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Wettability, reactivity and interfaces in the Gd/TiO_2 system

Patrycja Turalska[1], Marta Homa[1], Rafał Nowak[1], Grzegorz Bruzda[1], Natalia Sobczak[1,2], Ivan Kaban[3], Norbert Mattern[3], Jürgen Eckert[4,5]

[1]Foundry Research Institute, ul. Zakopianska 73, 30-418 Krakow, Poland
[2]Institute of Precision Mechanics, ul. Duchnicka 3, 01-796 Warsaw, Poland
[3]IFW Dresden, Institute for Complex Materials, Helmholtzstraße 20, 01069 Dresden, Germany
[4]Erich Schmid Institute of Materials Science, Austrian Academy of Sciences, Jahnstraße 12, 8700 Leoben, Austria
[5]Department Materials Physics, Montanuniversität Leoben, Jahnstraße 12, 8700 Leoben, Austria

E-mail: patrycja.turalska@iod.krakow.pl

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Abstract

High-temperature interaction of liquid Gd in contact with dense, polycrystalline TiO_2 substrate, was investigated. Wettability and reactivity tests were carried out at two different temperatures (1362°C and 1412°C) in flowing gas (Ar, 850−900 hPa) using the sessile drop method and classical contact heating of the examined couple of materials. The procedure was combined with a drop pushing procedure. During high temperature studies, images of the Gd/TiO_2 couple were continuously recorded by a high-resolution CCD camera. The results of wettability tests of liquid gadolinium on titanium dioxide substrate show that the Gd/TiO_2 system is non-wettable at both test temperatures (in either case the final contact angle was 100°). The results of structure examinations on the cross-sectioned samples show the dissolution of the TiO_2 substrate in liquid Gd and the presence of two sublayers at the drop/substrate interface: Gd_2TiO_5 (from the drop side) and $Gd_2Ti_2O_7$ (from the substrate side).

Keywords: *Gd, TiO_2, sessile drop, wettability, reactivity, interfaces*

1. Introduction

Gadolinium is a common alloying additive applied in order to improve functional and performance properties of advanced materials [1−2]. Many Gd-rich alloys are characterized by a liquid-liquid miscibility gap, which makes them attractive candidates for high performance metal-matrix composites fabricated by liquid assisted processing [3−4]. Therefore, establishing reliable data on critical temperatures of Gd-rich alloys is crucial in terms of their practical applications. On the other hand, high melting points, high chemical reactivity and affinity to oxygen strongly hinder their melting and casting, makes it difficult for an experimental evaluation of the thermophysical properties of such materials by conventional container/crucible-assisted methods. Thus, a selection of non-wetting and non-reactive materials that could be applied as crucibles for high temperature examinations of liquid alloys with additions of reactive elements (such as Gd or Ti), is deemed a demanding task.

In this study, the TiO_2 substrate as a potentially promising material for contact with Gd-rich alloys was selected for testing based on the thermodynamic stability data of oxides [5] and the authors' own experience.

2. Experimental procedure

For the wettability tests, dense, polycrystalline TiO_2 substrate (about 98% of the theoretical density) was prepared from powder with a purity of 99.90% by high pressure sintering. Prior to testing, the substrate was mechanically polished to a roughness of about 120 nm, using the same TiO_2 powder from which it was sintered, in order to avoid foreign phase inclusions in the substrate. Subsequently, it was purified in C_3H_8O (isopropanol) alcohol for 5 minutes using an ultrasonic cleaner, to remove impurities and to degrease the test surface. The prepared material served as a substrate for studying the wetting behavior of liquid gadolinium (99.99% – Sigma Aldrich).

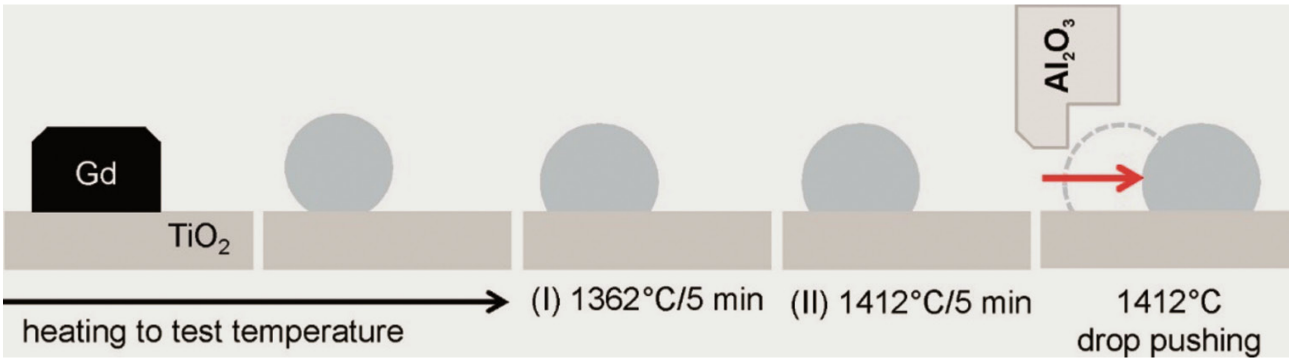


Fig. 1. Sessile drop method combined with classical contact heating and the drop pushing procedure used during the wettability tests

Studies of the Gd/TiO_2 interaction were carried out using a sessile drop method combined with contact heating of the examined couple of materials and a drop pushing procedure (Fig. 1). The original apparatus described in detail in [6] served as test equipment. The same test procedure as was used for the Gd/ZrO_2 system was applied [7]. High-temperature studies of the interaction between liquid Gd and TiO_2 substrates were conducted in an inert gas Ar atmosphere (99.9992% purity) at two different temperatures 1362°C and 1412°C, holding the system for 5 minutes at each temperature. These temperatures are 50°C and 100°C above the melting point of pure gadolinium T_m = 1312°C and they were selected for the purpose of future works devoted to measurements of thermophysical properties of Gd-rich alloys.

During wettability tests, the images of the Gd/TiO_2 couple were recorded with a high-resolution Microtron 1310 digital camera at a speed of 1 frame per second during heating of the system to the desired test temperature and during cooling to room temperature. During melting of gadolinium and subsequent tests carried out at 1312°C and 1462°C, the images were recorded at a rate of 10 frames per second. For calculating the contact angle θ, the obtained images were analyzed by ASTRA2 computer software developed by IENI-CNR, Genua, Italy [8,9].

Examinations of the sample surface and the cross-section structure after the wettability studies were carried out using a Zeiss Observer.Z1m optical microscope (OM) and a Hitachi TM3000 scanning electron microscope (SEM) equipped with an EDS (Energy Dispersive Spectroscopy) analyzer for chemical analysis.

Measurements of the microhardness of individual phases using a Vickers indenter were performed on the sample cross-section using a multifunctional measurement platform for testing the mechanical properties of solid materials and the properties of coatings and layers subjected to nano- and microscale loading using HV0.1 N.

3. Results and discussion

It was found that the Gd/TiO_2 system is non-wettable during heating to and at the test temperatures of 1362°C and 1412°C. The registered final value of the contact angle was θ_f = 100° and it is the same for both temperatures.

After the wettability tests, the solidified Gd/TiO_2 couple (Fig. 2a) shows a color changeover of the initially white TiO_2 substrate to dark gray, which might be related to oxygen loss and the formation of nonstoichiometric TiO_{2-x}, while heating the system to the test temperature [10]. A similar behavior was observed in the case of ZrO_2 substrate [7] during the study of its interaction with liquid Gd conducted under the same testing conditions. As discussed in detail in [11], this phenomenon is common for transition metal oxides that can lose oxygen with the formation of nonstoichiometric phases at high temperature, particularly in contact with a strong oxidizer.

The visual top-view observation (Fig. 2a) shows that the Gd drop has an asymmetric shape after high temperature exposure, probably due to the attempts to move it over the surface of the oxide substrate directly in the test chamber, when the drop pushing procedure was applied. Unfortunately, this attempt was not fully successful because the pusher was made of alumina, which was well wettable by liquid gadolinium. In addition, a light gray ring on the TiO_2 substrate around the solidified drop is well distinguished both by visual observation (Fig. 2a) and under SEM (Fig. 2b).

Figure 3 displays the results of detailed SEM observations of the structure of this ring. Area 1 corresponds to the structure of the drop/substrate interface formed during wettability tests and revealed at the highest test temperature of 1412°C during drop pushing. Areas 2−7 represent the structures of the gray layer at different distances from the drop. EDS analysis showed that the gray layer is composed of fine Gd-rich crystals densely packed in the vicinity of the Gd drop. With increasing distance from the drop, the number of crystals decreases

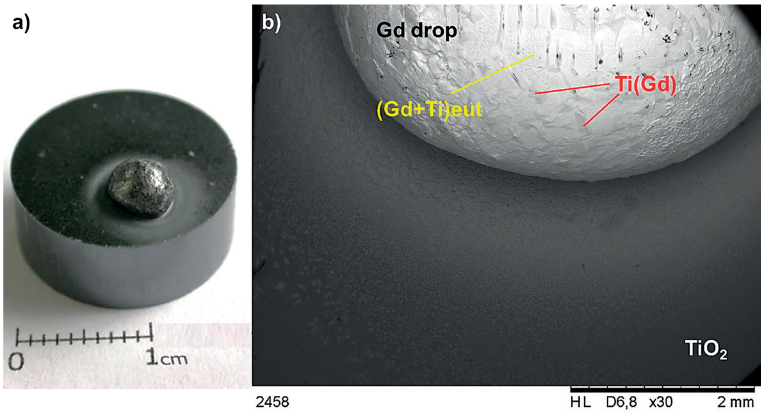


Fig. 2. The Gd/TiO_2 couple after wettability tests: a) photo, b) SEM top-view image

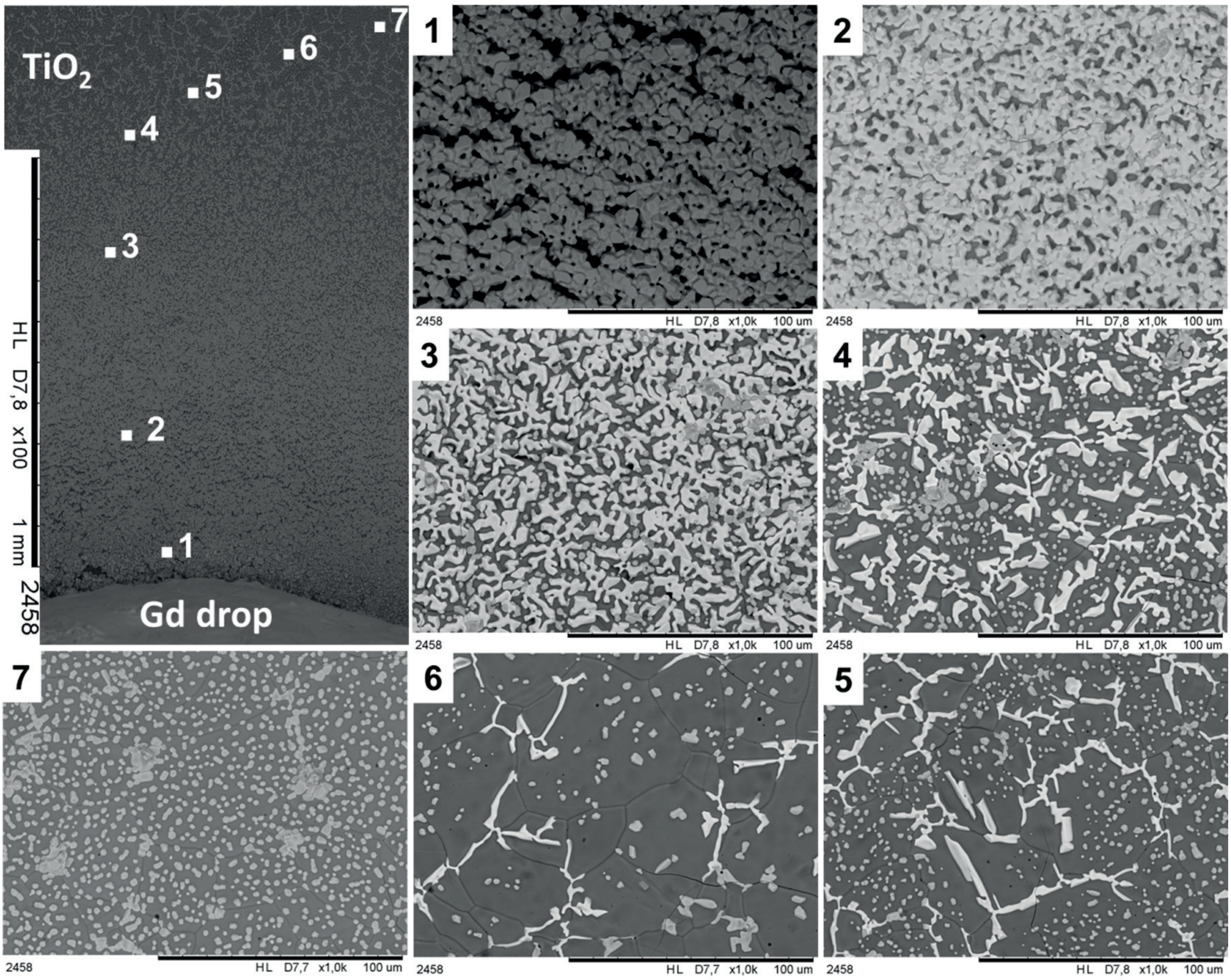


Fig. 3. SEM top-view images of the structure of a grey layer formed on the TiO_2 surface around the Gd drop at different distances from the drop: area 1 – corresponds to the structure of the drop/substrate interface formed during wettability tests and revealed at the highest test temperature of 1412°C during drop pushing, areas 2−7 – correspond to the structure of the layer formed by Gd evaporation-condensation mechanism

and are accompanied by a change of their shape. Since the crystals are located both inside the grains and along the grain boundaries of the substrate, we suggest that the Gd evaporation-condensation mechanism is responsible for the formation of gray rings on the substrate surface around the Gd drop. This phenomenon will be discussed in detail in the next publication devoted to comparative studies on high temperature interaction of liquid Gd with different Ti-rich substrates, including TiO_2, pure Ti, and oxidized Ti.

The structural investigations of cross-sectioned specimens were carried out separately for the Gd drop (Figs. 4, 5a) and the TiO_2 substrate (Fig. 5b) because the drop was detached from the substrate during cooling of the Gd/TiO_2 couple after the wettability tests.

Figure 4 shows the microstructure of the cross-sectioned Gd/TiO_2 couple as observed by OM. The analysis of the drop/substrate interface indicates that it is composed of two sublayers with different shades of grey. The dark gray continuous sublayer #1 at the drop-side interface with a thickness of about 100 μm and a microhardness of 513 HV is composed of crystals with an irregular shape and the surface more developed on the drop side. Additionally, numerous cracks were also detected in this zone. The sublayer #2 extending over the entire length of the substrate-side interface has a much brighter color. It is about 50 μm thick and has a compact structure without cracks. Its microhardness is 257 HV, while the microhardness of the TiO_2 substrate and the Gd-matrix material are 195 HV and 67 HV, respectively.

Figure 5 demonstrates the structures of the drop-side (Fig. 5a) and substrate-side (Fig. 5b) interfaces recorded under different magnifications by scanning electron microscopy (the substrate was in situ detached from the drop during cooling of the Gd/TiO_2 couple). SEM observations proved the results of OM characterization (Fig. 4) that are demonstrated by the presence of new phases in the initially pure Gd drop and the existence of two interfacial sublayers of dissimilar structure, chemistry, hardness and color. SEM/EDS analysis of both the drop surface (shown in Fig. 2b) and the cross-sectioned drop (shown in Fig. 5a) displayed numerous Ti-rich precipitates and areas of typical (Gd + Ti) eutectic structure predominantly located between Gd grains.

It should be emphasized that reliable chemical analysis of the Gd drop as well as the drop-side interface (shown in Fig. 5a) was difficult due to smearing of gado-

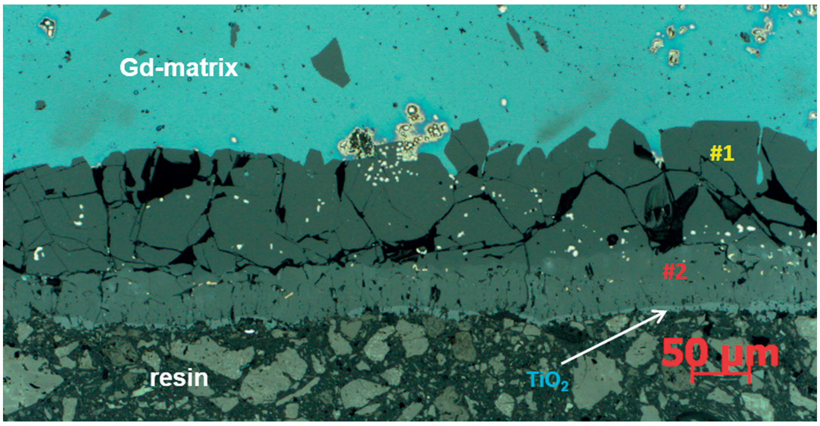
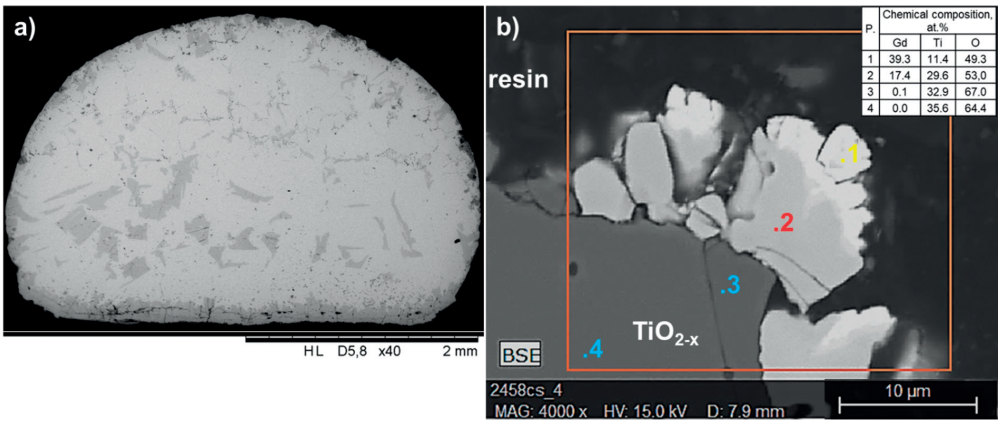


Fig. 4. Structure of the Gd/TiO_2 interface from the drop side after the wettability tests (OM)



P.	Chemical composition, at.%		
	Gd	Ti	O
1	39.3	11.4	49.3
2	17.4	29.6	53,0
3	0.1	32.9	67.0
4	0.0	35.6	64.4

Fig. 5. a) SEM image of the detached Gd drop of the Gd/TiO_2 couple, b) SEM/EDS analysis of the substrate-side interface of the Gd/TiO_2 couple performed on the substrate in situ detached after the wettability test

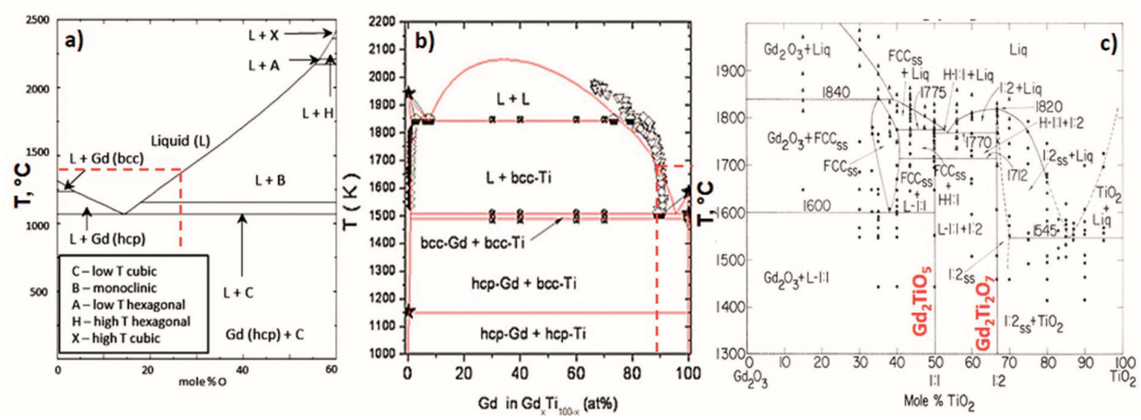


Fig. 6. Phase diagram data: a) Gd-O [12], b) Gd-Ti [13], c) Gd_2O_3-TiO_2 [14]

linium on the specimen surface during polishing and due to its fast oxidation. Due to methodological problems, the EDS analysis of the sublayers was performed on the cross-sectioned substrate in situ detached from the drop during cooling the Gd/TiO_2 couple. The most representative results of EDS analysis of interfaces are given in Figure 5b. The bright grey sublayer #1 (Fig. 5b, P.1) located at the drop side is mainly composed of oxygen and gadolinium with dissolved Ti (up to 11.4 at. %). The light grey sublayer #2 (Fig. 5b, P.2) located at the substrate side is mainly composed of oxygen and titanium and contains 17.4 at. % gadolinium. The EDS analysis of the titanium dioxide substrate (Fig. 5b, P.3−4) proves that it lost oxygen during the high temperature test that in turn caused the shift of the substrate chemistry to nonstoichiometric composition of TiO_{2-x}.

According to the literature data, liquid gadolinium is capable of dissolving in about 30 at. % oxygen [12] and about 12 at. % titanium [13] at a temperature of 1412°C. According to the equilibrium phase diagram Gd_2O_3-TiO_2 [14] the existence of ternary compounds, such as Gd_2TiO_5 and $Gd_2Ti_2O_7$, has been reported. Based on the chemical analysis of the reactively formed interfacial sublayers we may suggest that the sublayers #1 and #2 correspond to two phases, i.e. Gd_2TiO_5 (formed at the drop-side interface) and $Gd_2Ti_2O_7$ (formed at the substrate-side interface), respectively.

A comparison of the results of this study with those obtained in our previous work [7] on the wetting and reactivity of the Gd/ZrO_2 system [7], shows that in both Gd/TiO_2 and Gd/ZrO_2 systems, the interaction is accompanied with the dissolution of the substrate in liquid Gd and the formation of an interfacial layer. The difference between the two systems is related to the structure of this layer: it is composed of only one phase ($Gd_2Zr_2O_7$) in the Gd/ZrO_2 couple while in the Gd/TiO_2 couple, two layers of dissimilar structure, chemistry and microhardness are very distinguishable (Gd_2TiO_5, $Gd_2Ti_2O_7$). These observations are in agreement with the existing phase diagrams of the Gd_2O_3-ZrO_2 [15] and Gd_2O_3-TiO_2 [14] systems, respectively.

It should be highlighted that the formation of two compounds in the Gd/TiO_2 couple proves high reactivity between Gd and titanium dioxide. However, liquid Gd-Ti-O drop, produced after interaction with TiO_2 substrate, forms a high contact angle on the interfacial Gd_2TiO_5 sublayer at the drop-side interface. Thus one may conclude reactively formed Gd_2TiO_5 phase is non-wetting behavior combined with the formation of interfacial reaction products, that prevents further interaction of liquid Gd with the TiO_2 and plays the role of self-crucible, which can be beneficial for melting of Gd and Gd alloys in the TiO_2-based crucibles.

4. Summary

The results of wettability tests of the Gd/TiO_2 system performed in flowing Ar at temperatures of 1362°C and 1412°C show that, liquid gadolinium does not wet titanium dioxide substrate and at both test temperatures, it forms high contact angles of 100°.

Based on top-view SEM observations and cross-sectional SEM/EDS analysis of the solidified Gd/TiO_2 couple, it can be concluded that the following phenomena occur in the investigated system at high temperatures:

1) the evaporation of Gd and its deposition on the TiO_2 substrate around the Gd drop;
2) the dissolution of the TiO_2 substrate in liquid Gd;
3) the formation of two sublayers at the drop/substrate interface, i.e. Gd_2TiO_5 (from the drop side) and $Gd_2Ti_2O_7$ (from the substrate side) that prevent further interaction of liquid Gd with the TiO_2 substrate;
4) despite the fact that the Gd/TiO_2 system is reactive, liquid Gd-Ti-O drop, produced after interaction with TiO_2 substrate, forms a high contact angle on the reactively formed interfacial Gd_2TiO_5 sublayer.

Non-wetting behavior of the Gd/TiO_2 couple combined with the formation of interfacial reaction products can be beneficial for melting of Gd and Gd alloys in the TiO_2-based crucibles as a self-crucible concept.

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