczak N. Wettability, Spreading, and Interfacial Phenomena in High-Temperature Coatings, JOM-e, 2000, 52 (1), <http://www.tms.org/pubs/journals/JOM/0001/Asthana/Asthana-0001.html>
- [3] Eustathopoulos N, Sobczak N, Passerone A, Nogi K. Measurements of contact angle and work of adhesion at high temperatures. J. Mater. Sci., 2005, 40 (9/10): 2271–2280.
- [4] Sobczak N. Wetting phenomenon as a factor affecting structure and properties of metal-ceramic materials produced by liquid phase processes. Foundry Research Institute, Krakow, Poland, 2004. (in Polish)
- [5] Sobczak N, Singh M, and Asthana R. High-temperature wettability measurements in ceramic-metal systems – some methodological issues. Current Opinion in Solid State & Materials Science, 2005, 9(4–5): 241–253.
- [6] Sobczak N, Nowak R, Radziwill W, et al. Experimental complex for investigations of high temperature capillarity phenomena. Materials Science and Engineering A, 2008, 495 (1–2): 43–49.
- [7] Sobczak N. Wettability, interface structure and properties in Al/Al₂O₃ system. Kompozyty, 2003, 3(7): 301–312. (in Polish)
- [8] Sobczak N, Asthana R. The role of wetting phenomenon in the structure and bonding of metal-ceramic interfaces: Some recent developments. Recent Research Developments in Materials Science, Research Signpost (Publisher), 2001, 2: 135–160.
- [9] Sobczak N. Wettability and reactivity between molten aluminum and selected oxides. Solid State Phenomena (Bulk and Graded Nanometals), 2005, 101–102: 221–226.
- [10] Sobczak N. Effects of titanium on wettability and interfaces in aluminum/ceramic systems. Ceramic Transactions, 2004, 146: 83–90.
- [11] Sobczak N, Asthana R, Radziwill W, et al. The role of aluminum oxidation in the wetting-bonding relationship of Al/oxide couples. Archives of Metallurgy and Materials, 2007, 52 (1): 55–65.
- [12] Laurent V, Chatain D, Eustathopoulos E. Wettability of SiO₂ and Oxidized SiC by Aluminium. Materials Science and Engineering A, 1991, 135: 89–94.
- [13] Zhou X B, Hosson J T M De. Reactive wetting of liquid metals on ceramic substrates. Acta Materialia, 1996, 44(2): 421–426.
- [14] Sobczak N, Nowak R, Radziwill W, et al. Effect of carbon film on wettability and bonding in Al/Al₂O₃ and AlTi6/Al₂O₃. Ceramics (Polish Ceramic Bulletin), 2005, 80: 669–676.
- [15] Purgert R M, Sobczak N, Nowak R, et al. Interaction between molten inconel 740 alloy and oxide ceramics. Abstract Book, Int. Conference Cast Composites' 2009, Oct. 11–14, Kocierz, Poland, Foundry Research Institute, 2009: 84.
- [16] Sobczak N, Nowak R, Sienicki E, Stobierski L. Wettability and reactivity between liquid aluminum and Y₂O₃-containing ceramics. Abstract Book, Int. Conference Cast Composites' 2009, Oct. 11–14, Kocierz, Poland, 2009: 53–54.
- [17] Nogi K, Iwamoto N, Ogino K. Wetting phenomena at high temperature. Transactions JWRI, 1992, 21: 141–146.
- [18] Sobczak N, Nowak R, Asthana R. Wetting in high-temperature materials processing: the case of Ni/MgO and NiW10/MgO. Scripta Materialia, doi:10.1016/j.scriptamat.2010.03.003.
- [19] Zhu J, Kamiya A, Yamada T, et al. Surface tension, wettability and reactivity of molten titanium in Ti/yttria-stabilized zirconia system. Materials Science and Engineering, 2002, 327(2): 117–127.
- [20] Karwinski A, Sobczak N, Nowak R. et al. Interaction between liquid titanium and ZrO₂-based ceramics containing CeO, ZrO₂, Y₂O₃ and CaO nanoparticles. Abstract Book, Int. Conference on High Temperature Capillarity, Athens, Greece, 2009: 147.
- [21] Liu Aihui Li Bangsheng Nan Hai , et al. Interaction between γ-TiAl alloy and zirconia, China Foundry, 2008 5(1): 44–46.
- [22] Nowak R, Sobczak N, Ricci E, et al. Surface tension of γ-TiAl based alloys. Journal of Materials Science, 2010, 45: 1993–2001.