THE EFFECT OF TESTING PROCEDURE ON DSC MEASUREMENTS OF Gd-Ti-Zr ALLOY USING ZrO_2 CONTAINER

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Abstract

Differential Scanning Calorimetry (DSC) was applied to determine the critical temperatures of phase transformations in the Gd40Ti30Zr30 alloy (wt%). The comparative measurements were carried out using three types of measuring devices at a temperature RT- 1650°C in the same flowing gas (Ar, 99.9992%) but applying different testing procedures, which allowed obtaining dissimilar oxygen contents in the surrounding atmosphere. The high temperature interaction and reactivity taking place between molten alloy samples and ZrO_2 container during DSC tests were evaluated by structural analysis of the resulting interfaces using alloy samples solidified inside the ZrO_2 containers. The conducted research has demonstrated methodological difficulties accompanying measurements of the thermophysical properties of Gd-rich alloys by the container-assisted DSC method, particularly when the tests are performed in flowing argon atmosphere with significantly reduced oxygen content. Under non-oxidizing conditions, the degradation of ZrO_2 container can take place during DSC testing because the selected Gd40Ti30Zr30 alloy reacts with the ZrO_2 to form a continuous interfacial reaction product layer. Under slightly oxidizing conditions, the gadolinium oxide formed in situ on the alloy surface, plays the role of a barrier for direct contact between molten alloy and container and thus may suppress or even prevent the degradation of the container and its subsequent strong bonding with the holder.

Keywords: DSC; Gd-rich alloys; ZrO_2 container; Reactivity; Interfaces

1. Introduction

Progressive development of the technology of metallic materials with particular emphasis on alloys containing reactive constituents such as Gd and Ti requests the search for new refractory ceramics enabling melting and casting of these alloys and the determination of their thermophysical properties by container- or support-assisted methods, e.g. measurements of the critical temperatures of phase transformations, viscosity, surface tension, density, and electrical or thermal conductivity. Knowledge of these properties is the fundamental guideline for practical use of liquid metals and alloys and also for modeling and computer simulation of many industrial liquid-assisted processes.

Monotectic alloys are of a high interest mainly due to the possibility of using the phenomenon of liquid state demixing for the synthesis of a new class of metal matrix composites (MMCs) by means of liquid-phase routes. Multi-component Gd-Ti-X alloys (X - Co or Zr) are excellent candidates for the manufacture of such materials. They have a very large potential of applications due to the combination of two or more phases with significantly different properties coexisting in one alloy [1].

Fabrication of composite materials based on the Gd-Ti-X system needs reliable and reproducible data on their critical temperatures. In turn, its experimental determination by container- or support-assisted methods requires appropriate container material that should be non-wettable and non-reactive in contact with the liquid alloy.

Technical literature offers only few pieces of information on materials used for high temperature testing of thermophysical properties of both solid and liquid gadolinium-containing alloys at high temperatures (Table 1). Analysis of the published data reveals that Al_2O_3 and ZrO_2 containers have been used in the thermal analysis of Gd-containing alloys and compounds: Al_2O_3 – for differential thermal analysis (DTA) in works [2-4], ZrO_2 – for DTA and differential

Table 1. *Literature data on materials used as containers for testing thermophysical properties of gadolinium-containing alloys and compounds [2-6]*

Material	Temperature, °C	Atmosphere	Methods	Material of support/container	Ref.
ZrO_2-$REO_{1.5}$ RE=La, Nd, Sm, Gd, Dy, Yb	1700	-	DTA	Al_2O_3	[2]
Gd-Ti	1300	Ar	DTA	Al_2O_3	[3]
Gd-Ti-Al-Cu	1300	Ar	DTA	Al_2O_3	[3]
Mn50Gd50	1027	N_2	DTA	Al_2O_3	[4]
Mn70Gd30	1127	N_2	DTA	Al_2O_3	[4]
Mn75Gd25	1127	N_2	DTA	Al_2O_3	[4]
Mn80Gd20	1127	N_2	DTA	Al_2O_3	[4]
Gd70Ti30	1677	He	DTA	ZrO_2	[5]
Gd20Ti80	1677	He	DTA	ZrO_2	[5]
Gd40Ti30Zr30	1600	Ar	DSC	ZrO_2	[6]
Gd90Ti5Zr5	1550	Ar	DSC	ZrO_2	[6]

scanning calorimetry (DSC) in works [5,6]. The choice of these containers is obviously dictated by their availability; at least no other specific justification can be found in Refs. [2-6]. Moreover, there is no detailed information about the chemical composition of containers used, which can be of great practical importance for other works with Gd-containing alloys.

Chemical reaction between an alloy and a container material may considerably impact the recorded data or even seriously damage the DSC device. Mattern et al. [5] reported the disturbances in data recording during DTA measurements of the Gd20Ti80 and Gd70Ti30 alloys in ZrO_2 containers and the occurrence of chemical reaction between Gd-Ti alloys and the container material. By applying the sessile drop method, Kaban et al. [1] examined the wettability of Gd40Ti60 and Gd60Ti40 alloys on ZrO_2 substrates stabilized with different amounts of Y_2O_3. They demonstrated that reducing the Y_2O_3 stabilizer content from 5 wt% to 3 wt% results in a better stability and lower reactivity of ZrO_2 substrate in contact with the Gd-Ti alloys in a wide temperature range up to approx. 1650°C. This effect was explained by the formation of a layer of the reaction product containing Gd, Zr and O at the drop/substrate interface. Even though the layer is thin, it inhibits the transport of constituents and further growth of reaction zone. Based on the available literature data, it can be concluded that ZrO_2 might be a suitable material for high temperature container-assisted testing of molten Gd-rich alloys.

The present work is focused on the methodological aspects of high temperature studies of the thermophysical properties of the Gd-rich Gd40Ti30Zr30 alloy by differential scanning calorimetry (DSC) using commercial ZrO_2 containers (delivered by NETZSCH, Selb, Germany). To determine the effect of the testing procedure applied in DSC measurements on the high temperature interaction between molten alloy and ZrO_2, the microstructure and chemistry of the alloy/container interface were examined in the samples solidified inside the ZrO_2 containers.

2. Experimental

The ternary Gd-based alloy containing 40% Gd, 30% Ti and 30% Zr (nominal composition given in wt%) was studied in this work (Fig. 1a). The alloy was prepared by arc-melting from the chemically pure Gd, Ti and Zr elements (Sigma Aldrich) [7] under argon atmosphere using a nonconsumable tungsten electrode and it was re-melted two times to improve its homogeneity. The initial oxygen content in the master alloy after arc-melting was not determined. Three samples were cut out from thus prepared alloy ingot using an Accutom-50 precision cutting machine (Struers).

Three comparative DSC tests (Table 2) were carried out in similar temperature ranges and the same flow gas atmosphere (Ar, 99.9992%) using the same types of ZrO_2 containers (Fig. 1b) commercially available at NETZSCH. The experiments were performed using the following three devices:

#1: STA 449 F3 Jupiter NETZSCH;
#2: DSC 404C Pegasus, NETZSCH;
#3: DSC 404 F1 Pegasus, NETZSCH.

Besides different maximum temperature permitted in these devices, the main difference in the DSC tests was dissimilar testing procedure caused by different design of DSC devices. In particular, the oxygen content in the surrounding atmosphere was different. For test #1 performed in device #1, the testing chamber was filled and cleaned with flowing argon for 30 min without any preliminary evacuation (no

pre-vacuum). In contrast, for the test performed in devices #2 and #3, the experimental chamber was evacuated before filling it with Ar. In device #2, only a rotary pump was used allowing the decrease in pressure inside the chamber up to a value of about 10^{-2} bar. In device #3, two-stage evacuation with rotary and turbo molecular pumps up to a rest pressure of about 10^{-5} bar was done.

Sensitivity and temperature calibrations of the DSC devices were made with five pure metals (In, Zn, Bi, Au, Ni) with heating rate of 20 K/min (#1, #3), 15 K/min (#2), under flowing Ar gas using the same type of zirconia containers. The details of testing conditions are summarized in Table 2.

After DSC tests, the ZrO_2 containers with solidified samples were subjected to detailed visual observation and structural examination. The structure and chemistry of cross-sectioned alloy/container couples were investigated by scanning electron microscopy (Hitachi TM3000 and FEI Scios™) coupled with energy dispersive X-ray spectroscopy (SEM+EDS analysis).
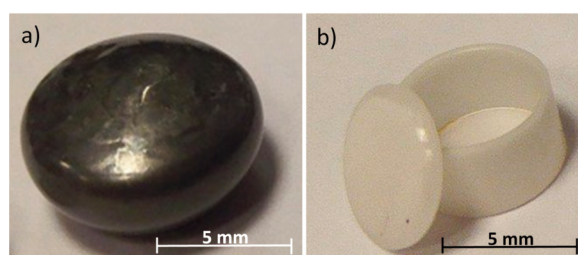

Figure 1. *Photos of as cast Gd40Ti30Zr30 alloy (a) and ZrO_2 container used in a DSC test*

3. Results and Discussion

The DSC curves recorded during heating the alloy samples in different DSC devices are presented in Figure 2. To clearly present the data, it is shown separately for the temperatures below 1000°C (Figs. 2a-c) and above 1000°C (Figs. 2d-f). The most important quantitative parameters extracted from these DSC curves are summarized in Table 3.

For all tests up to 1000°C, one endothermic event was observed at a temperature of ~620°C. Above 1000°C, certain discrepancies were noticed on the DSC curves measured in different experiments. In test #2 two endothermic peaks were detected (Fig. 2e - peak 2 and peak 3), while three endothermic peaks were recorded in test #1 (Fig. 2d - peak 2, peak 3 and peak 5) and test #3 (Fig. 2f - peak 2, peak 4 and peak 6). Moreover, in test #3, the exothermic peak occurred at 1591°C.

From the analysis of experimental data collected in this study (Table 3) and information on phase equilibria in the Gd-Ti-Zr system provided by Mattern et al. [8], three critical temperatures can be distinguished on DSC curves, for which the following endothermic phase transformations occur in the Gd40Ti30Zr30 alloy upon heating:

Peak 1: solid state transition *hcp*-(Ti, Zr) → *bcc*-(Ti, Zr) at a temperature of about 620°C;

Peak 2: solid state transition *hcp*-Gd → *bcc*-Gd at a temperature of about 1200°C;

Peak 3: melting of *bcc*-Gd phase at a temperature of approximately 1300°C;

Peak 4: complete melting of the alloy *L+bcc*-(Ti, Zr) → L at a temperature of approximately 1400°C.

Table 2. *DSC devices and experimental conditions applied in the present study*

| Test	Device	Pressure inside test chamber, bar	Atmosphere	Temperature range, °C	Heating rate, °C/min	Sample mass, mg
#1	STA 449 F3 Jupiter, NETZSCH	-	flowing Ar, 99.9992%	25-1550	I) 20 II) 20	58.742
#2	DSC 404C Pegasus, NETZSCH	10^{-2} bar (by rotary pump only)		25-1500	I) 15 II) 5	20.170
#3	DSC 404C F1 Pegasus, NETZSCH	10^{-5} (by rotary and turbo molecular pumps)		25-1650	I) 20 II) 5	156.610
Legend:						
I - 1st step of heating; II - 2nd step of heating.						
Notes:						
1. Higher heating rate in the 1st step was used to reduce the interaction time between the alloy and the container						
2. Lower heating rate in the 2nd step was used for better temperature control						
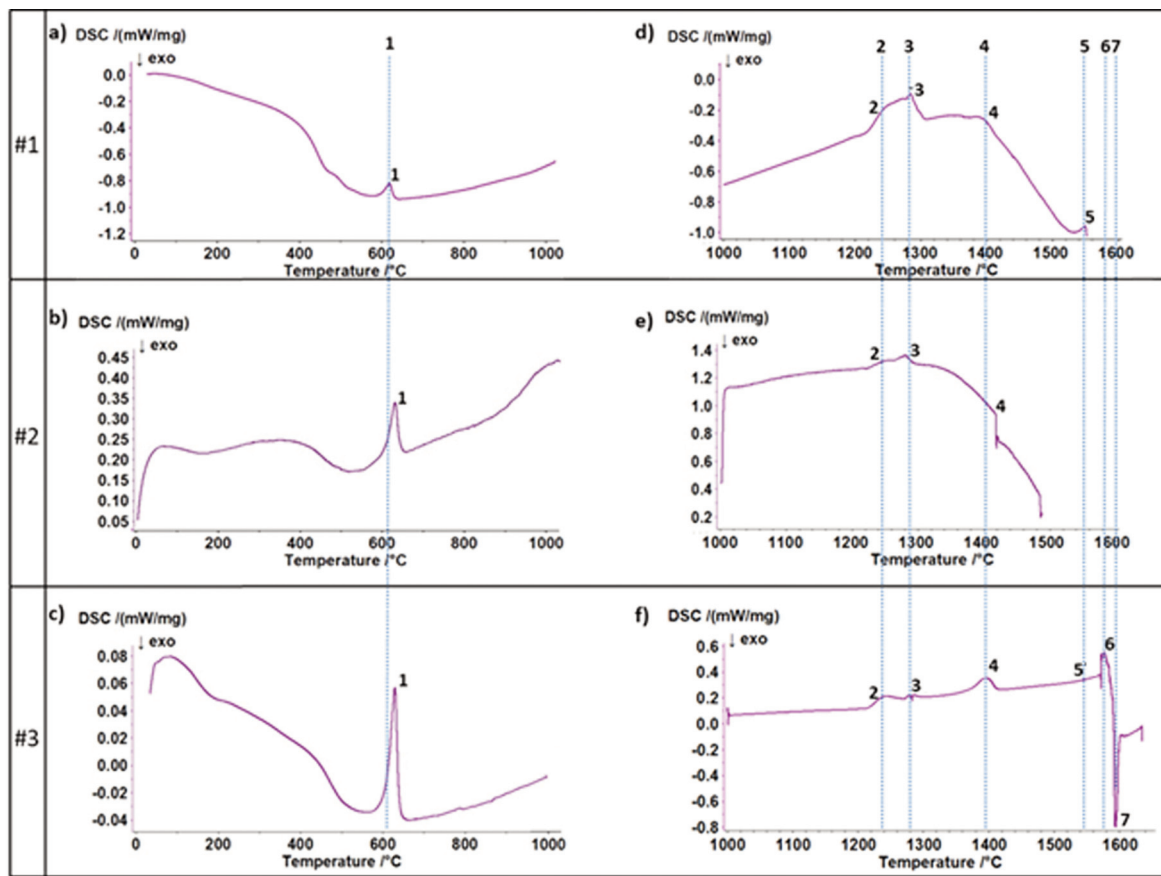
Figure 2. *Fragments of DSC curves from tests #1, #2 and #3 recorded during heating in the temperature range: a-c) RT-1000°C; d-f) T>1000°C*

Table 3. *The results of DSC tests carried out on the Gd40Ti30Zr30 alloy*

No.	Peak	ENDO		EXO	Color after DSC test	
		Onset, °C	Peak, °C	Onset, °C	Alloy sample	ZrO_2 container
Test #1	1	596	618	-	white surface	inside: white outside: white
	2	1218	-			
	3	1281	1284			
	4	-	1393			
	5	1553	1549			
Test #2	1	605	625	-	matt surface	inside: dark ring around sample outside: white
	2	1222	-			
	3	1264	1280			
	4	-	-	1418		
Test #3	1	609	629	-	bright metallic surface	inside: dark outside: dark
	2	1217	1238			
	3	1277	-			
	4	1373	1395			
	5	-	-			
	6	1572	1577			
	7	-	-	1591		

To further clarify the effect of testing procedure on the results of DSC measurements, an important piece of information can be gained from the visual observation of the DSC samples before and after high temperature DSC tests. The images of alloy samples solidified inside zirconia containers are shown in Figures 3a-c, whereas the photos of the bottom of these containers are shown in Figures 3d-f.

In the case of test #1, visual examination of the metal sample revealed the following:

1) the alloy surface was covered with a white layer (Fig. 3a);

2) the sample was not adhering to the container material and thus was easily detached from the container bottom.

These observations prove that under the experimental conditions of test #1, the alloy has undergone oxidation during heating, which resulted in the formation of a surface oxide layer acting as a barrier to the diffusion process of constituents at the alloy/container interface. Moreover, the ZrO_2 container did not change its initially white color during high temperature measurements and prolonged contact with molten alloy. This is additional evidence for the presence of oxidizing conditions in test #1, because it is well-known that at high temperature and under non-oxidizing conditions ZrO_2 is easily transformed to non-stoichiometric ZrO_{2-x} with an accompanying change in color from white to black [8-10].

Visual observations of the samples and containers from tests #2 and #3 did not reveal the presence of the white oxide on the sample surface. In both cases, the solidified samples had the shape of regular drops with a matt gray surface (Fig. 3b and Fig. 3c, respectively). In both tests, a permanent bond was formed between the alloy and the container material. Moreover, in test #3, the ZrO_2 container was also bonded to the Pt sample carrier, which was totally damaged during the attempt to separate it. In contrast to test #1, the initially white ZrO_2 container has changed its color to a light gray (test #2) or dark gray (test #3). This phenomenon is typical for oxides of transition metals MeO_2 (Me – Zr, Ti, Hf) and is due to the loss of oxygen and the formation of non-stoichiometric oxides MeO_{2-x}, when heated in a non-oxidizing atmosphere [8-10]. Thus the above observations give an experimental evidence that in tests #2 and #3, the amount of oxygen in the chamber was significantly lower than in test #1, which is in agreement with the different testing procedures applied (i.e. higher vacuum accompanied by lower oxygen content was produced in tests #2 and #3).
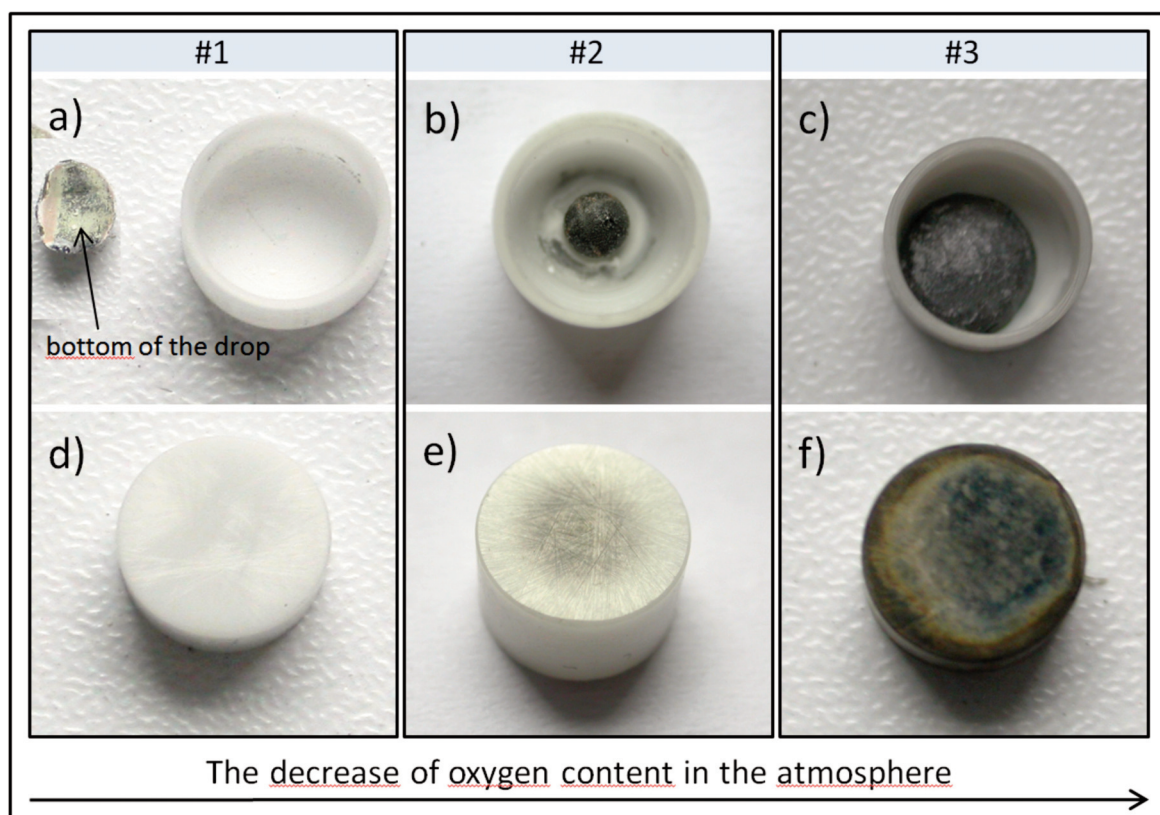

Figure 3. Photos of alloy/container couples after DSC tests: a-c) top views of the inside of zirconia containers; d-f) bottom views of ZrO_2 containers only

Based on the visual observations of samples and their structural characterization after DSC tests, it was concluded that as soon as a liquid Gd-rich phase is formed in the alloy samples (T~1300°C), a chemical reaction proceeds between the molten alloy and the container material. This reaction affects the shape of the DSC curve and is particularly well visible on the DSC curve obtained in test #3 (exothermic peak 7).

The microstructures of cross-sectioned ZrO_2 containers with adhered Gd40Ti30Zr30 alloy after tests #2 and #3 are shown in Figures 4a, b and c, respectively. In both cases, in the area where the alloy had a direct contact with the container, the presence of interfacial reaction product layer (RPL) of a light gray color is well distinguished under SEM due to the difference in the color of the alloy, the ZrO_2 container and the reactively formed layer. The RPL formed in test #2 contains 41.6-43.7% Gd, 48.7-49.3% O, 7.3-8.3% Zr and 0.3-0.8% Ti (at.%) and its thickness is approximately 70 μm (Figs. 4a and b). The RPL formed in test #3 contains 52.9-56.2 Gd and 43.8-47.1 O (at.%), while its thickness is 200 μm (Fig. 4c). In both cases, the RPL is continuous and somewhat extends beyond the direct contact area of the alloy and the container. Since the mass of the alloy sample in test #3 was almost eight times larger than that in test #2, the molten alloy in test #3 completely covered the container bottom and had side contacts with the container walls (Fig. 4c). The formation of a long continuous RPL at the alloy/container interface is responsible for a good bonding and strong joint between the alloy and the container. The RPL growing outside the alloy/ZrO_2 contact area in tests #2 and #3 is composed of large whisker-like crystals visible in Fig. 4b and Fig. 4c, respectively. Similar phenomenon was observed in the vicinity of the Gd-Ti drop in the sessile drop wettability tests performed with the gadolinium-rich binary Gd-Ti alloys on the ZrO_2 substrates in work [1].

The above discussed observations prove the reactive character of the interaction between the molten Gd40Ti30Zr30 alloy and the ZrO_2 container. High reactivity of Gd-Ti-Zr alloys with zirconia should therefore be taken into consideration when carrying out high temperature DSC tests, since it may contribute to unreliable measurements and results: 1) appearance of an additional thermal effect on the DSC curve; this phenomenon is recorded as an exothermic peak that might be overlapping with the endothermic peak related to the alloy melting process; 2) change in the alloy chemical composition. Moreover, high reactivity of the Gd-Ti-Zr/ZrO_2 couples results in their strong bonding, which may damage the DSC container.

Particularly highly-aggressive conditions of DSC tests are created when highly "clean" environment is generated as that in test #3 after using two-stage gas evacuation from the test chamber by means of a rotary pump and a turbo molecular pump. Under such conditions, at a high temperature, ZrO_2 is transformed into a metallic-like non-stoichiometric ZrO_{2-x} oxide that, in turn, easily forms a strong joint with the Pt holder during DSC test, consequently resulting in the holder damage during any attempt to separate it. Therefore, it is believed that peak 6 corresponds to the decomposition of $ZrO_2 \rightarrow ZrO_{2-x} + O_2$ while oxygen, released at the alloy/container interface, reacts with Gd to form the reaction product layer of Gd_2O_3 (Fig. 4c). From this point of view, slightly oxidizing conditions at the beginning of the DSC tests seem to be more beneficial since a native gadolinium oxide film formed on the surface of the alloy sample plays the role of a barrier suppressing the reactivity between molten Gd-rich alloy and ZrO_2 container. But in this case, it should be taken into consideration that the exothermic peak of alloy oxidation may affect the DSC curve shape, in particular the endothermic peak corresponding to the alloy melting process. Moreover,
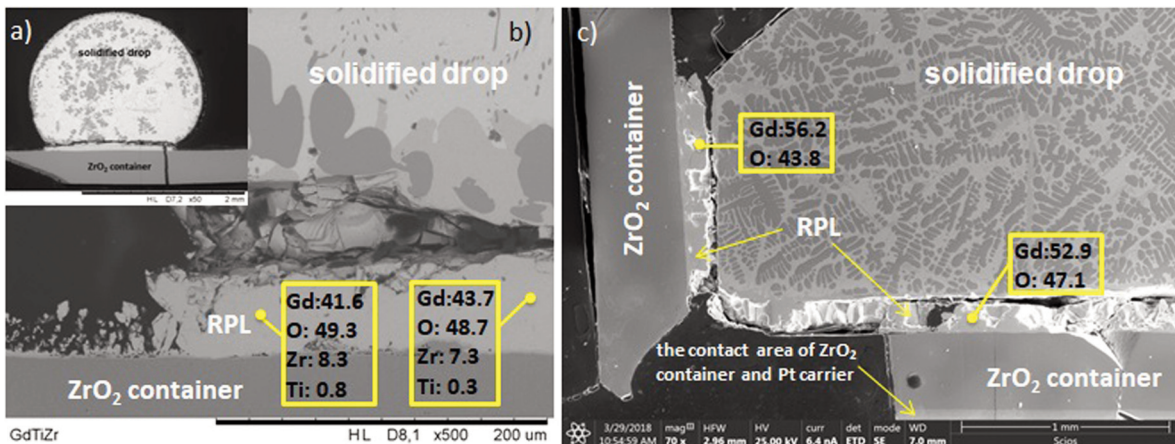

Figure 4. *SEM images of cross-section of Gd40Ti30Zr30 alloy sample solidified in the ZrO_2 container after DSC measurements: a, b) test #2; c) test #3*

for oxidizing conditions, a larger sample mass is recommended to keep the structure and chemistry of the alloy sample more homogenous, since for a smaller sample, the formation of surface oxide on the alloy may contribute to notable changes in the alloy chemical composition.

4. Summary

The experimental investigations carried out in this work have demonstrated methodological difficulties of the high temperature testing of highly reactive Gd-rich alloys by the container-assisted method such as differential scanning calorimetry. Under non-oxidizing conditions, the degradation of ZrO_2 container can take place during DSC testing because the selected Gd40Ti30Zr30 alloy reacts with the ZrO_2 to form a continuous interfacial reaction product layer. On the DSC curves, this phenomenon is recorded as an exothermic peak that might be overlapping with the endothermic peak related to the alloy melting process.

On the contrary, under slightly oxidizing conditions, the gadolinium oxide formed in situ on the alloy surface, plays the role of a barrier for direct contact between molten alloy and container and thus may suppress or even prevent the degradation of the container and its subsequent strong bonding with the holder. Despite the fact that in this case, the exothermic peak of alloy oxidation may affect the DSC curve shape, particularly the endothermic peak corresponding to the alloy melting process, slightly oxidizing conditions are more beneficial for container-assisted measurements at high temperatures.

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EFEKAT POSTUPKA ISPITIVANJA NA DSC MERENJA Gd-Ti-Zr LEGURE KORIŠĆENJEM ZrO$_2$ KONTEJNERA

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Apstrakt

Da bi se odredile kritične temperature faznih transformacija u Gd40Ti30Zr30 leguri (wt%) primenjena je diferencijalna skenirajuća kalorimetrija. Komparativna merenja su izvedena korišćenjem tri tipa uređaja za merenje pri temperaturi RT-1650°C u istom protočnom gasu (Ar, 99.9992%) ali uz primenu različitih postupaka ispitivanja što je omogućilo dobijanje različitih sadržaja kiseonika u okolnoj atmosferi. Interakcija visoke temperature i reaktivnosti koja se desila između rastopljenih uzoraka legure i ZrO$_2$ kontejnera tokom DSC testova vrednovane su pomoću strukturne analize rezultirajućih međufaza korišćenjem uzoraka legure koja se stvrdla u ZrO$_2$ kontejneru. Sprovedeno istraživanje pokazalo je metodološke poteškoće koje prate merenja termofizičkih osobina legura bogatih Gd DSC metodom potpomognutom kontejnerom, pogotovu kada se testovi izvode u atmosferi protočnog argona sa značajno smanjenim sadržajem kiseonika. Pod neoksidirajućim uslovima, degradacija ZrO$_2$ kontejnera se može desiti tokom DSC testiranja zato što izabrana Gd40Ti30Zr30 legura reaguje sa ZrO$_2$ da bi formirala međufazni sloj proizvoda. Pod slabo oksidirajućim uslovima, gadolinium oksid formiran in situ na površini legure ima ulogu barijere za direktan kontakt između otopljene legure i kontejnera i tako može da smanji ili čak i spreči degradaciju kontejnera i njegovo kasnije čvrsto vezivanje sa držačem.

Ključne reči: DSC; Legure bogate Gd; ZrO$_2$ kontejner; Reaktivnost; Interfejsi