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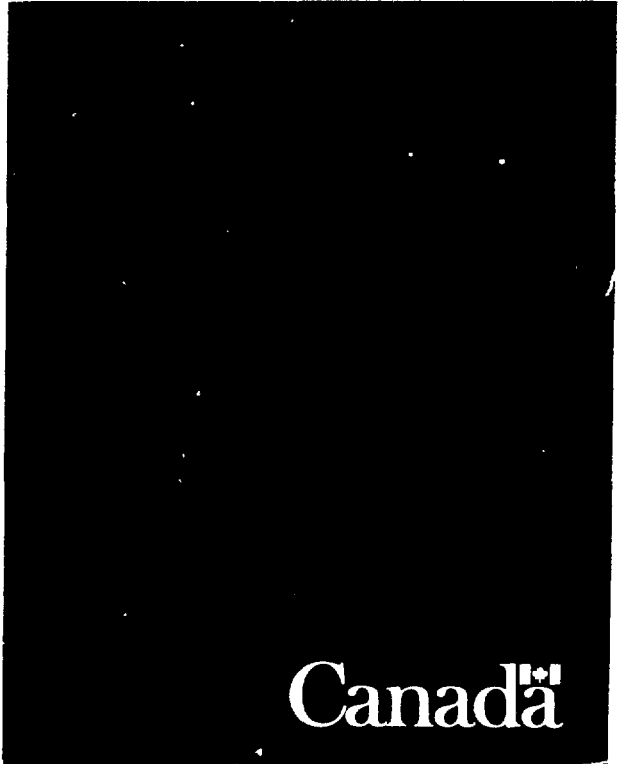
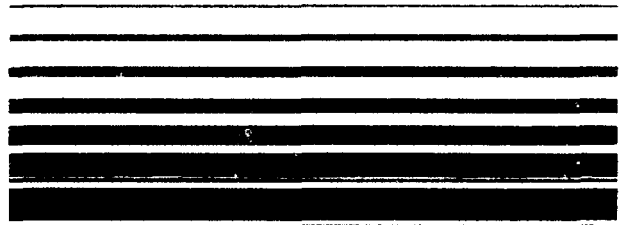
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**HYDROGEN ABSORPTION-DESORPTION
AT METAL SURFACES**

by

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A research report prepared for the
Atomic Energy Control Board
Ottawa, Canada

Project No. 2.174.1

Completed April, 1990
Published April, 1991

Canada

Research report

HYDROGEN ABSORPTION-DESORPTION AT METAL SURFACES

This work was produced by the Thermodynamics and Kinetics Laboratory, Department of Mechanical Engineering, 5 King's College Road, University of Toronto, Toronto, Canada, under contract to the Atomic Energy Control Board (contract no. 87055-9-4053/01-SZ).

ABSTRACT

On the basis of experimental studies, it has been proposed that when zirconium oxide (ZrO_2) is exposed to hydrogen at $300^\circ C$ or higher, a reaction occurs to produce metallic zirconium and water, thereby increasing the electrical conductivity of the oxide film and its permeability to hydrogen. It is conventionally proposed that when ZrO_2 is exposed to a reducing atmosphere, the oxide undergoes these changes because of oxygen diffusing to the substrate and leaving behind anion vacancies. To distinguish these two mechanisms, a series of experiments has been performed in which specimens of zirconium and zirconium-2.5% niobium were either hydrided or deuterided in a furnace at a temperature between $300^\circ C$ and $800^\circ C$ and in an atmosphere that consisted primarily of either hydrogen (H_2) or deuterium (D_2). After cooling a specimen to room temperature, it was placed in a thermogravimetric analyzer that was equipped with a mass spectrometer, TGA-MS. Each specimen was then heated to $1200^\circ C$ at a controlled rate in a primarily helium atmosphere that was monitored with the mass spectrometer. It was observed that light water (H_2O) evolved from the hydrided specimens and heavy water (D_2O) from the deuterided ones and that there was a weight loss of the specimens that accompanied the water evolution. A series of experiments was then conducted to determine if the oxygen for the reaction was coming from the oxide layer. It was found that the specimens having approximately the same amount of hydride but more oxide also evolved more H_2O , and that the H_2O did not come from reactions between impurity H_2 and oxygen (O_2) in the TGA-MS. The concept that emerges is that heating a zirconium or zirconium alloy specimen that contains a hydride or deuteride phase within and an oxide layer on its surface causes the hydrogen to diffuse toward the surface and when it encounters the oxide a reaction follows that produces water. Since there is a low solubility for the water in the solid, it evolves into the gas phase. This evolution gives rise to a weight loss of the specimen and can be slow or sudden depending on where the reaction takes place and the difficulty that the water has in leaving the specimen. The conventional mechanism for the dissipation of the imperviousness of ZrO_2 to H_2 that results from the oxide being exposed to a reducing atmosphere will not explain the water production observed in these experiments. However, the existence of the proposed reaction can account for the elevated hydrogen concentration in an oxide film that has been observed to accompany the aqueous corrosion of zirconium and the effects on both the electrical conductivity and hydrogen permeability that follows from exposing the oxide to a reducing atmosphere.

RÉSUMÉ

À partir d'études expérimentales, on propose que, si de l'oxyde de zirconium (ZrO_2) est exposé à de l'hydrogène à des températures supérieures à 300 °C, il réagit et produit du zirconium métal et de l'eau, augmentant ainsi la conductivité électrique de la couche d'oxyde et sa perméabilité à l'hydrogène. On croit traditionnellement que, si du ZrO_2 est exposé à une atmosphère réductrice, l'oxyde réagit ainsi parce que l'oxygène se disperse vers le substrat et laisse des fautes d'empilement d'anions derrière. Pour distinguer ces deux mécanismes, on a procédé à une série d'expériences où des échantillons de zirconium et de zirconium contenant 2,5 pour 100 de niobium en poids ont été soit hydrurés soit deutériés dans un four à des températures variant de 300 à 800 °C et dans une atmosphère comprenant surtout de l'hydrogène (H_2) ou du deutérium (D_2). Après avoir été refroidi à la température de la pièce, l'échantillon a été placé dans un analyseur thermogravimétrique doté d'un spectromètre de masse (TGA-MS). Chaque échantillon a ensuite été chauffé à 1200 °C à un débit progressif dans une atmosphère principalement composée d'hélium qui a été contrôlée à l'aide du spectromètre de masse. On a observé que de l'eau légère (H_2O) et de l'eau lourde (D_2O) se formaient respectivement à partir des spécimens hydrurés et deutériés et que les échantillons perdaient du poids par suite de la formation d'eau. Une série d'expériences a ensuite été effectuée pour déterminer si l'oxygène de la réaction provenait de la couche d'oxyde. On a découvert que les échantillons avaient environ la même quantité d'hydrure, mais que plus d'oxyde produisait plus de H_2O , et que le H_2O ne provenait pas des réactions entre les impuretés de H_2 et d'oxygène (O_2) dans le TGA-MS. Le principe qui ressort est que, si l'on chauffe du zirconium ou un alliage de zirconium qui comporte une phase d'hydruration ou de deutériuration à l'intérieur et une couche d'oxyde à sa surface, l'hydrogène se diffuse vers la surface, réagit au contact de l'oxyde et produit du H_2O . Comme l'eau est peu soluble dans le solide, elle s'évapore. Cette évaporation entraîne une perte de poids lente ou soudaine de l'échantillon selon l'endroit où la réaction se produit et la difficulté de l'eau à s'en échapper. Le mécanisme classique de dissipation de l'imperméabilité du ZrO_2 au H_2 qui découle de l'exposition de l'oxyde à une atmosphère réductrice ne peut expliquer la production d'eau dans ces expériences. Toutefois, l'existence de la réaction proposée peut expliquer la concentration élevée d'hydrogène dans la couche d'oxyde qui, selon les observations, accompagne la corrosion aqueuse du zirconium et les effets autant de la conductibilité électrique que de la perméabilité à l'hydrogène après l'exposition de l'oxyde à une atmosphère réductrice.

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A. INTRODUCTION

The oxide layer formed on the surface of the *Zr* alloy pressure tubes during manufacture acts as a barrier to further corrosion of the material when it is in-service. It is known that this oxide layer does not provide protection for an indefinite period. The observation has been that the corrosion rate of these tubes when they are initially put in service is relatively low and that the deuterium absorbed into the substrate is also relatively low, but with time the corrosion rate accelerates as does the rate of deuterium absorption [1]. This suggests that the ZrO_2 layer progressively loses its protective capacity and that the rate of loss accelerates with time.

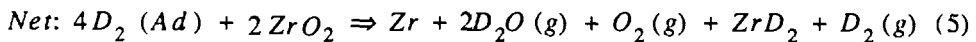
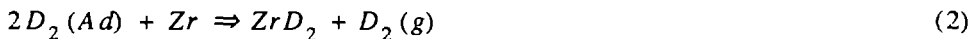
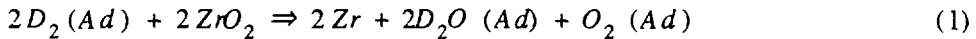
Ideally one would like to be able to predict the time for which the oxide layer would protect the pressure tubes from significant corrosion, deuterium ingress and embrittlement because that would allow one to know the period of safe operation of the pressure tubes. However, the mechanisms of corrosion remain an area of current interest and the subject of debate [1, 2].

It is known that if an oxide layer covering a zirconium substrate is exposed to a hydrogen atmosphere, the electrical conductivity of the film progressively increases as does the permeability of the oxide to hydrogen [3]. The explanation that was originally given by Shannon [3] for these observations was that when the oxide was exposed to a reducing atmosphere, oxygen from the ZrO_2 diffuses through the oxide and goes into physical solution in the *Zr* substrate. The anion vacancies created by this process were suggested to provide a pathway for hydrogen to penetrate the oxide layer and to give rise to the increased electrical conductivity. Shannon also showed that exposing the oxide layer to a vacuum gave rise to an increase in the electrical conductivity and therefore created the anion vacancies. If O_2 or H_2O (*v*) were present at sufficient concentrations in the otherwise hydrogen atmosphere, it was found that the electrical conductivity of the ZrO_2 film did not change and that the hydriding of the substrate *Zr* was prevented. Shannon interpreted this as indicating that the O_2 or H_2O (*v*) repaired the protective ZrO_2 by further corrosion which prevented the O^{2-} vacancies from forming. We would note that Shannon did not monitor the gas phase during these experiments so any possible reaction between the hydrogen gas and ZrO_2 would not have been detected by him.

That more is involved in the dissipation of the protective properties of the oxide than suggested by Shannon was indicated by the results reported by Woolsey and Morris [4] who used deuterium as a tracer, O^{18} and an ion beam method to examine oxygen and hydrogen (as deuterium) transport in corrosion films of Zircaloy-2 that were autoclaved in water at 355°C. In pre-breakaway films they found results that indicated oxygen was diffusing along grain boundaries and they found results that indicated the reason for the post-breakaway corrosion

is the generation of new diffusion pathways in the previously protective oxide. The mechanism by which these new pathways are generated in post-breakaway film was not discussed. Importantly, however, Woolsey and Morris were able to measure the deuterium concentrations in the films. They found "unexpectedly high concentrations of deuterium".

Another piece of information regarding the dissipation of the protective properties of ZrO_2 became available as a result of a study [5] in which a thin film of Zr was deposited under ultrahigh vacuum conditions on the inside surface of a glass sphere. The film was then oxidized by exposing it to O_2 at $300^\circ C$ for twenty-four hours. The gas phase contacting the ZrO_2 was monitored with a (quadrupole) mass spectrometer and the pressure in this phase could be reduced to $\sim 7 \times 10^{-10}$ Torr with the system at $300^\circ C$. After the ZrO_2 film had been prepared, the vessel was evacuated, and then D_2 was dosed into the volume and allowed to adsorb onto ZrO_2 film for several minutes. The vessel was then evacuated until no D_2 , O_2 or D_2O could be detected in the gas phase with the mass spectrometer, thus leaving primarily D_2 adsorbed on the ZrO_2 surface. Then a valve was closed isolating the glass vessel and film from the vacuum system, but leaving it so that the gas phase of the vessel could be monitored with the mass spectrometer. It was found that all three components D_2 , O_2 and D_2O appeared in the gas phase, indicating that a spontaneous reaction was taking place between the D_2 and ZrO_2 at $300^\circ C$. The results were consistent with the following reaction mechanism



where (Ad) or (g) after a component indicates that the component is adsorbed or in the gas phase.

One of the principal steps in this possible reaction mechanism is the reaction of $D_2 (Ad)$ with ZrO_2 to produce metallic Zr and D_2O , ZrD_2 and O_2 . We note first of all that this reaction provides an explanation for the observations of Shannon [3]. Basically, the increased electrical conductivity of the ZrO_2 film that followed the exposure of ZrO_2 to hydrogen would, according to this reaction mechanism, result from the production of metallic Zr and would produce an increased electrical conductivity of the film. The decrease in electrical

conductivity of a $Zr - ZrO_2$ film that was observed to follow from increasing the concentrations of D_2O and O_2 in the gas phase would be the expected result since this would shift the equilibrium composition of the oxide layer to the left, giving a higher concentration of ZrO_2 and thus a lower electrical conductivity.

The observation of Woolsey and Morris of an "unexpectedly high concentration" of D_2 in the oxide that was found in their study would also be explained by this mechanism since deuterium would be bound to the metallic Zr that is produced in the reaction. Thus the concentration of D_2 in the film would be much higher than what would have been expected by the conventional mechanism [6] that suggests



and that the O^{2-} diffuses through the oxide to the metal-oxide interface where it reacts to produce thicker oxide.



The electrons diffuse back through the oxide to discharge the H^+ and produce hydrogen gas



that does not remain there, but leaves as hydrogen gas.

Although the mechanism proposed above in Eqs. 1–5 appears to explain the change in the hydrogen permeability of a ZrO_2 film that has been observed to follow from exposing the film to a reducing atmosphere and the observed hydrogen concentration within oxide films resulting from aqueous corrosion, the evidence supporting its existence was obtained with a thin film of ZrO_2 that was exposed to D_2 under high vacuum conditions [5]. The possibility exists that the oxygen participating in the reaction was only loosely bound (adsorbed) to the ZrO_2 rather than actually being chemically bound [7]. If this were the only oxygen that was involved in the reaction, it would only proceed to a very limited extent, since the concentration of surface bound oxygen is small.

A second way in which the mechanism proposed above can be examined is by considering what could be expected if a zirconium sample containing H_2 , either dissolved or as a hydride, were heated in an environment containing little hydrogen. If the mechanism of dissipation of the protective properties of the ZrO_2 layer discussed by Shannon is valid, one would expect to see only H_2 evolve into the gas phase.

Whereas if the mechanism in Eqs. 1–5 is valid, one would also expect to see H_2O in the gas phase that would have been produced when the hydrogen within the Zr diffused outward, came in contact with the ZrO_2 layer, and reacted to produce H_2O . One would expect the H_2O to come out of the layer because its solubility is very small; however, depending on where (i.e. how deep) within the ZrO_2 layer the H_2O was produced, it may not come out immediately, but it may be retained in the specimen until it builds up sufficiently to force its way out. Below we describe the results of a series of experiments in which this distinction between the conventional mechanism of the dissipation of the protective properties of ZrO_2 and the mechanism proposed in Eqs. 1–5 is used to identify the actual mechanism. The components produced in the gas phase when a ZrO_2 - Zr specimen containing hydrogen is heated in an atmosphere that is initially free of hydrogen is used as a means of distinguishing these mechanisms.

B. EXPERIMENTAL APPARATUS, MATERIALS AND PROCEDURES

1. Apparatus

There are two principal pieces of apparatus that were used in the study. One was a hydrogen tube furnace that allowed a Zr or Zr alloy specimen to be placed in a crucible, the crucible to be enclosed in a steel tube and inserted in an electrically heated furnace. The environment of the specimen could be controlled by flowing a gas into the tube. In the experiments we conducted, the gas admitted was either protium (99.99%) or deuterium (99.5%).

The second principal piece of apparatus used was a combined thermogravimetric analyzer and (quadrupole) mass spectrometer (*TGA-MS*) that are shown schematically in Fig. 1. A specimen that had been prepared in the hydrogen tube furnace was then placed in the crucible of the thermogravimetric analyzer. After closing the system, the crucible and specimen could be heated to 1500°C at a controlled rate while being weighed and the gas phase of the furnace monitored with the mass spectrometer. Helium was used as the carrier gas. It flowed continuously into the analyzer during a measurement. Its purity was 99.9999 %. The gas sample for the mass spectrometer was continuously drawn through a heated stainless steel tube that was connected to a vacuum pump. The pressure in this tube at the entry to the vacuum pump was set at approximately 13.3 *Pa*. A portion of the gas flowing through this tube was drawn through the mass spectrometer head by a second vacuum that was set at 0.133 *mPa*. Thus three important parameters could be measured simultaneously: the specimen weight at a particular temperature and ideally the presence of any gas component that was evolved from the specimen by the heating process. However, the presence of the *He* carrier gas masked any component that had a molecular weight near its value, e.g. D_2 .

2. Materials

Two types of materials were used in the study. One was *Zr* wire (1.0 mm diameter) that was obtained commercially and contained hafnium as an impurity but was otherwise 99.99 % pure. The other specimens were *Zr - 2.5% Nb*. They were taken from a sample of pressure tube. Specimens were cut from three perpendicular directions: one parallel to the longitudinal axis of the tube, one in the radial direction and one in the circumferential direction. Some of both types of specimen were then rolled to different thicknesses and specimens cut from them.

3. Specimen Preparations in H_2 Tube Furnace

After the experiment had been carefully weighed and enclosed in the tube, it was first rinsed with N_2 for thirty minutes and then with H_2 or D_2 . During this period, the furnace was pre-heated to the temperature chosen for a particular preparation. With the H_2 or D_2 flow rate maintained, the tube containing the specimen was then inserted in the pre-heated furnace and maintained there for the period chosen.

At the end of an experiment, the tube with the enclosed specimen was withdrawn from the furnace and allowed to cool to room temperature with the hydrogen flow continuing. After the tube had reached room temperature, the hydrogen flow was stopped and the specimen taken out and weighed again. They were then ready for examination in the thermogravimetric analyzer.

4. Examination of Specimens in the Thermogravimetric Analyzer-Mass Spectrometer

With the furnace open to the atmosphere, a *Zr* or *Zr* alloy specimen was placed in the ceramic crucible (Al_2O_3) of the *TGA-MS*. The furnace was then closed and the flow of the *He* into it was initiated. The system was rinsed with *He* for twenty minutes. During this period, the pressures of the sampling system and of the mass spectrometer were adjusted to the chosen values. After the rinse had been completed, the specimen was heated at the particular rate chosen to a maximum temperature of 1200°C. The flow rate of the *He* was constant during this process and was sufficiently high so that the pressure in the furnace was at all times above atmospheric.

C. RESULTS

The results obtained with the various specimen examined in this study are summarized in Table 1. The initial observations with several specimen was that they underwent a sudden weight loss when they were reheated in the thermogravimetric analyzer. The mass spectrometer was not employed in these cases. Because of our experience with the study of

Ref. 5, it was decided to examine the possibility that this weight loss was associated with water leaving the specimens. A series of experiments was then run with the mass spectrometer used in the analog mode. These specimens are listed in Table 1 as specimen III.0, IV.1, VI.1, VI.3. The indication for these studies was that indeed water was being evolved during the weight loss period. Then the mass spectrometer was changed to the digital mode and the appropriate sensitivity was set for each of the components monitored: O_2 , H_2 , H_2O , N_2 and D_2O . The results are described in Table 1 by listing the temperatures at which water and hydrogen were initially detected and the temperature at which each reached its maximums. These temperatures are not given for specimens III.0, IV.1, VI.1 and VI.3, since the settings of the mass spectrometer were chosen to have different values when the mass spectrometer was employed in the digital mode. However, for all of the other 22 specimens, the same settings of the mass spectrometer were employed; thus one may examine the results obtained with these latter specimen on a comparative basis. (The spectrums obtained from specimens, VI.5, VIII.2 and IX.3/3 were inadvertently destroyed.) To illustrate the conclusions that can be drawn from the results obtained with these 22 specimens, we have selected certain specimens for discussion.

The phase diagram for *Zr-H* system is shown in Fig. 2. As may be seen there, if a *Zr-H* specimen is brought into equilibrium with pure H_2 at one ATA pressure and 800°C , the *H/Zr* atomic ratio is approximately 1.6. Thus the specimen would consist partially of ZrH_2 and partially of *Zr*. One group of specimens was prepared under these conditions in the hydrogen furnace. This would mean that the maximum percentage weight increase from the hydriding reaction alone for these specimens would be 1.73%. As may be seen in Table 1, all of the specimens that were prepared under this condition had greater than 3% increase in their weight. We shall assume this to mean that some of the *Zr* reacted with oxygen, water or with nitrogen that would have been present in the hydrogen furnace as impurities to produce ZrO_2 and possibly ZrN [8, 9]. Thus the specimens that were prepared in a hydrogen atmosphere of 1 ATA and 800°C would be expected to have a significant layer of oxide and some nitride present on their surface and a hydride phase present inside when they were cooled to room temperature before being transferred to the thermogravimetric analyzer for further analysis.

The type of results obtained with *Zr* specimens prepared in this fashion is indicated by specimen VII.1, Figs. 3–6. In each of these figures, as in those for other specimens, the weight change of the sample is expressed as a percentage of the weight increase of the sample that occurred as a result of its processing in the hydrogen furnace. In Fig. 3, the oxygen content of the primarily *He* atmosphere in the thermogravimetric analyzer is shown.

Each of the other components monitored in the gas phase of thermogravimetric analyzer, i.e. H_2 , H_2O and N_2 are shown in Figs. 4–6, along with the percentage change in the weight.

The composition of the gas phase in the thermogravimetric analyzer was also measured when no *Zr* specimen was present. One set of results are shown in Figs. 7–10. The difference in the composition of the gas phase when the empty crucible was put through a *TGA-MS* cycle as compared with that when a specimen and the crucible were put through the same cycle in the *TGA-MS* indicates the effect of a specimen on the gas phase of the *TGA-MS* during the analysis of a specimen. Thus comparing the results in Fig. 3 and Fig. 7 indicates that specimen VII.1 was taking up O_2 throughout the period in the *TGA-MS*, but that hydrogen was coming from the sample in the temperature range from 900°C to 1100°C as may be seen by comparing Figs. 4 and 8. Also water was coming from the specimen in the temperature range from 800°C to 1200°C (see Figs. 5 and 9). Small amounts of N_2 were observed to be given up by the specimen throughout the temperature range (see Figs. 6 and 10).

One of the possible interpretations of these results is that when the specimen is placed in the *He* atmosphere of the *TGA-MS* and heated, the hydrogen that had been taken-up by the specimen in the hydrogen furnace diffuses toward the surface, encounters the oxide and reacts to produce water. The outer oxide layer resists the release of the water until its build up is sufficient to break through the oxide. Then the water comes out rapidly. According to Ref. 5, the reaction between ZrO_2 and hydrogen takes place readily at 300°C and more rapidly at higher temperatures.

To examine this possibility further, another *Zr* specimen, VI.6, was prepared in the hydrogen furnace under similar conditions as those used for VII.1, but for specimen VI.6, D_2 was used in the furnace at the same temperature, pressure and for the same period of time as was used with VII.1 when it was exposed to H_2 in the furnace. The weight gain in the case of VI.6 was larger than 4.47%. The maximum that could be attributed to the formation of ZrD_2 would be 2.17%. The difference, 2.3%, would approximate the weight gain of the specimen due to the formation of the oxide and nitride. For specimen VII.1, this difference was approximately 2.0%. Thus the oxide layers of specimens VI.6 and VII.1 would be expected to be of the same magnitude.

If the water forms as a result of the hydrogen absorbed into the bulk of the specimen reacting with the oxide, then one would expect D_2O to appear in the gas phase when VI.6 specimen was examined in the *TGA-MS*. The results obtained are shown in Figs. 11–15, the most important of which is Fig. 14. The other results are similar to those seen in Figs. 3–6. As may be seen in Fig. 14, D_2O was produced in the gas phase. Thus it would appear that the hydrogen put into the sample does react with oxygen to produce the water, and it is not any

impurity H_2 that reacts to produce water. The question that we now wish to address is whether the oxygen for this reaction comes from the oxide. To examine this possibility, specimens were prepared which had a reduced amount of oxide as compared with specimen VI.6.

Before proceeding and for future reference, we first show that the $Zr - 2.5\% Nb$ specimen behaved in a similar fashion when prepared in the same manner. The results for one such specimen, XIX.3, is shown in Figs. 16–19. (For the $Zr - 2.5\% Nb$ samples, the first Arabic numeral in their number denotes the direction at which the specimen was cut from the pressure tube sample. No significant variation was found with this variable.) It was exposed to hydrogen at one ATA and 800°C for five hours and had a weight gain of 3.91%. This specimen had an initial weight gain when examined in the TGA-MS. By comparing the O_2 content of the empty crucible experiment with the results in Fig. 16, one finds that the impurity O_2 was probably reacting with the specimen throughout most of the temperature range, and this was responsible for the initial weight gain of the specimen. A similar comparison indicates H_2 and H_2O were emitted by the specimen and they were responsible for the weight loss of the specimen. Small amounts of N_2 appears to have been emitted from the specimen in the temperature range from room to 400°C and then during the period of weight gain, 400°C to 800°C, both N_2 and O_2 were taken-up by the specimen.

To determine if the oxygen in the oxide layer is participating in the reaction that produces the H_2O , we prepared both Zr and $Zr - 2.5\% Nb$ specimens under conditions that would be expected to produce a smaller amount of oxide on the sample when it entered the TGA-MS. If one examines the composition isotherms shown in Fig. 2, then one finds that for specimens prepared at a hydrogen pressure of one ATA, the amount of hydride increases as the temperature is lowered. Thus at 500°C and this pressure, one finds (if the composition isotherm is extrapolated) that specimens brought to equilibrium would consist of pure hydride, ZrH_2 and therefore no oxide. However, there is no assurance that the specimens were in equilibrium; thus if specimens were prepared at even lower temperatures, oxide would perhaps be reduced further than for those prepared at 500°C. We have prepared specimens at a hydrogen pressure of one ATA and temperatures of 500°C and 300°C.

The results obtained for a Zr sample, IX.3, are shown in Figs. 20–23. It was exposed to hydrogen at one ATA and 500°C for five hours, and had a weight gain of 2.7% which is less than those samples prepared at 800°C. This suggests that, as expected, it had more hydride and less oxide. Note from Table 1 that for the samples prepared at 500°C, a weight gain of this amount is approximately an equilibrium value. When the hydrided sample was placed in the (almost) hydrogen free environment of the TGA-MS and heated, the oxygen appears to have reacted with the sample throughout the temperature range. Perhaps this was because

the hydride on the surface decomposed allowing the *Zr* to react. The O_2 concentration in this experiment was less than that of the empty crucible experiment throughout this temperature range. The hydrogen concentration was not significantly different than the background until very high temperatures were reached. The N_2 appears to have reacted with the specimen throughout the temperature range. There was no significant weight change of the specimen until approximately 900°C at which time the weight rose sharply and then decreased even more rapidly. Since only H_2O was leaving the specimen during this latter period, it must be responsible for the weight decrease. However, it is important to compare the amount of H_2O coming from this *Zr* specimen with that from a *Zr* specimen prepared to have more oxide, such as specimen VII.1. This latter specimen was prepared at 800°C and thus would be expected to have slightly less hydride and more oxide. As may be seen by comparing Fig. 5 with Fig. 22, the specimen having the most oxide produced the most H_2O . This suggests that indeed the oxygen for the production of water is coming from the oxide of the specimen.

To examine this further, a *Zr* - 2.5% *Nb* sample, XVIII.3/4, was prepared at an even lower temperature, 300°C . When cut from a pressure tube, it was 1.5 mm in thickness. It was then rolled to a thickness of 0.1 mm. This reduces the time required for the specimen to be brought to equilibrium at the lower temperature. After being rolled, specimen XVIII.3/4 was exposed to hydrogen at one ATA and 300°C for a period of 300 hours. This gave rise to a 1.07% increase in sample weight. If the sample had been fully hydrided, the sample weight could have increased by as much as 2.17%. Thus all of the weight increase could have been from hydrogen absorption; no doubt there was some oxide.

By comparison with sample XIX.3 that had a weight increase of 3.91% as a result of being exposed to hydrogen at one ATA, 800°C , one could certainly expect that sample XVIII.3/4 had less oxide on its surface than did sample XIX.3 when the samples entered the TGA-MS. The results obtained in the TGA-MS and, in particular, the water generated by the two samples are quite different as may be seen by comparing Figs. 18 and 26 with the background, Fig. 9. For the sample having the least oxide (XVIII.3/4), one observes that up to 800°C in the TGA-MS the H_2O content is not significantly above the background but that it then rises to a maximum at approximately 900°C that is approximately four times the background. Whereas for the more fully oxidized specimen (XIX.3), the H_2O content becomes greater than the background at approximately 750°C and at 800°C is approximately twelve times greater than the background. The water content then rises to a maximum that is approximately seventeen times greater than the background. Clearly then the specimen having the most oxide is also the one that produces the most H_2O when the hydrogen is

desorbed. This result supports the suggestion that as the hydrogen diffuses towards the surface of the specimen that it encounter the oxide and reacts to produce H_2O .

Since O_2 is always present in the gas phase of the *TGA-MS*, it is possible that this O_2 reacts with the impurity H_2 to be partially responsible for the H_2O that is observed in the gas phase when a *Zr* or *Zr - 2.5% Nb* sample that has been exposed to H_2 in the furnace is examined in the *TGA-MS*. This possibility was examined further by examining in the *TGA-MS* a *Zr* sample, XXI, that had not been exposed to hydrogen in the furnace. The results obtained with this untreated sample are shown in Figs. 28–31. As may be seen by comparing Fig. 28 with O_2 content in the empty crucible experiment, Fig. 7, O_2 was taken-up by the specimen. Also the impurity H_2 and impurity N_2 was taken-up by the untreated specimen. However, no significant H_2O was generated by the untreated *Zr* sample. The H_2O content is less than or equal to the background H_2O at all times. It should also be noted that the weight of the *Zr* specimen continued to increase throughout the temperature range. This is consistent with the observed concentrations of O_2 , H_2 , H_2O and N_2 since if there was any change in their concentration it was a decrease.

A similar result was obtained with a *Zr - 2.5% Nb* sample, XX, that was examined in the *TGA-MS* without exposing it to the H_2 in the furnace. The results are shown in Figs. 32–35. If there was any change in the concentration of O_2 , H_2 , H_2O or N_2 in the gas phase of the *TGA-MS* when the *Zr - 2.5% Nb* specimen was present as compared to the empty crucible experiment, it was a decrease. This indicates that these components were being taken-up by the specimen. The weight increase of this specimen was continuous, except at one point where it decreased by 0.1 mg.

The fact that the specimens that were not exposed to H_2 at elevated temperatures did not produce any water nor did they show significant sudden weight loss, when they were examined in the *TGA-MS*, indicates that the impurity O_2 and impurity H_2 were not responsible for the water production observed to come from the specimens that did have hydrogen present when they were examined in the *TGA-MS* and that the weight loss of the specimen is produced by the water generated by the reaction between the hydrogen present in the *Zr* and the oxide.

D. DISCUSSION AND CONCLUSION

When the above results are considered along with the results of Ref. 4, it appears that reaction mechanism in Eqs. 1–5 can be used to explain both sets of observations. Suppose a *Zr* or *Zr - 2.5% Nb* specimen is prepared so that it contains hydrogen within either in physical solution or as a hydride and ZrO_2 on the outside surface. Also suppose that the specimen is then heated in an environment that contains (ideally) no hydrogen. The results

discussed above indicate that as the hydrogen diffuses to the oxide, it reacts with the oxide to produce water, in agreement with the reaction mechanism in Eqs. 1–5. What happens to the water once it has formed depends on the state of the oxide. If it is porous, then it can simply evaporate out; however, if the oxide is fully intact, then it may be necessary for the water to build up until it suddenly breaks out as it did for the specimen shown in Figs. 5, 13, 14, 18 and 22. This release of the water gives rise to a sudden decrease in the weight of the specimen.

That it is the hydrogen present inside the sample that participates in the reaction to produce the H_2O is indicated by the experiments in which D_2 was first absorbed into the Zr . This was found to give rise to the production of D_2O as seen in Fig. 14.

The possibility that it is the impurity oxygen that reacts with hydrogen coming from the specimen was examined in several ways. A series of specimens were prepared so that they had progressively less oxide. The indication was that this led to progressively less H_2O being produced. The two extremes are shown in Figs. 18 and 26. There were several times more water produced by the specimen that had the most oxide. This conclusion is supported by the results that were obtained when samples of Zr and $Zr - 2.5\% Nb$ that had not been exposed to H_2 in the furnace before they were examined in the $TGA-MS$. There was no significant H_2O production by these samples (see Figs. 30 and 34). Thus it could not be the impurity O_2 and impurity H_2 that was responsible for the H_2O production observed when the samples containing hydrogen were exposed in the $TGA-MS$.

The weight loss of the specimen appears to result from the H_2O leaving the sample. When the samples that had not been exposed to hydrogen in the furnace were examined with the $TGA-MS$ their weight was observed to steadily increase, as seen in Figs. 33 and 34, indicating a reaction of these specimens with the impurities N_2 , O_2 , H_2 and H_2O . For a sample that had been exposed to hydrogen in the furnace and then examined in the $TGA-MS$, these reactions were presumably taking place as well. The reaction of the hydrogen with the oxide to produce water would have had the opposite effect on the sample weight than would the reaction with the impurities. Thus depending on which of these reactions dominates determines the shape of the sample weight curve.

This is not a good experiment to determine the temperature dependence of the reaction between hydrogen and ZrO_2 because water may not appear in the gas phase immediately. Depending where the water forms within the specimen, it may have difficulty in escaping into the gas phase where it could be detected.

The results of Ref. [5] indicate that the reaction in Eqs. 1–5 occurs at 300°C and more rapidly at 350°C. The lowest temperature at which H_2O was detected in the gas phase of these experiments was when the specimen was at 500°C; however, the water would have been formed at a lower temperature since the water would have had to flow to the mass spectrometer head from its source in the furnace of the *TGA-MS* before it could have been detected.

The conventional mechanism for the corrosion of *Zr* could not be used to explain the observed production of water in these experiments nor the weight loss of these specimens. Further, the magnitude of the weight loss is much too large to be produced by any adsorbed O_2 [7].

The fact that the mechanism given in Eqs. 1–5 is supported by the results of two completely different sets of experiments [5] and that it can be used to explain the results of previous investigations that had been used as the experimental support for the conventional mechanism provides substantial experimental support for the new mechanism.

E. FUTURE WORK

The experimental results reported herein and those of Ref. [4] provide substantial support for the existence of the reaction mechanism given in Eqs. 1–5. However, if this mechanism is to be used to predict the corrosion rate and hydrogen pick-up rate of *Zr* alloy pressure tubes, it is necessary to establish the quantitative parameters describing the reaction. One of the first steps toward this goal would be to establish the equilibrium surface concentrations of *Zr*, ZrO_2 and ZrH_2 when the surface is exposed to a particular gaseous atmosphere at a particular temperature. Knowledge of this composition and of how the surface composition changes as a function of temperature and composition of the gas phase would serve as a basis for study of hydrogen permeation of ZrO_2 . If this could be done in terms of the relevant thermodynamic properties, such as the chemical potentials, then one would have a basis for relating the measurements to in-service conditions.

TABLE 1

Hydrogen Absorption/Desorption From Zr and Zr - 2.5% Nb

No.	III.0	IV.1	IV.2	IV.3	IV.4	VI.1	VI.2	VI.3
Sample	Zr (W)	Zr (W)	Zr (W)	Zr (W)	Zr (W)	Zr (W)	Zr (W)	Zr (W)
Absorpt. Temp. °C	700	800	800	800	800	800	800	800
Absorpt. Time	5 hrs.	15 min.	15 min.	15 min.	15 min.	5 hrs.	5 hrs.	5 hrs.
Furnace Flow Rate	High	High	High	High	High	Low	Low	Low
Gas	H ₂	H ₂	H ₂	H ₂	H ₂	D ₂	D ₂	D ₂
Surface Area/mm ²	70.05	37.38	32.04	33.30	68.17	35.19	34.87	35.81
Wt. Before Adsorpt./mg	111.57	58.22	49.54	51.73	108.50	54.90	54.30	55.92
Wt. After Adsorpt./mg	115.66	60.82	51.80	54.32	113.14	57.21	56.88	58.79
Wt. Increase / mg.	4.09	2.60	2.26	2.59	4.64	2.31	2.58	2.64
Wt. Increase %	3.54	4.27	4.36	4.77	4.11	4.04	4.54	4.51
TG Wt. Loss-Start °C	880	940	790	850	350 800	800	750	850
Wt. Loss Min. °C	1130	1015	1000	1015	400 950	1150	1100	1050
Rolled Thickness/mm	-	-	-	-	-	-	-	-
Water: Start. °C	-	-	500	-	500	-	800**	-
Max. at °C	-	-	970	-	930	-	1020	-
Gas Peak	-	-	H ₂	-	H ₂	-	-	-
Start at °C	-	-	550 1100	-	800	-	-	-
Max. at °C	-	-	600 1115	-	915	-	-	-
TG Flow Rate (Helium)	40	50	100	100	100	100	100	50
TG Ht. Rate (°C Min.)	30	30	30	30	30	30	30	30

* Zr (W) R: A Zr wire (1 mm Dia) that was rolled.

† Zr (Nb) R: A Zr - 2.5% Nb pressure tube sample, rolled.

** D₂O

TABLE 1

Hydrogen Absorption/Desorption From Zr and Zr - 2.5% Nb

No.	VI.4	VI.5	VI.6	VI.6	VII.1	VIII.2	VIII.3	IX.3
Sample	Zr (W)	Zr (W)	Zr (W)		Zr (W)	Zr (W)	Zr (W)	Zr (W)
Absorpt. Temp. °C	800	800	800		800	500	500	500
Absorpt. Time	5 hrs.	5 hrs.	5 hrs.		5 hrs.	26.5 hrs.	26.5 hrs.	36 hrs.
Furnace Flow Rate	Low	Low	Low		Low	Low	Low	Low
Gas	D ₂	D ₂	D ₂		H ₂	H ₂	H ₂	H ₂
Surface Area/mm ²	41.78	36.13	37.07		37.70	42.41	109.96	111.84
Wt. Before Adsorpt./mg	65.20	56.40	57.70		58.68	66.26	176.51	179.70
Wt. After Adsorpt./mg	68.61	59.20	60.40		60.93	68.15	181.25	184.70
Wt. Increase / mg.	3.41	2.80	2.70		2.25	1.89	4.74	5.00
Wt. Increase %	4.97	4.73	4.47		3.69	2.77	2.62	2.70
TG Wt. Loss-Start °C	850	840	800		800	800	800	1040
Wt. Loss Min. °C	1100	1000	1125		1100	900	1120	1180
Rolled Thickness/mm	-	-	-		-	-	-	-
Water: Start at °C	750**	-	850**	650	550	-	500	500
Max. at °C	925	-	1160	950	940	-	900	860
Gas Peak	-	-	H ₂	H ₂	H ₂	-	H ₂	H ₂
Start at °C	-	-	-	550 850	700 840	-	950	1025
Max. at °C	-	-	-	600 1000	750 1000	-	1170	1060
TG Flow Rate (Helium)	100	30	100	-	100	100	100	100
TG Ht. Rate (°C Min.)	30	15	45	-	30	30	30	30

* Zr (W) R: A Zr wire (1 mm Dia) that was rolled.

† Zr (Nb) R: A Zr - 2.5% Nb pressure tube sample, rolled.

** D₂O

TABLE 1

Hydrogen Absorption/Desorption From Zr and Zr - 2.5% Nb

No.	IX. 3/2	IX. 3/3	XV. 1/2	XV. 4/1	XVI. 1/2	XVII. 1/1	XVII. 1/2	XVII. 3/2
Sample	Zr (W)	Zr (W)	Zr (Nb) R [†]	Zr (W) R [*]	Zr (Nb) R [†]	Zr (Nb) R [†]	Zr (Nb) R [†]	Zr (Nb) R [†]
Absorpt. Temp. °C	500	500	500	500	500	500	500	500
Absorpt. Time	36 hrs.	36 hrs.	31 min.	31 min.	3 hrs.	6 hrs.	6 hrs.	6 hrs.
Furnace Flow Rate	Low	Low	Low	Low	Low	Low	Low	Low
Gas	H ₂	H ₂	H ₂	H ₂	H ₂	H ₂	H ₂	H ₂
Surface Area/mm ²	110.58	102.42	238.88	145.02	278.65	92.60	73.92	209.83
Wt. Before Adsorpt./mg	177.46	164.24	75.78	58.35	88.44	56.60	44.95	66.53
Wt. After Adsorpt./mg	182.41	168.86	77.71	59.43	90.15	58.20	46.22	68.56
Wt. Increase / mg.	4.95	4.63	1.93	1.08	1.71	1.60	1.27	2.03
Wt. Increase %	2.71	2.74	2.48	1.82	1.90	2.75	2.75	2.96
TG Wt. Loss-Start °C	770 1070	825	900	-	-	1000	1050	650
Wt. Loss Min. °C	840 1180	925	965	-	-	1050	1150	-
Rolled Thickness/mm	-	-	0.10	0.13	0.10	0.20	0.20	0.10
Water: Start at °C	700	-	700	-	-	600	600	600
Max. at °C	1100	-	920	-	-	950	950	1000
Gas Peak	H ₂	-	H ₂	-	-	H ₂	H ₂	H ₂
Start at °C	950 1075	-	750	-	-	900	900	800
Max. at °C	975 1125	-	940	-	-	1025	1025	1050
TG Flow Rate (Helium)	100	100	100	100	100	100	100	100
TG Ht. Rate (°C Min.)	30	30	30	30	45	45	45	45

* Zr (W) R: A Zr wire (1 mm Dia) that was rolled.

† Zr (Nb) R: A Zr - 2.5% Nb pressure tube sample, rolled.

TABLE 1

Hydrogen Absorption/Desorption From Zr and Zr - 2.5% Nb

No.	XVII. 4/1 R	XVIII.3/4	XIX.2	XIX.3	XX	XXI		
Sample	Zr (W)	Zr (Nb) R [†]	Zr (Nb)	Zr (Nb)	Zr (Nb)	Zr (W)		
Absorpt. Temp. °C	500	300	800	800	-	-		
Absorpt. Time	6 hrs.	300 hrs.	5 hrs.	5 hrs.	-	-		
Furnace Flow Rate	Low	Low	Low	Low	-	-		
Gas	H ₂	H ₂	H ₂	H ₂	-	-		
Surface Area/mm ²	146.61	211	62.70	94.01	76.67	102.10		
Wt. Before Adsorpt./mg	58.99	66.9	159.25	166.3	162.64	163.61		
Wt. After Adsorpt./mg	60.96	67.59	164.84	173.07	-	-		
Wt. Increase / mg.	1.97	0.69	5.59	6.77	-	-		
Wt. Increase %	3.23	1.02	3.39	3.91	-	-		
TG Wt. Loss-Start °C	-	-	800	800	-	-		
Wt. Loss Min. °C	-	-	1150	1175	-	-		
Rolled Thickness/mm	0.13	0.10	-	-	-	-		
Water: Start at °C	500	650	600	650	1000	-		
Max. at °C	900	900	900	900	1100	-		
Gas Peak	H ₂	H ₂	H ₂	H ₂	Untreated	Untreated		
Start at °C	800	800	950	750	-	-		
Max. at °C	975	975	1000	950	-	-		
TG Flow Rate (Helium)	100	100	100	100	100	100		
TG Ht. Rate (°C Min.)	30	45	45	45	45	45		

* Zr (W) R: A Zr wire (1 mm Dia) that was rolled.

† Zr (Nb) R: A Zr - 2.5% Nb pressure tube sample, rolled.

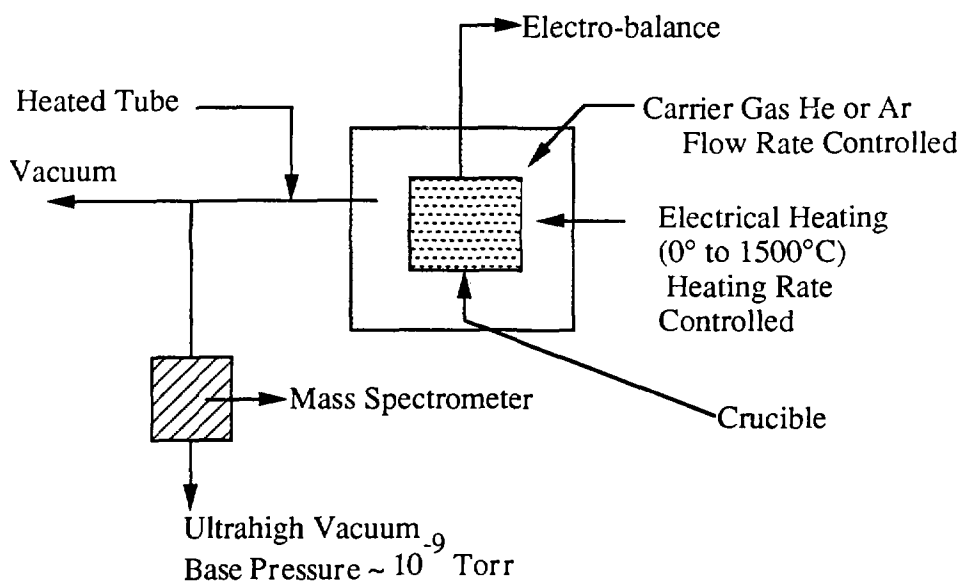


Figure 1: Schematic of the thermogravimetric analyzer and mass spectrometer used in the study.

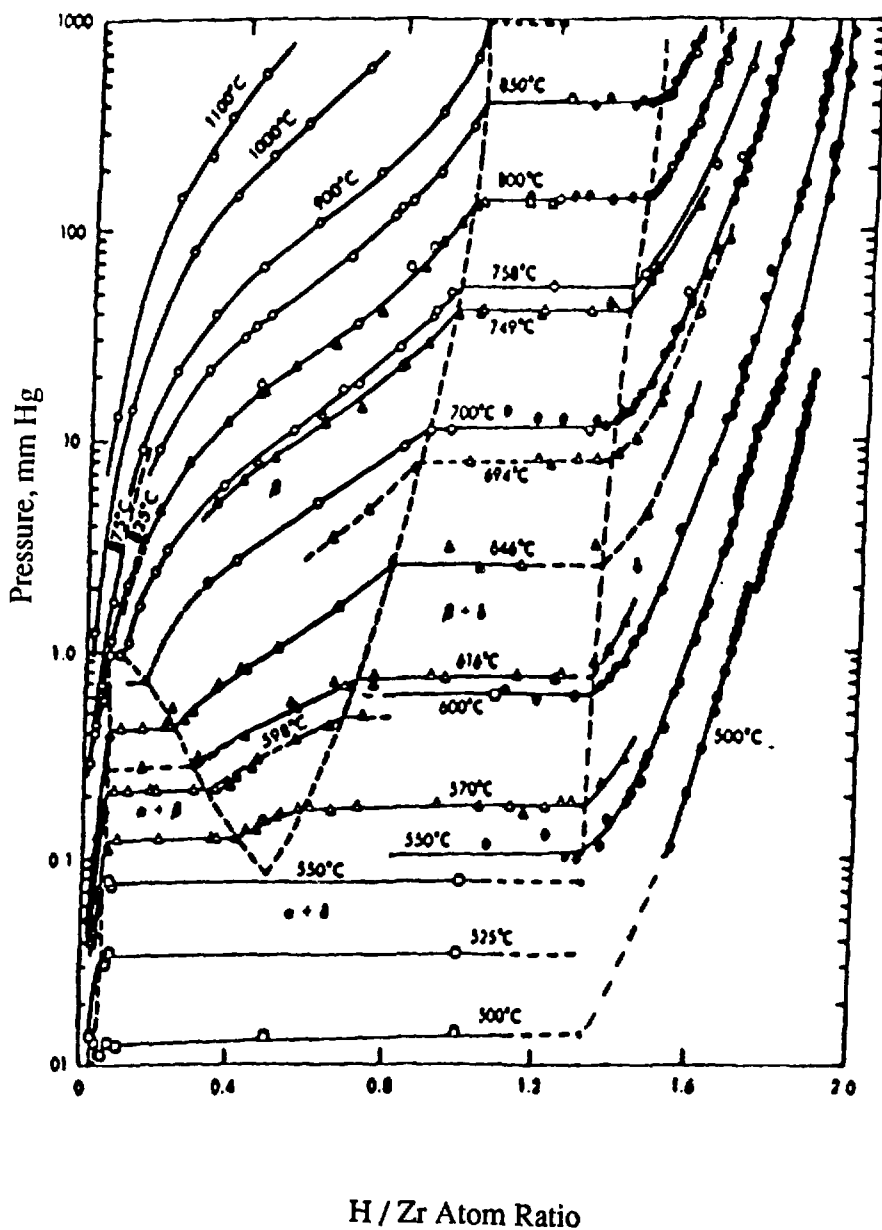


Figure 2: Pressure - composition isotherms for Zr - H systems, from Ref. 10.

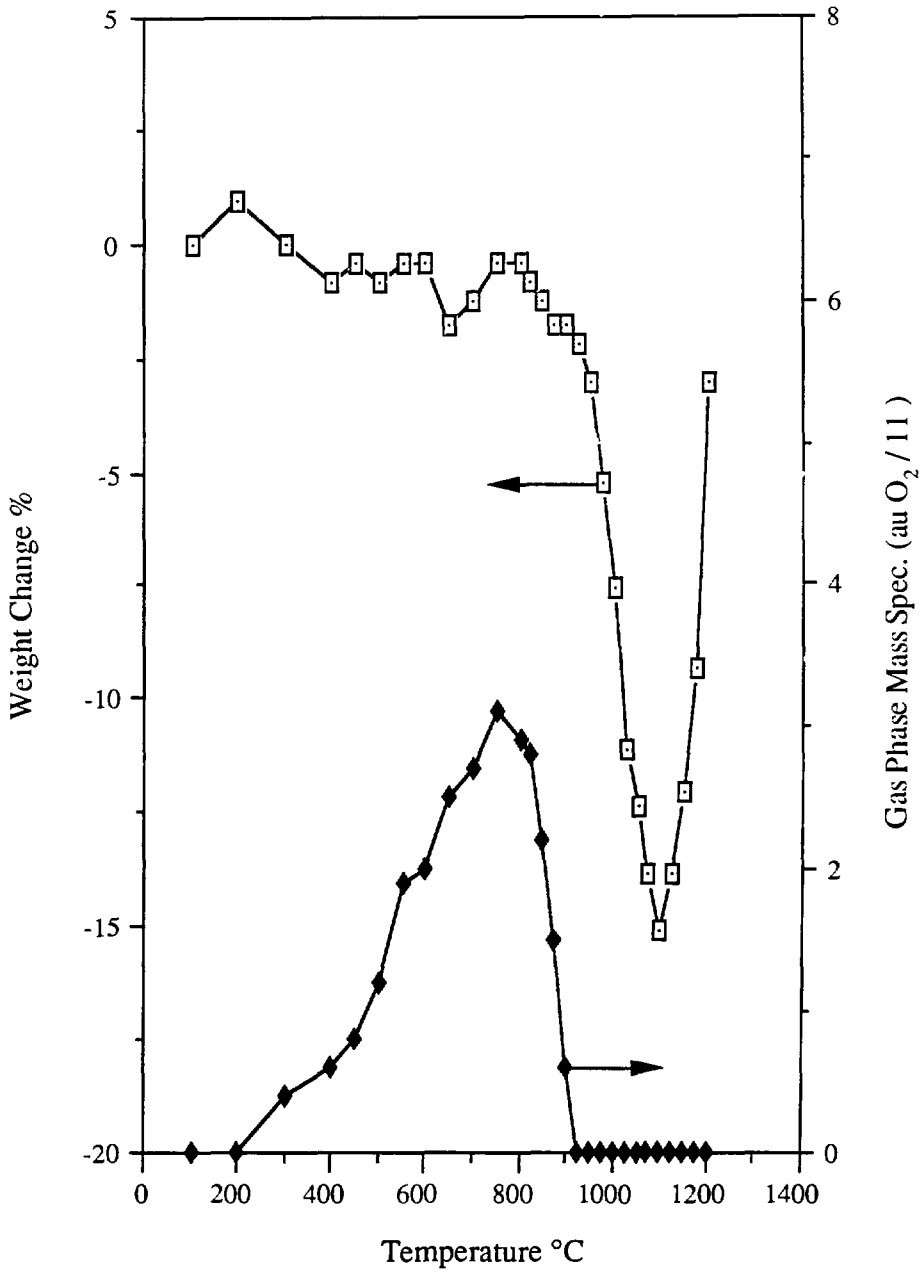


Figure 3: Percentage weight change and O₂ detected in the atmosphere of the Zr specimen VII.1 when examined in the thermogravimetric analyzer.

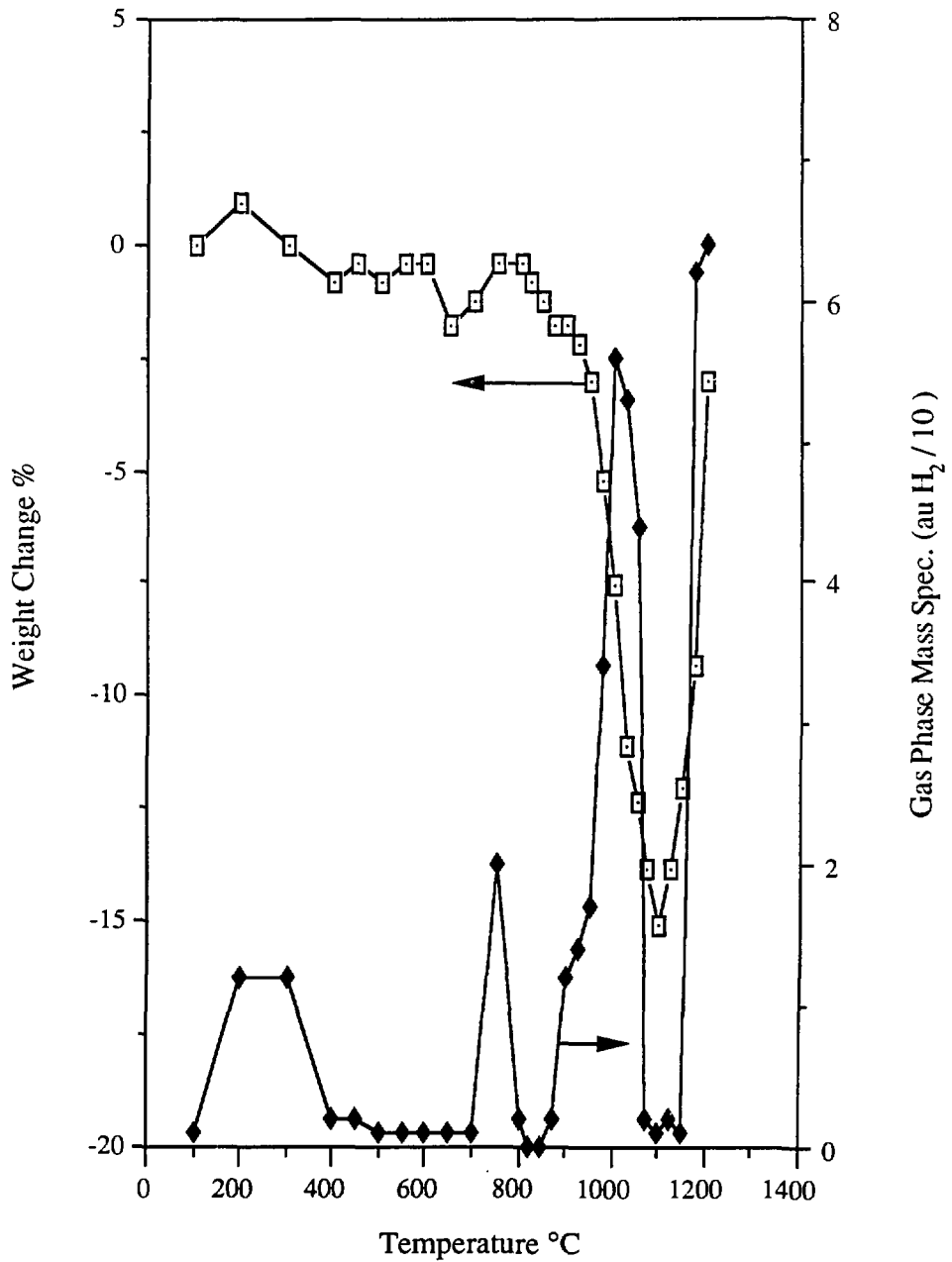


Figure 4: Percentage weight change and H₂ detected in the atmosphere of the Zr specimen VII.1 when examined in the thermogravimetric analyzer.

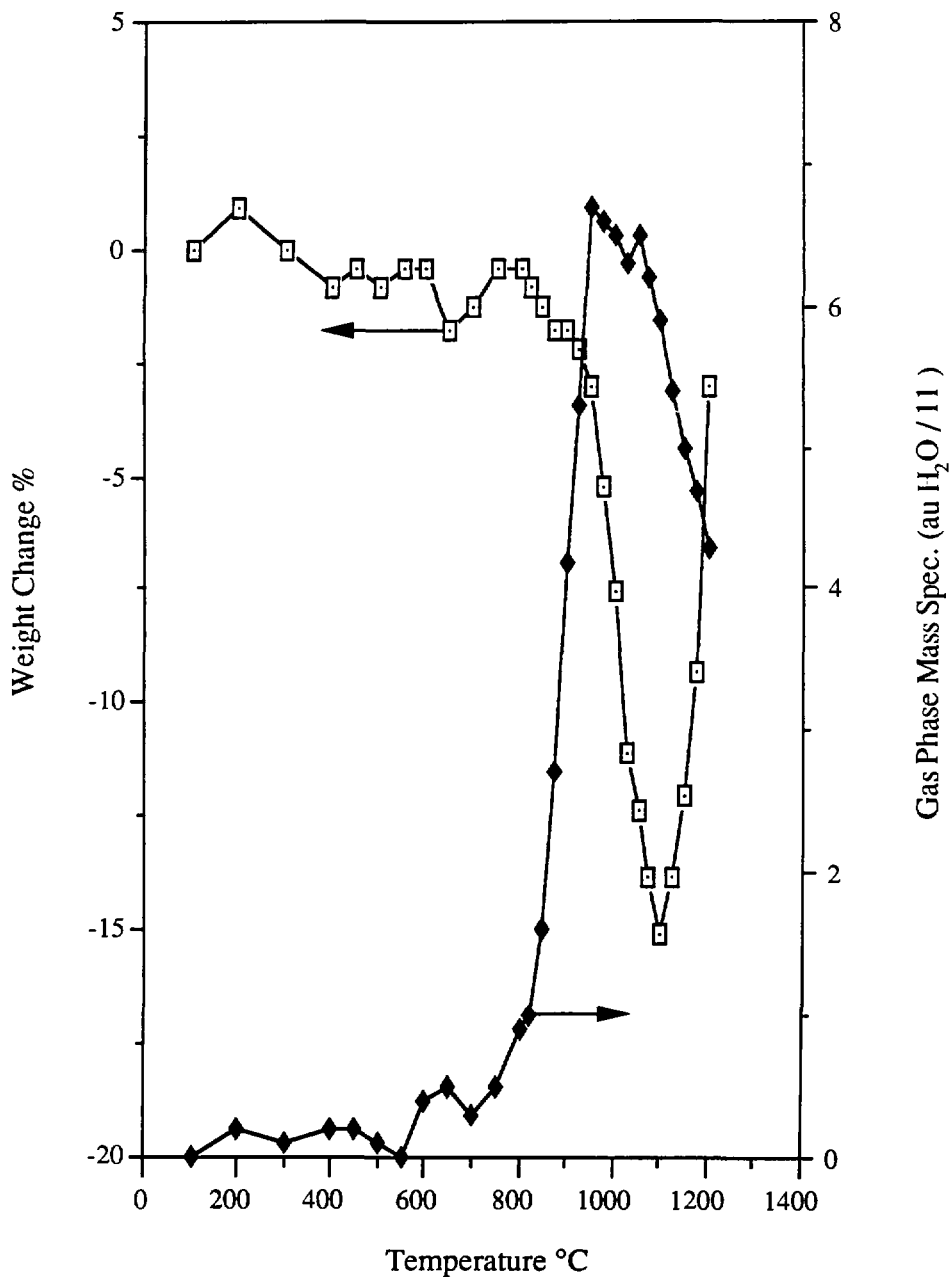


Figure 5: Percentage weight change and H₂O detected in the atmosphere of the Zr specimen VII.1 when examined in the thermogravimetric analyzer.

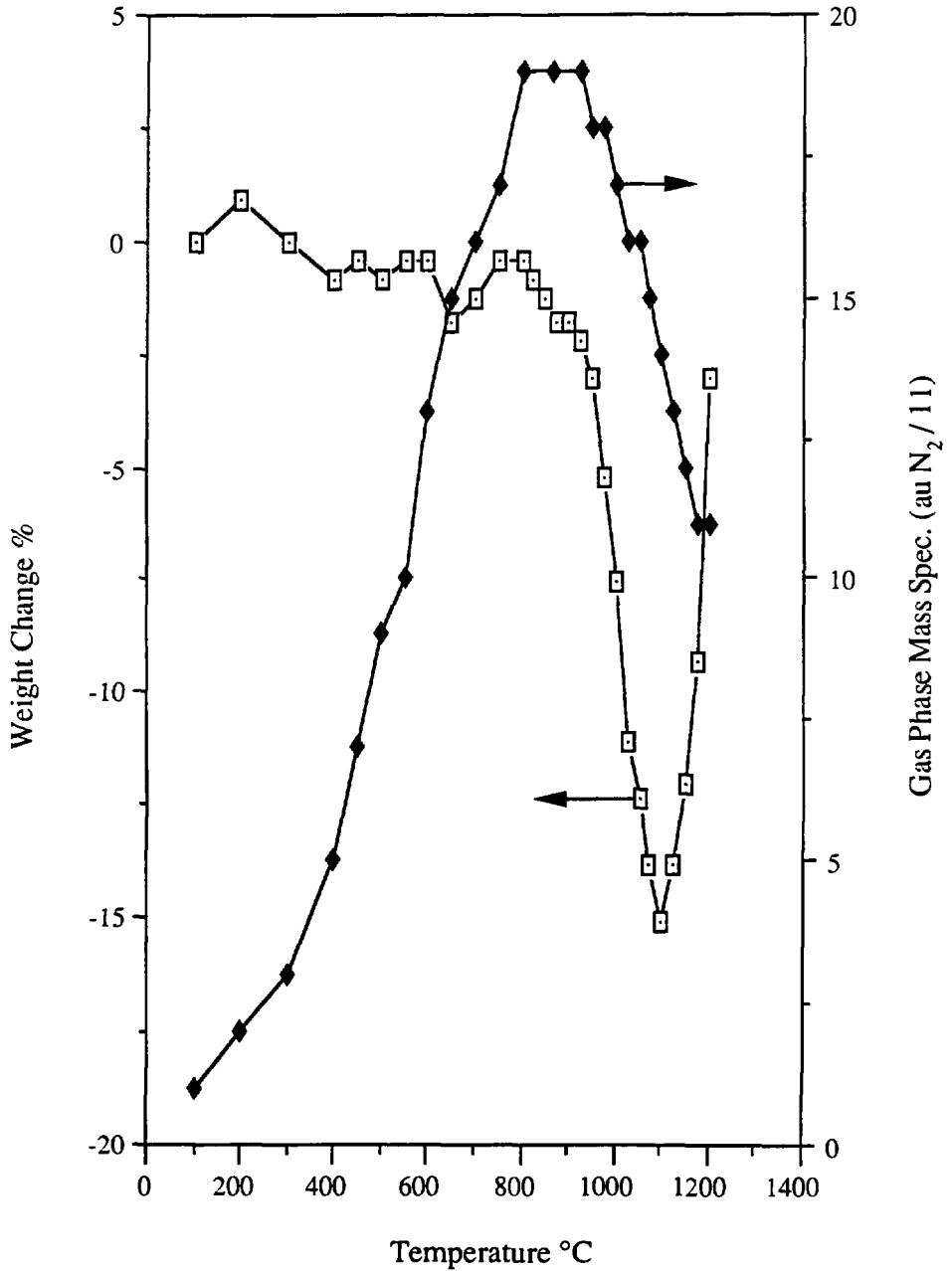


Figure 6: Percentage weight change and N₂ detected in the atmosphere of the Zr specimen VII.1 when examined in the thermogravimetric analyzer.

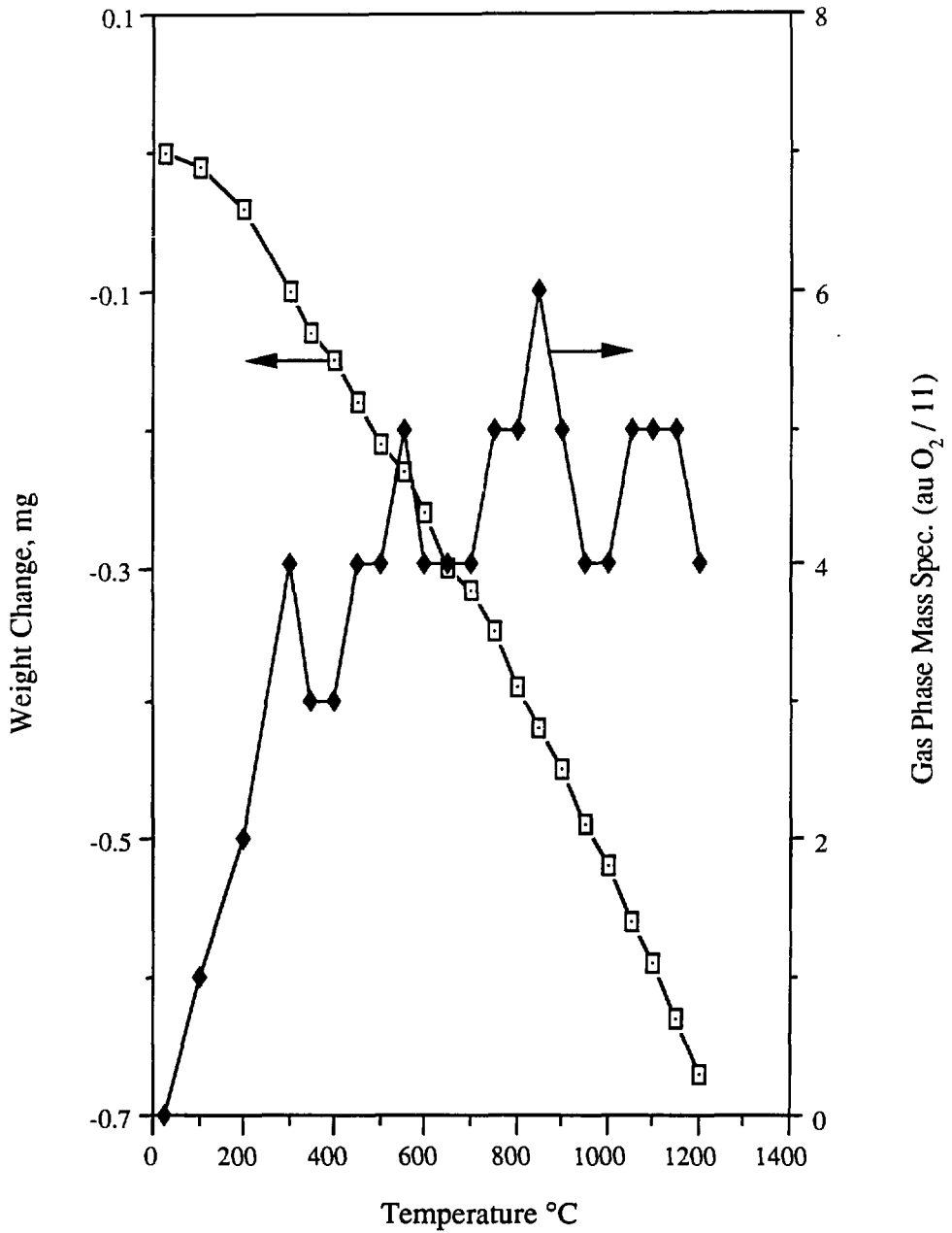


Figure 7: Weight change of the empty crucible and O₂ detected in the atmosphere of the thermogravimetric analyzer.

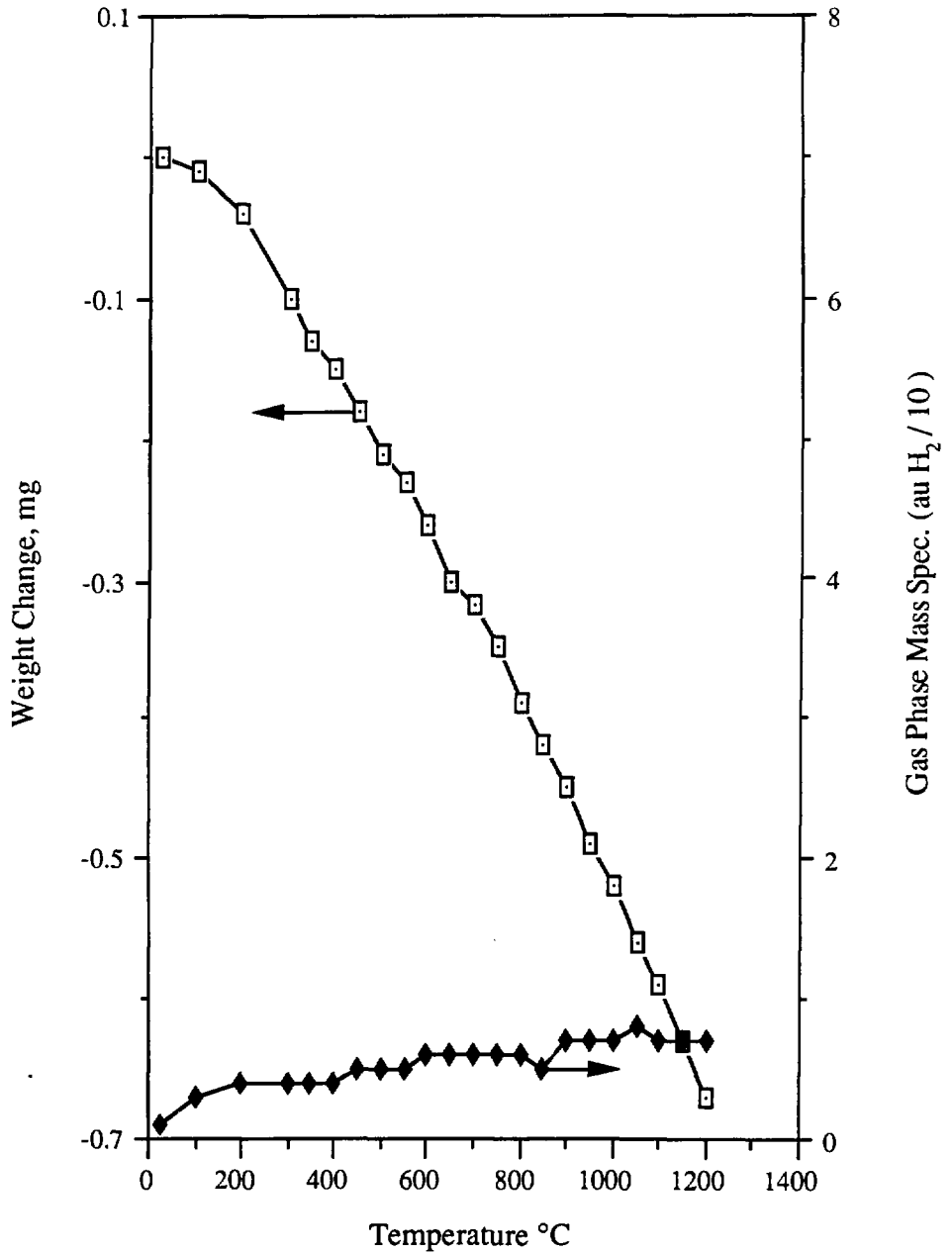


Figure 8: Weight change of the empty crucible and H₂ detected in the atmosphere of the thermogravimetric analyzer.

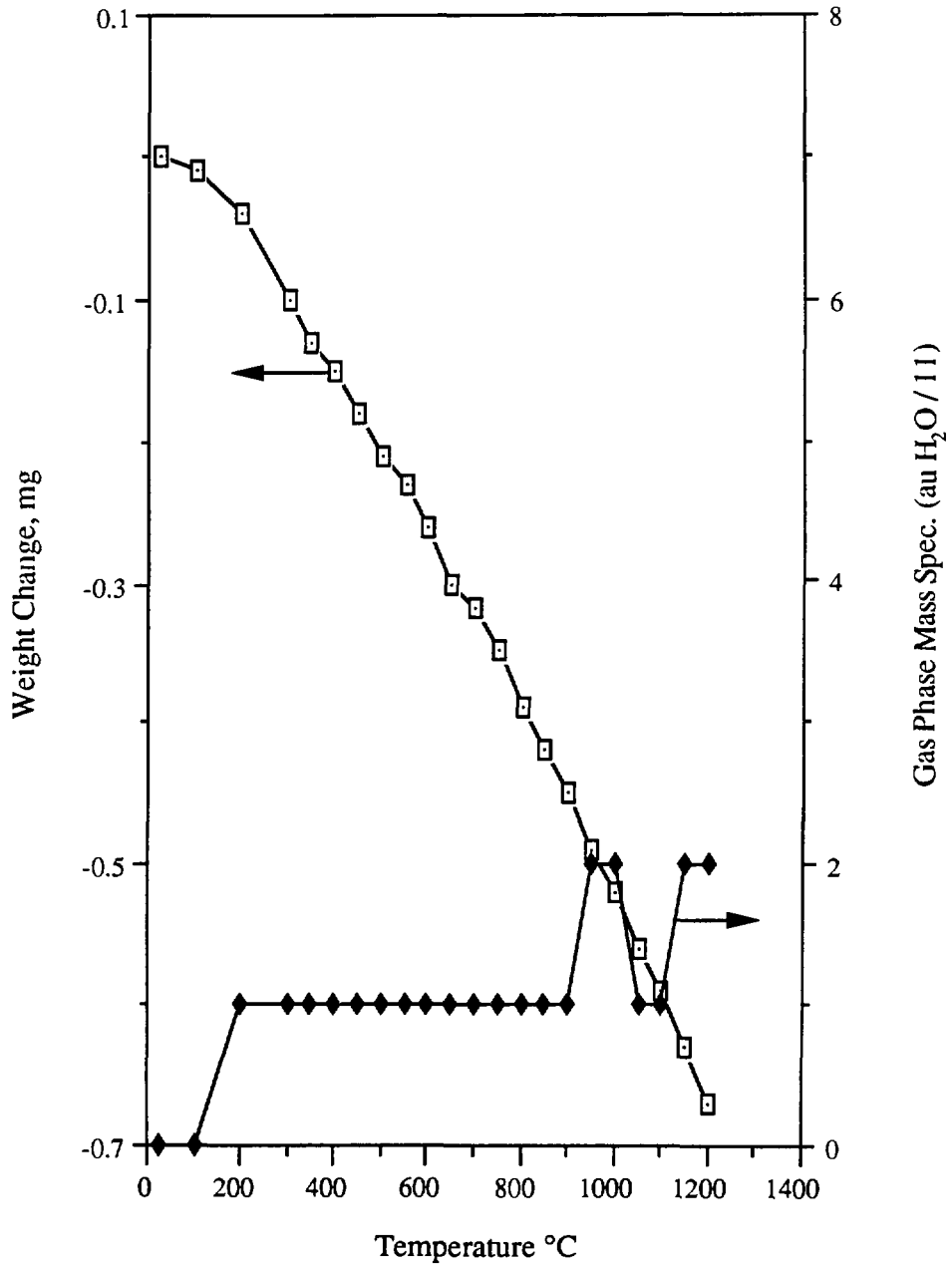


Figure 9: Weight change of the empty crucible and H₂O detected in the atmosphere of the thermogravimetric analyzer.

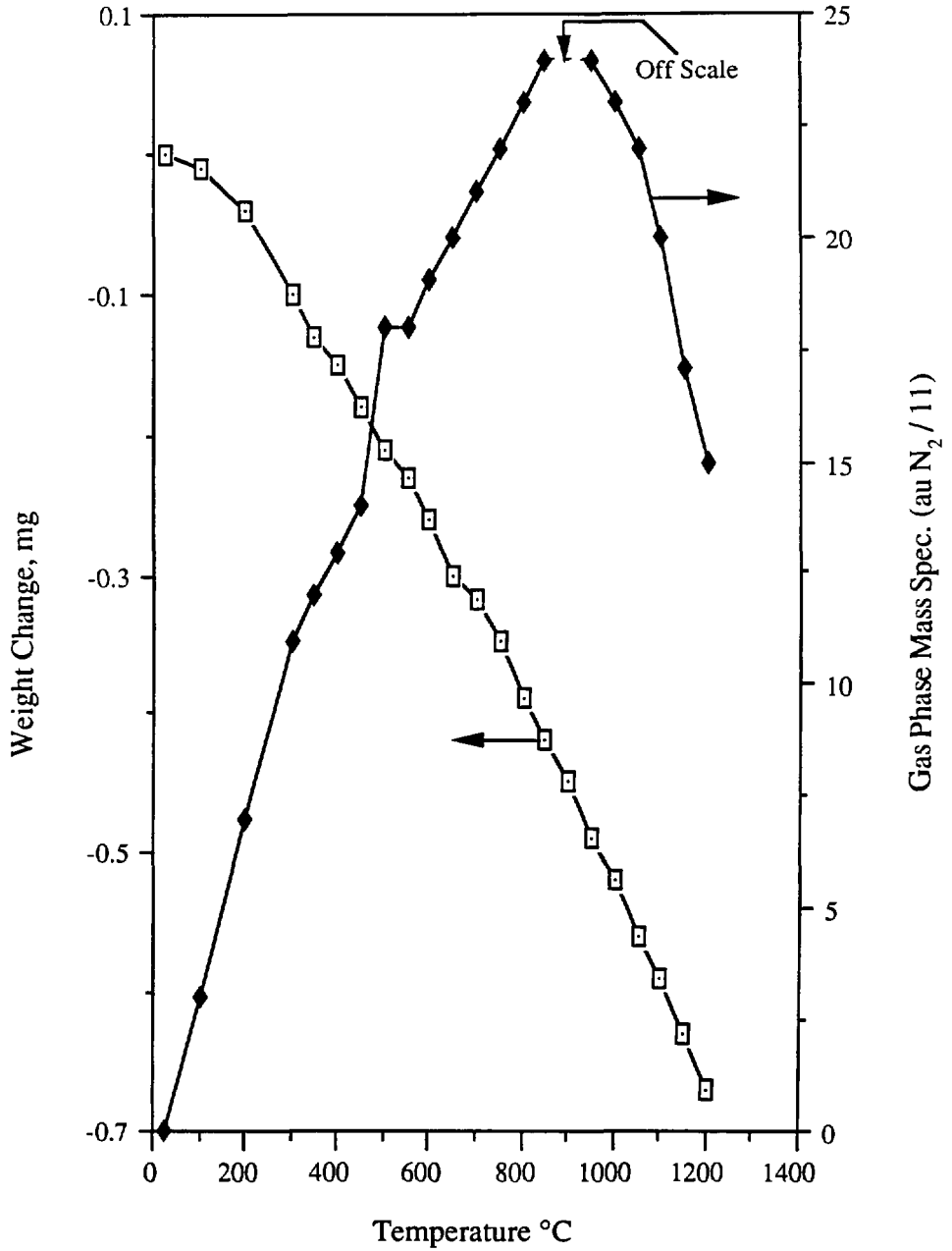


Figure 10: Weight change of the empty crucible and N₂ detected in the atmosphere of the thermogravimetric analyzer.

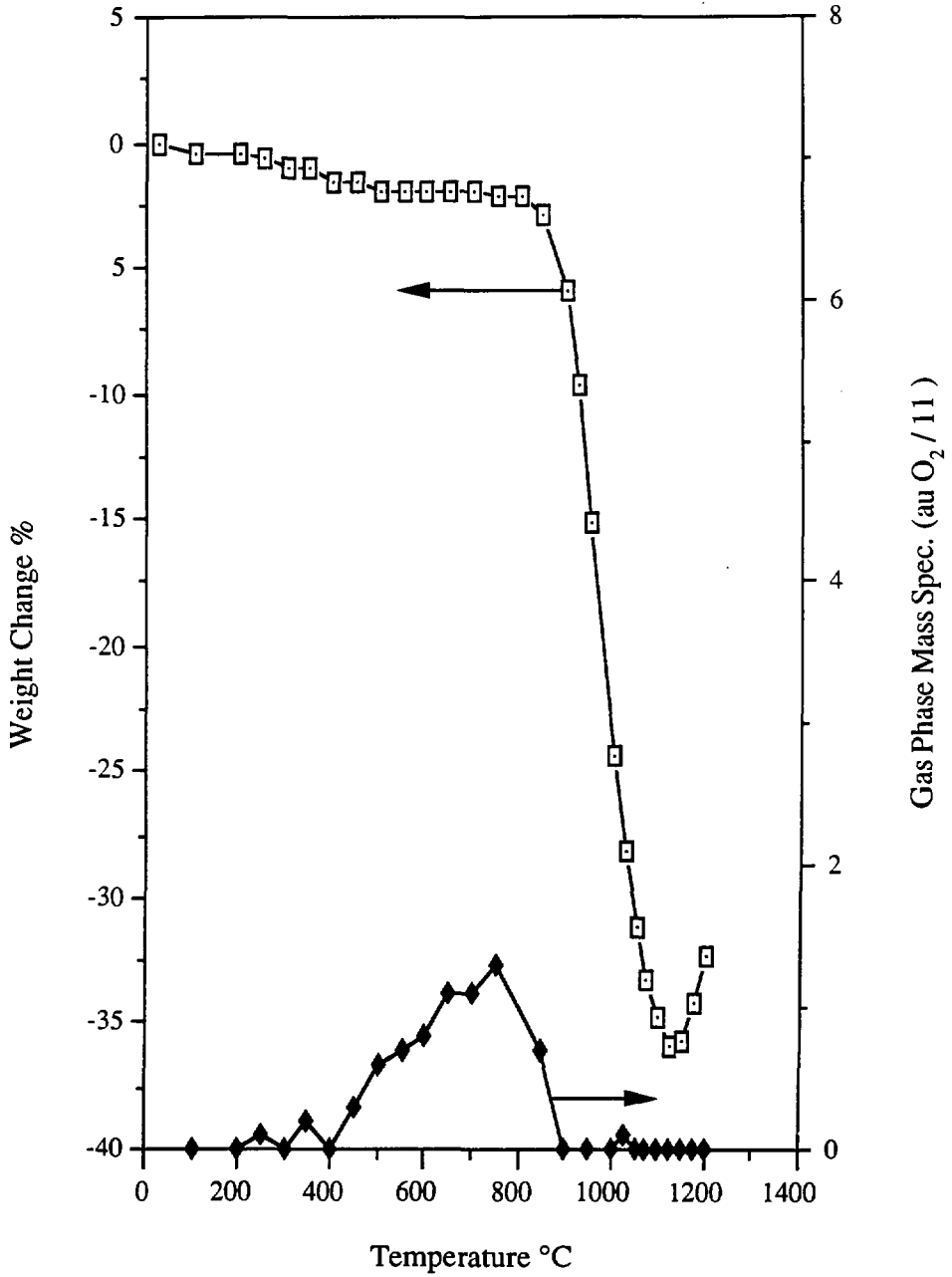


Figure 11: Percentage weight change and O₂ detected in the atmosphere of the Zr specimen VL6 when examined in the thermogravimetric analyzer.

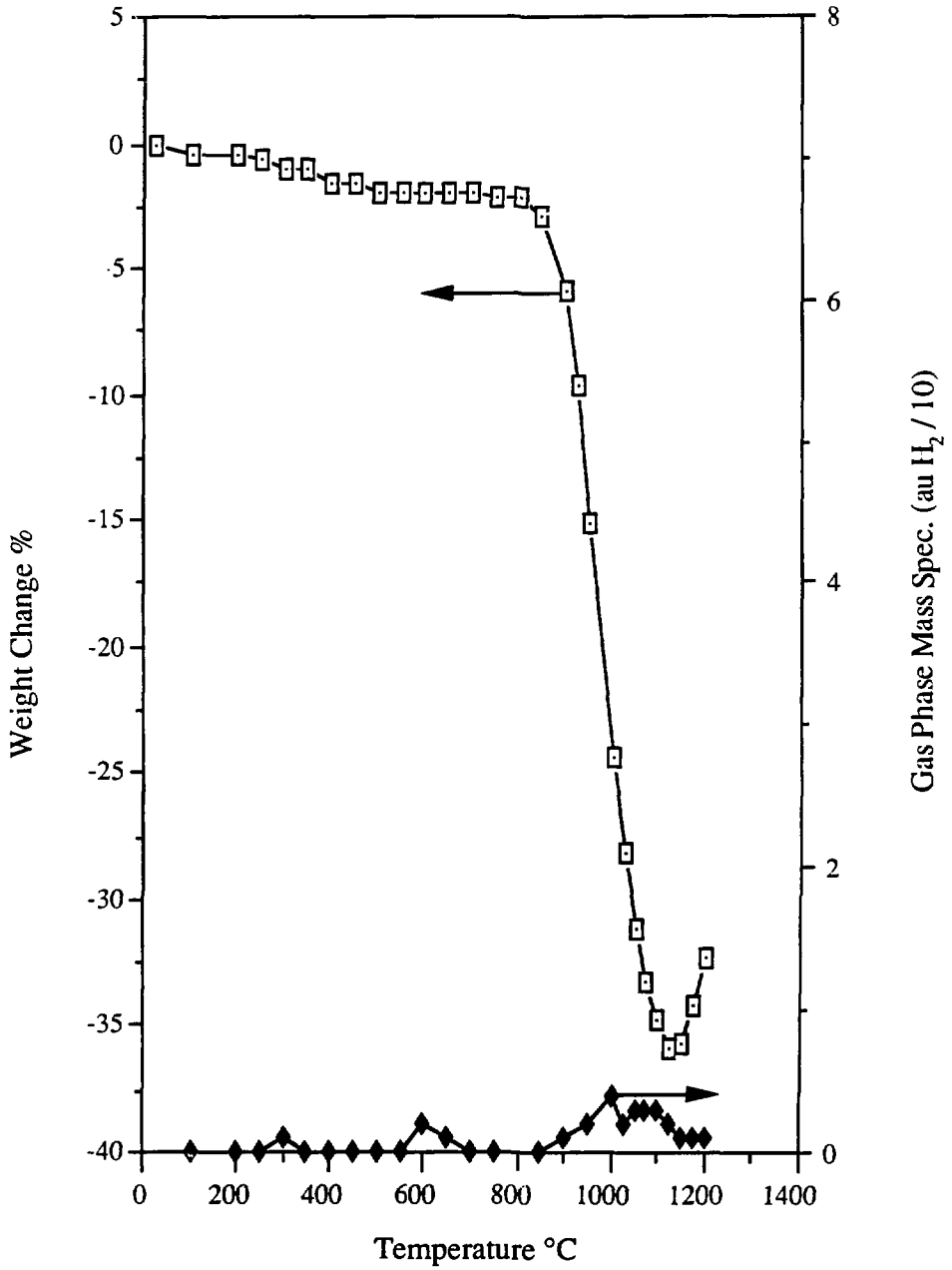


Figure 12: Percentage weight change and H₂ detected in the atmosphere of the Zr specimen VI.6 when examined in the thermogravimetric analyzer.

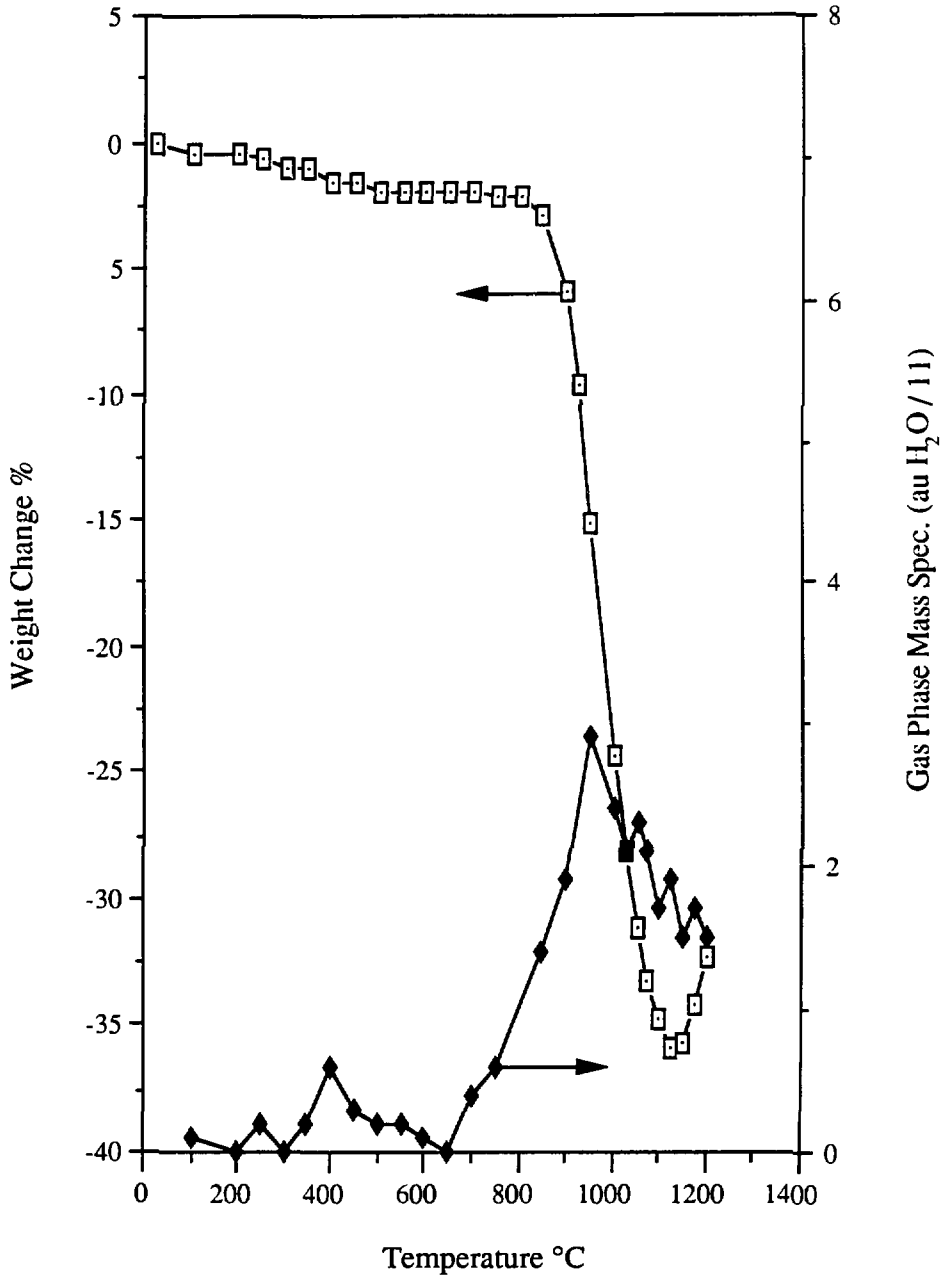


Figure 13: Percentage weight change and H₂O detected in the atmosphere of the Zr specimen VI.6 when examined in the thermogravimetric analyzer.

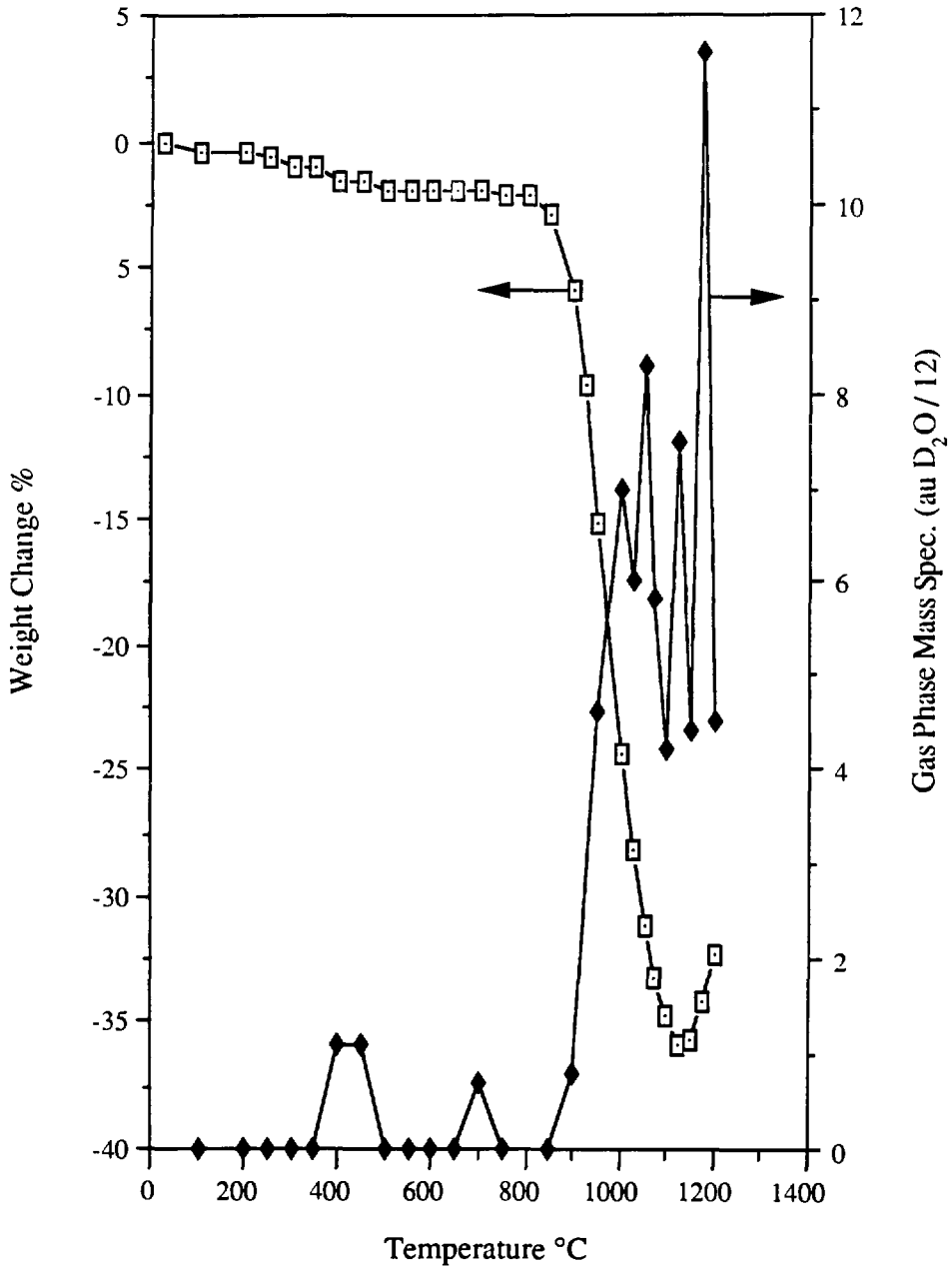


Figure 14: Percentage weight change and D₂O detected in the atmosphere of the Zr specimen VI.6 when examined in the thermogravimetric analyzer.

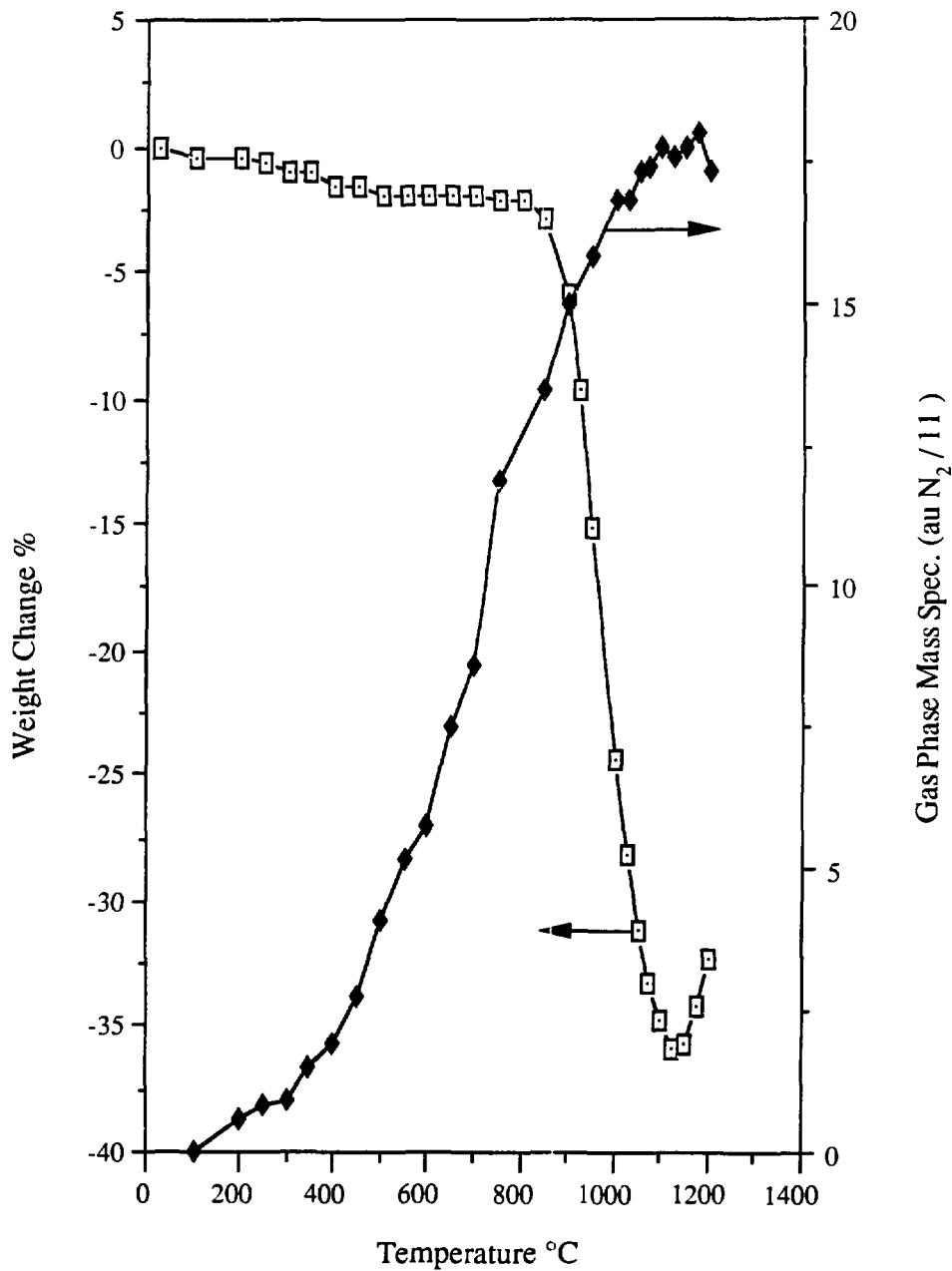


Figure 15: Percentage weight change and N₂ detected in the atmosphere of the Zr specimen VI.6 when examined in the thermogravimetric analyzer.

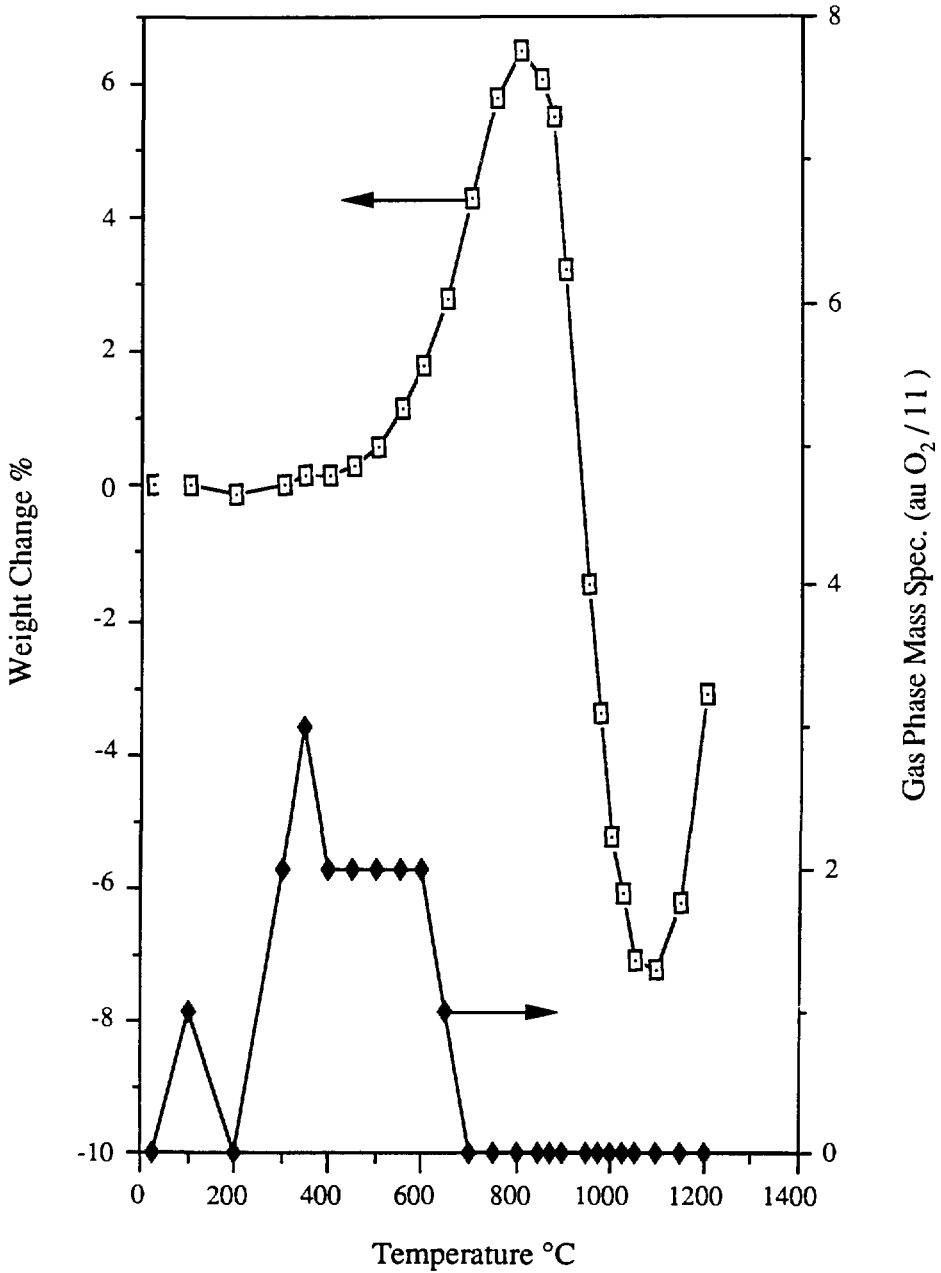


Figure 16: Percentage weight change and O₂ detected in the atmosphere of the Zr - 2.5% Nb specimen XIX.3 when examined in the thermogravimetric analyzer.

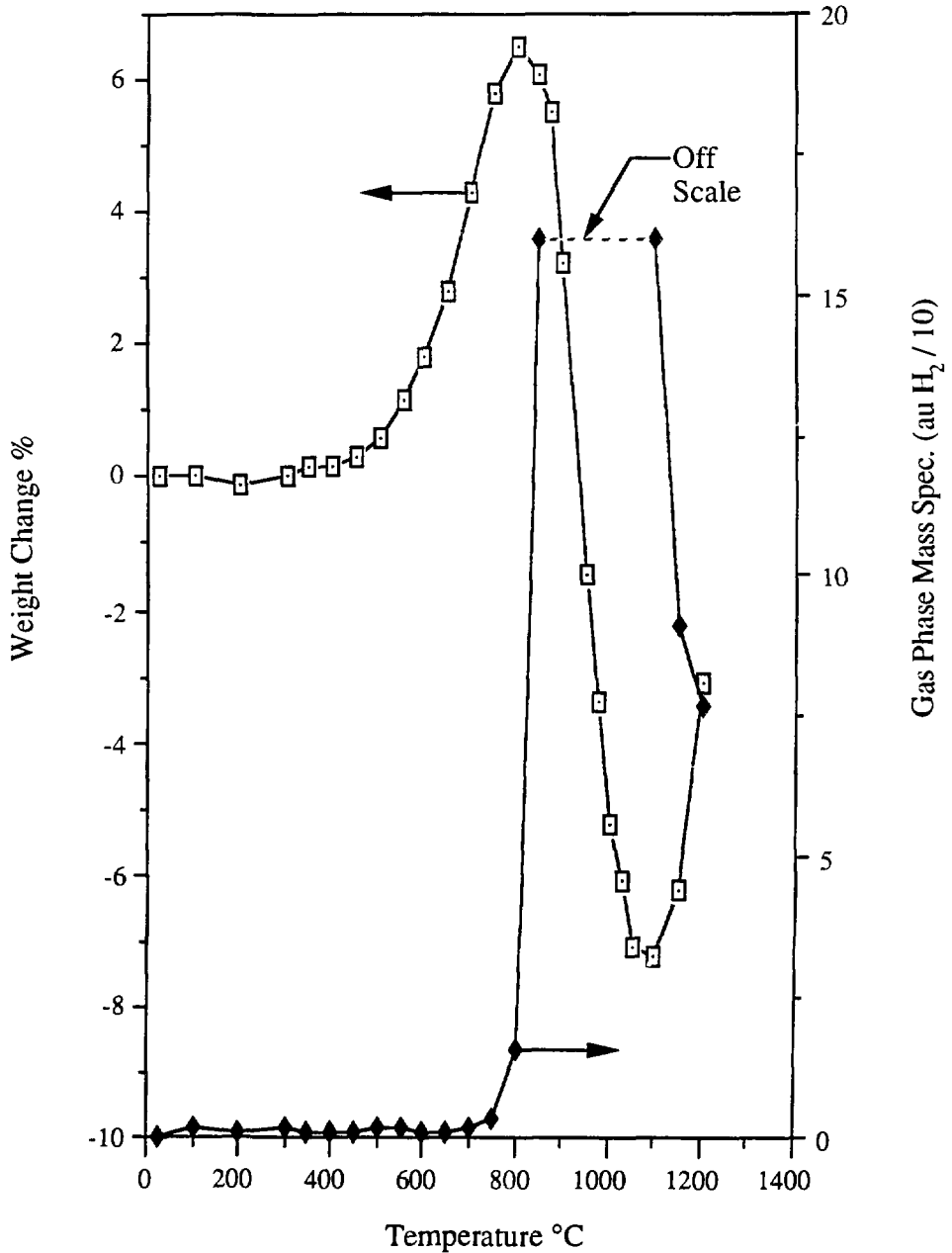


Figure 17: Percentage weight change and H₂ detected in the atmosphere of the Zr - 2.5% Nb specimen XIX.3 when examined in the thermogravimetric analyzer.

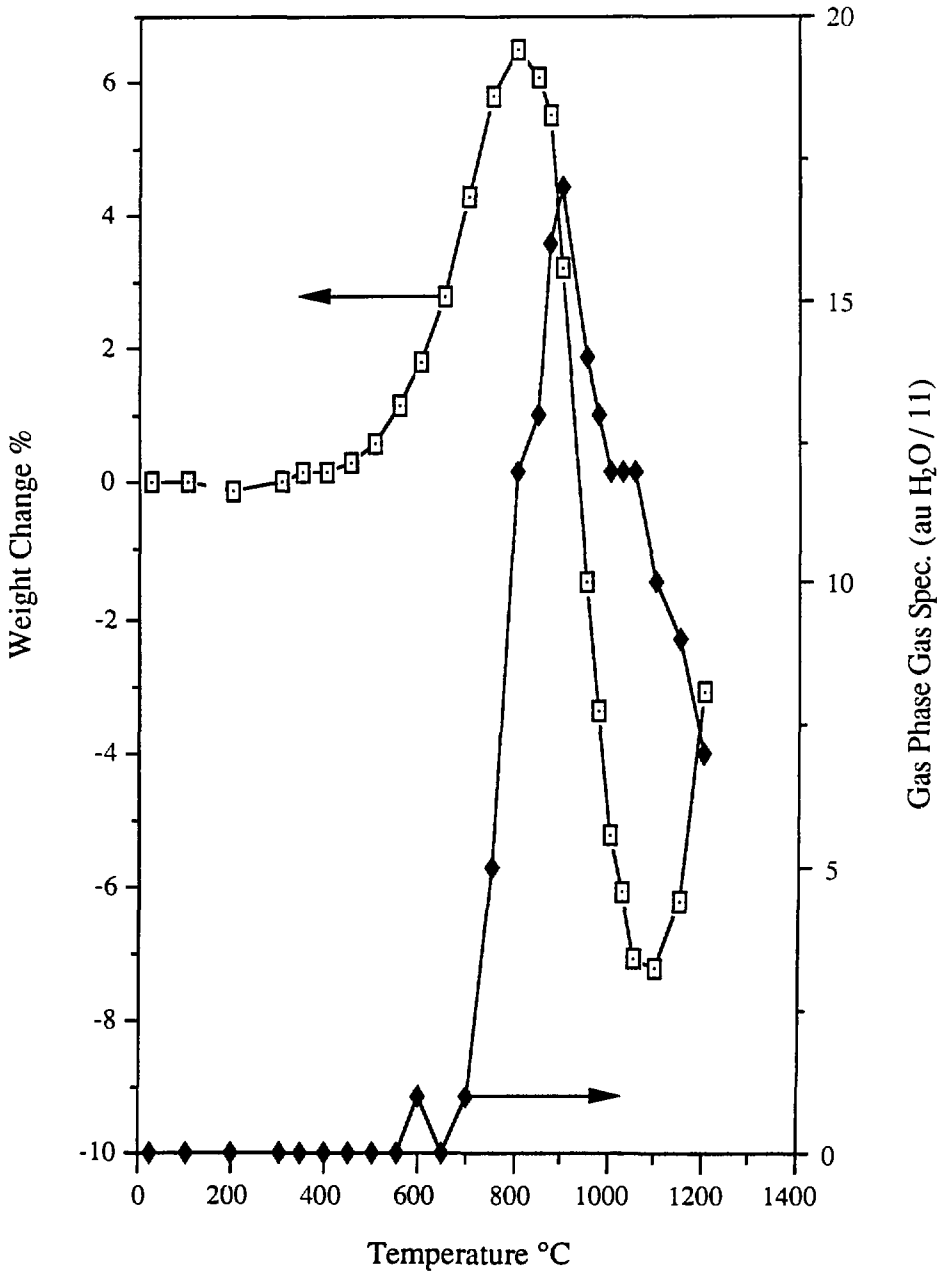


Figure 18: Percentage weight change and H₂O detected in the atmosphere of the Zr - 2.5% Nb specimen XIX.3 when examined in the thermogravimetric analyzer.

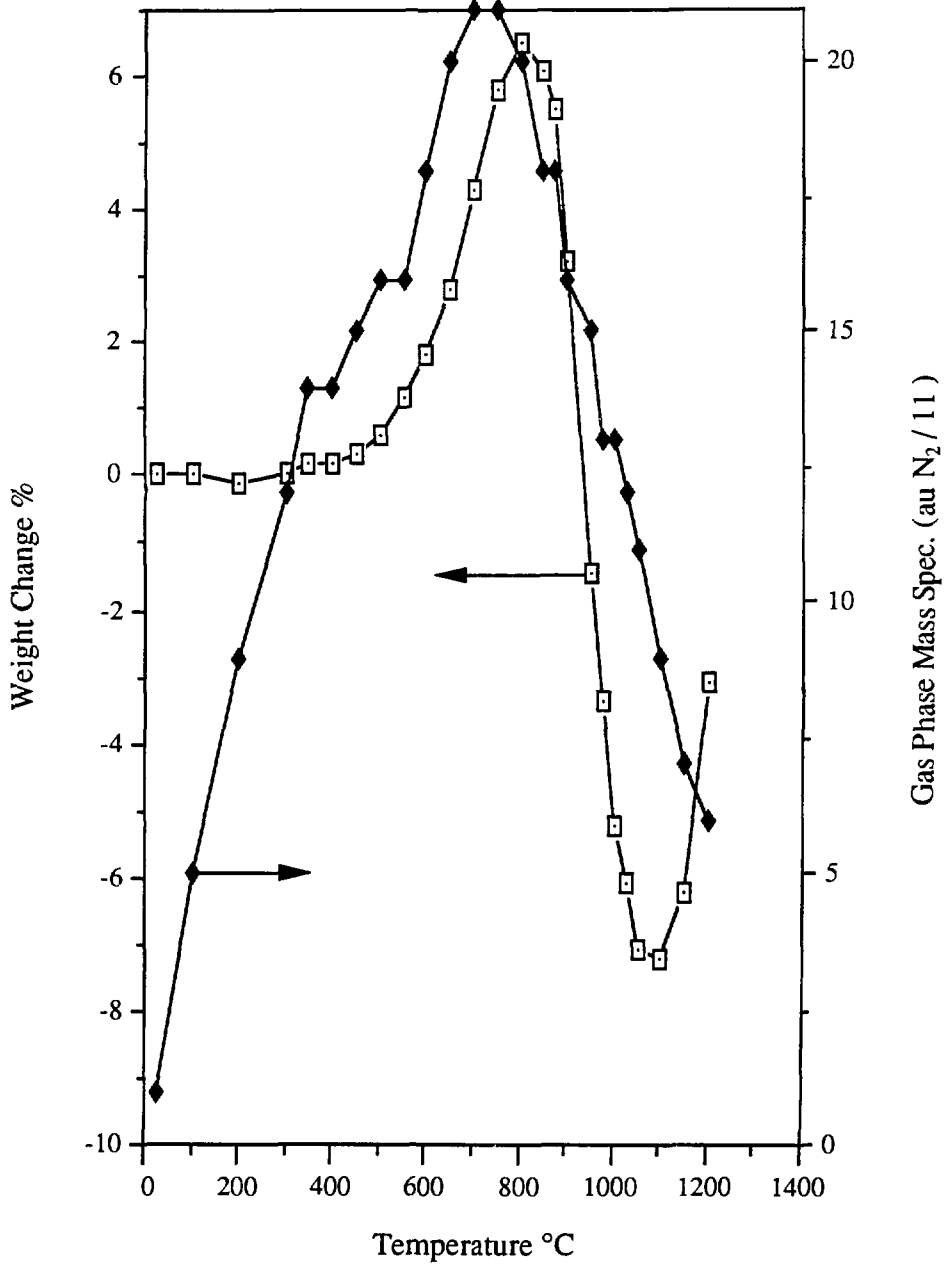


Figure 19: Percentage weight change and N₂ detected in the atmosphere of the Zr - 2.5% Nb specimen XIX.3 when examined in the thermogravimetric analyzer.

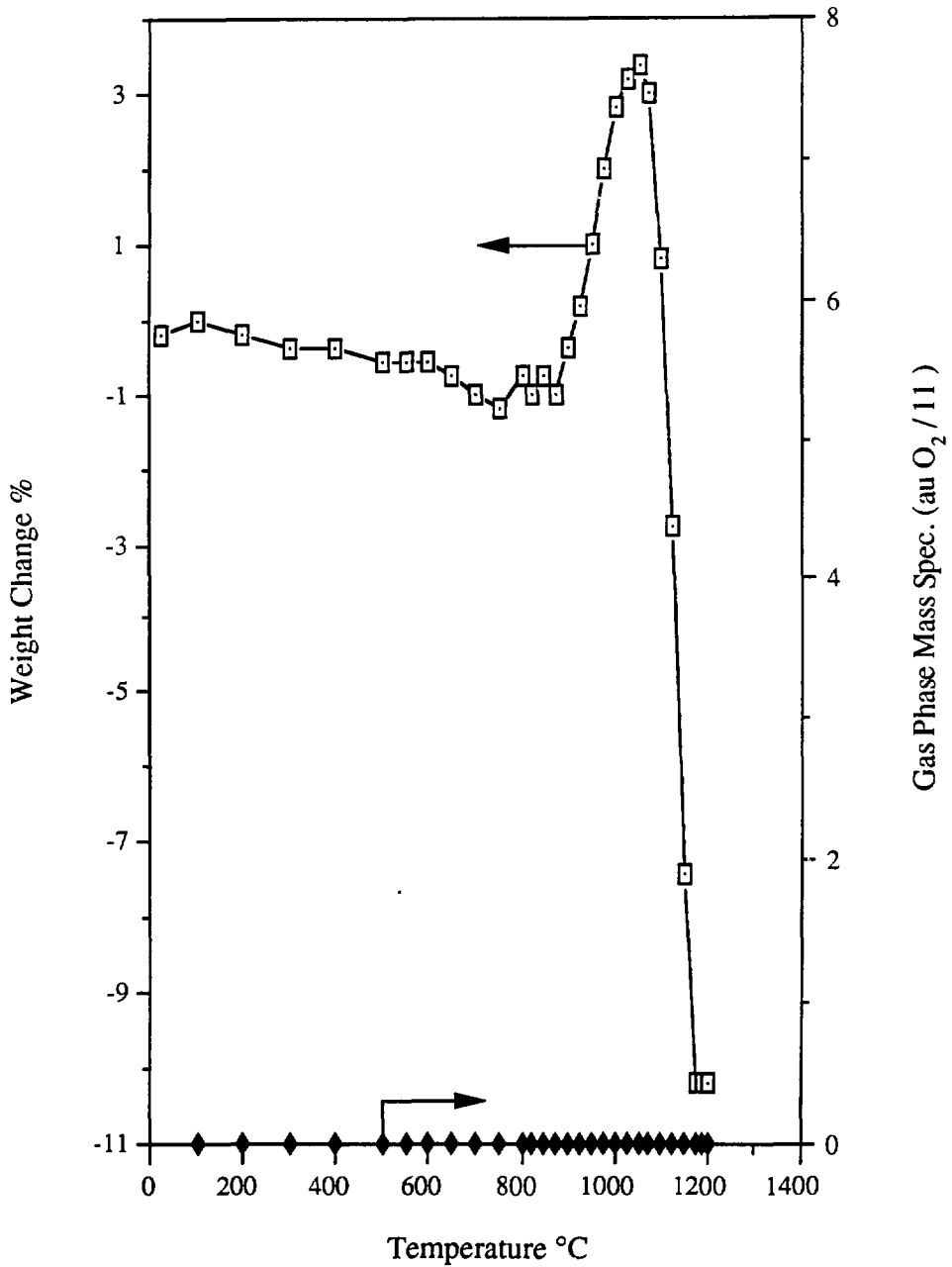


Figure 20: Percentage weight change and O₂ detected in the atmosphere of the Zr specimen IX.3 when examined in the thermogravimetric analyzer.

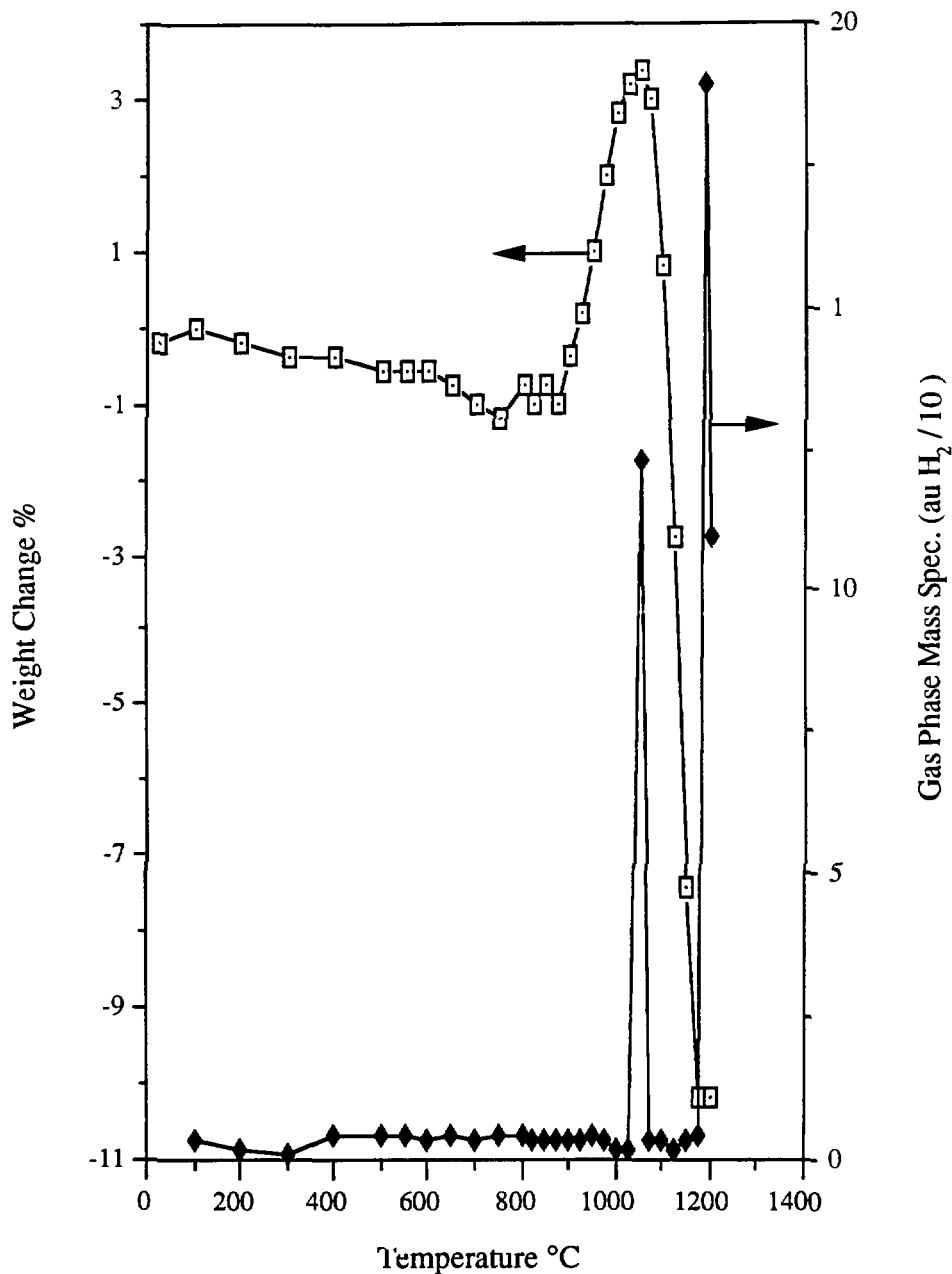


Figure 21: Percentage weight change and H₂ detected in the atmosphere of the Zr specimen IX.3 when examined in the thermogravimetric analyzer.

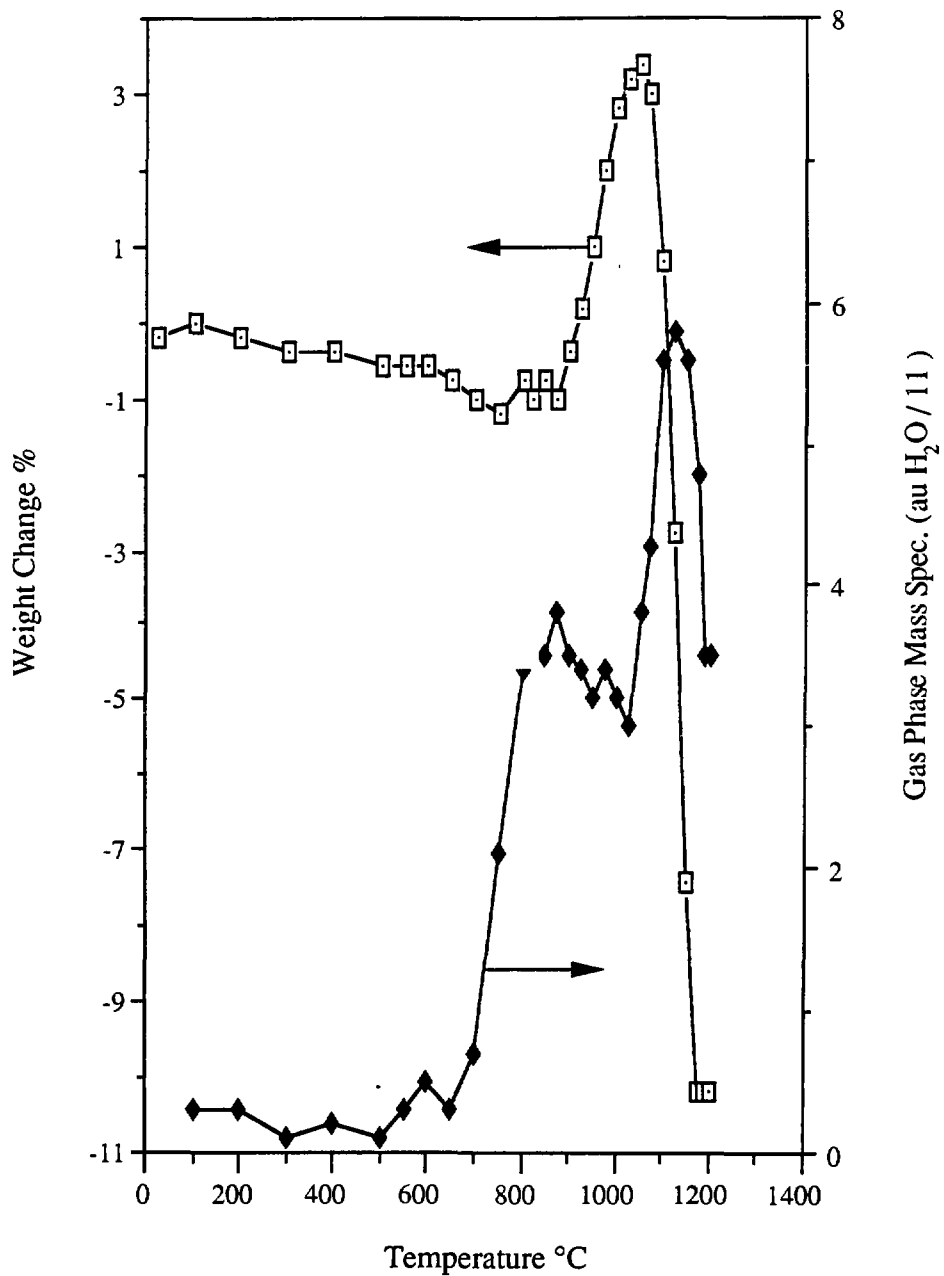


Figure 22: Percentage weight change and H₂O detected in the atmosphere of the Zr specimen IX.3 when examined in the thermogravimetric analyzer.

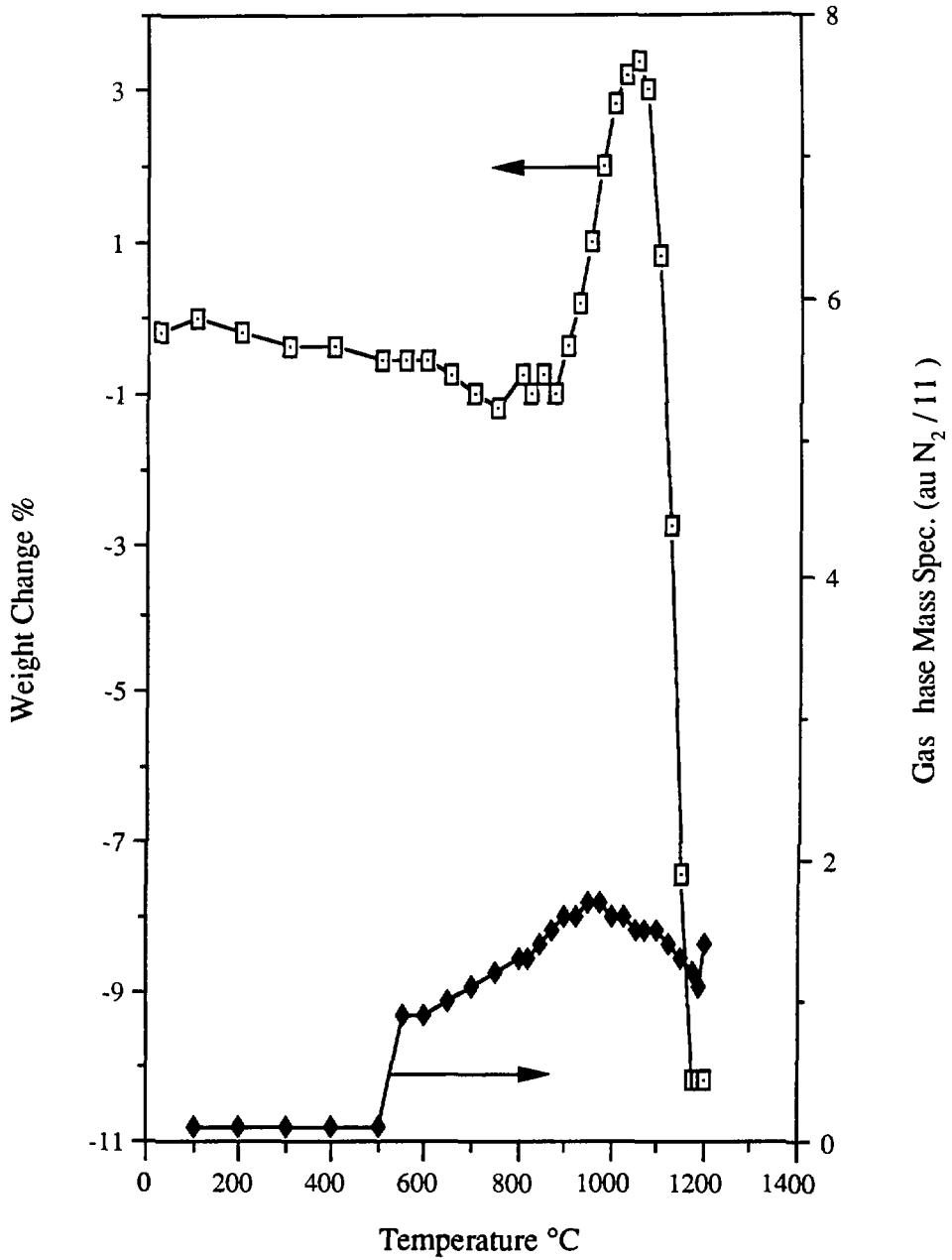


Figure 23: Percentage weight change and N₂ detected in the atmosphere of the Zr specimen IX.3 when examined in the thermogravimetric analyzer.

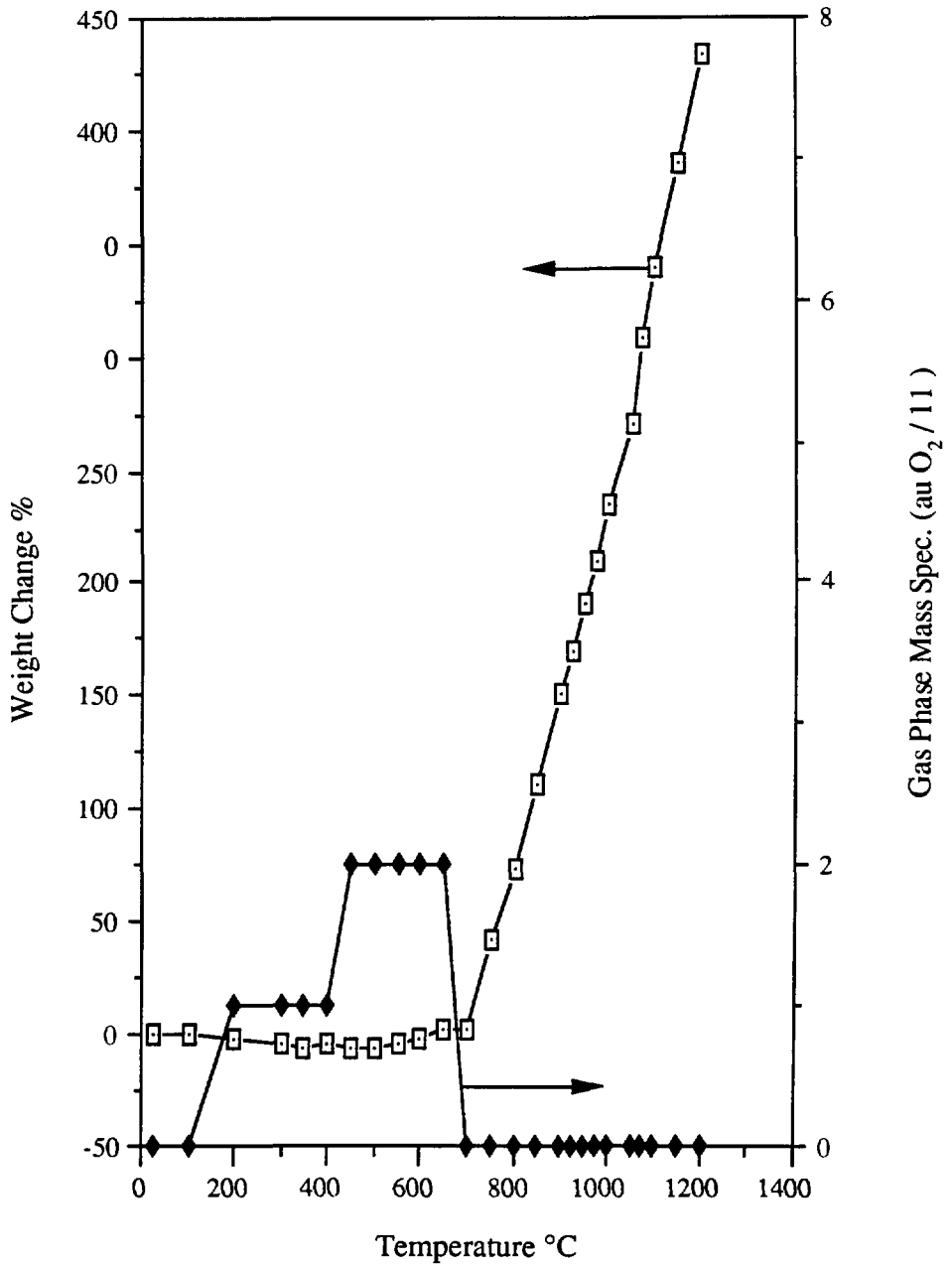


Figure 24: Percentage weight change and O₂ detected in rolled Zr - 2.5% Nb specimen XVIII.3/4 when examined in the thermogravimetric analyzer.

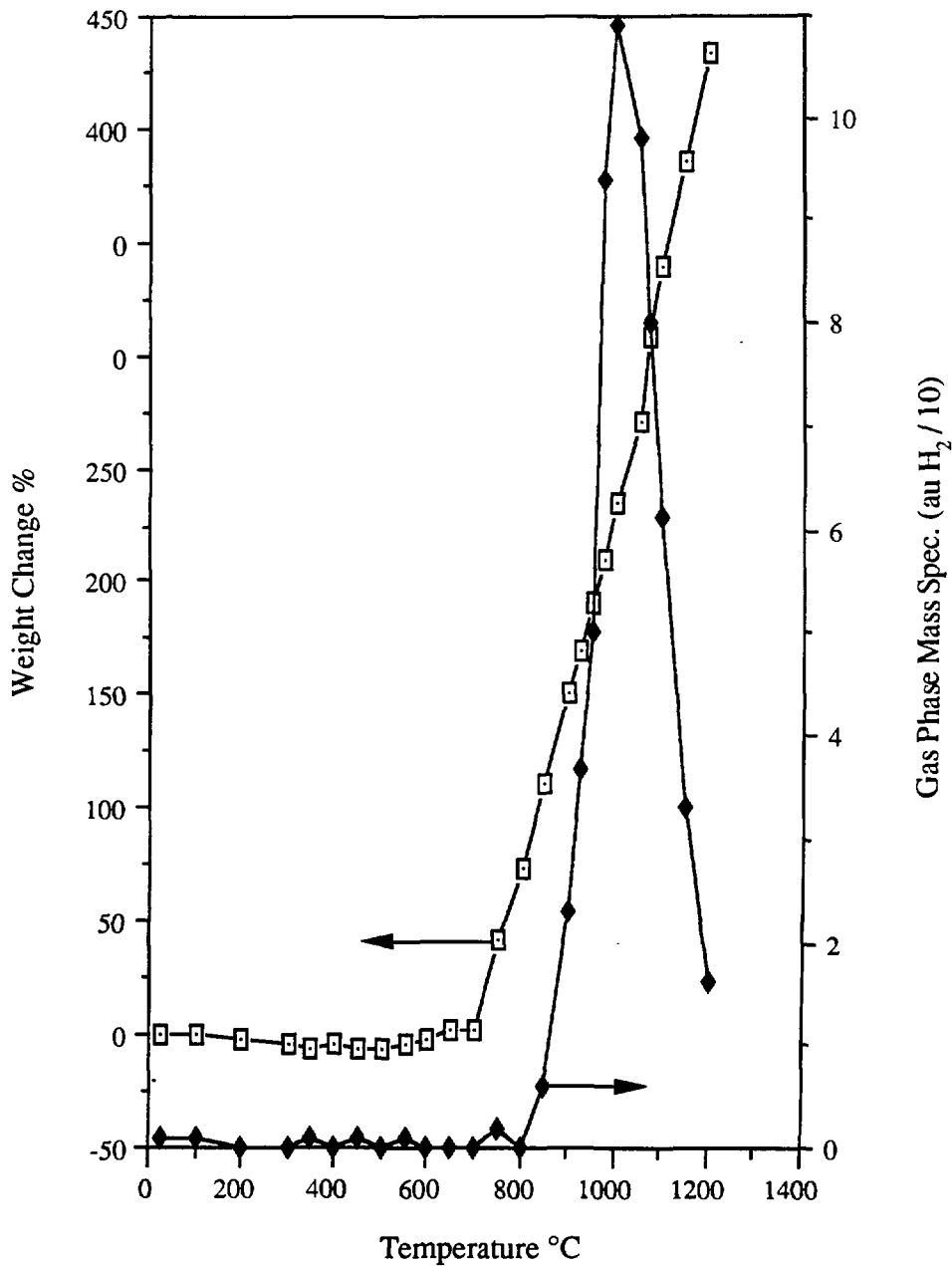


Figure 25: Percentage weight change and H₂ detected in rolled Zr - 2.5% Nb specimen XVIII.3/4 when examined in the thermogravimetric analyzer.

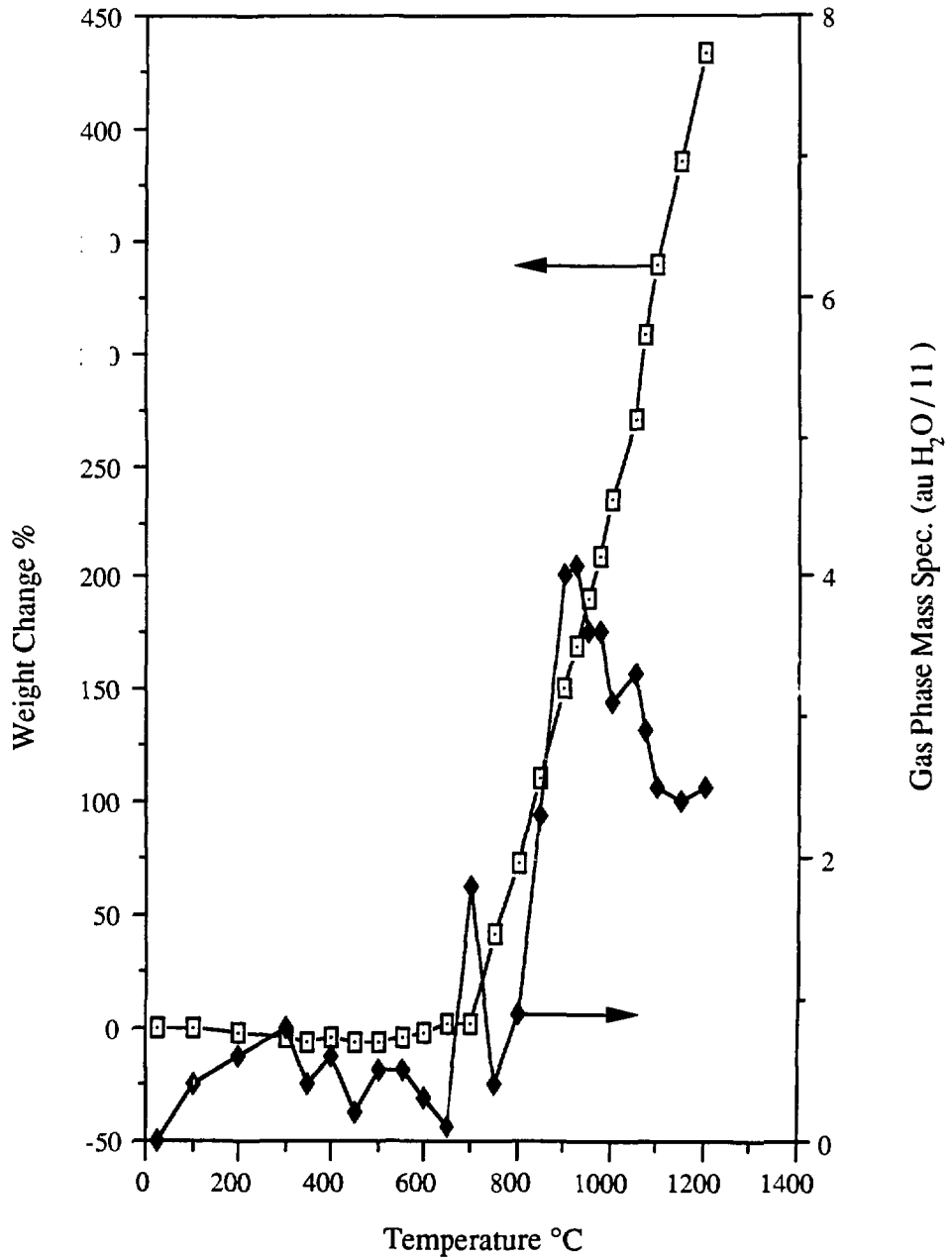


Figure 26: Percentage weight change and H₂O detected in rolled Zr - 2.5% Nb specimen XVIII.3/4 when examined in the thermogravimetric analyzer.

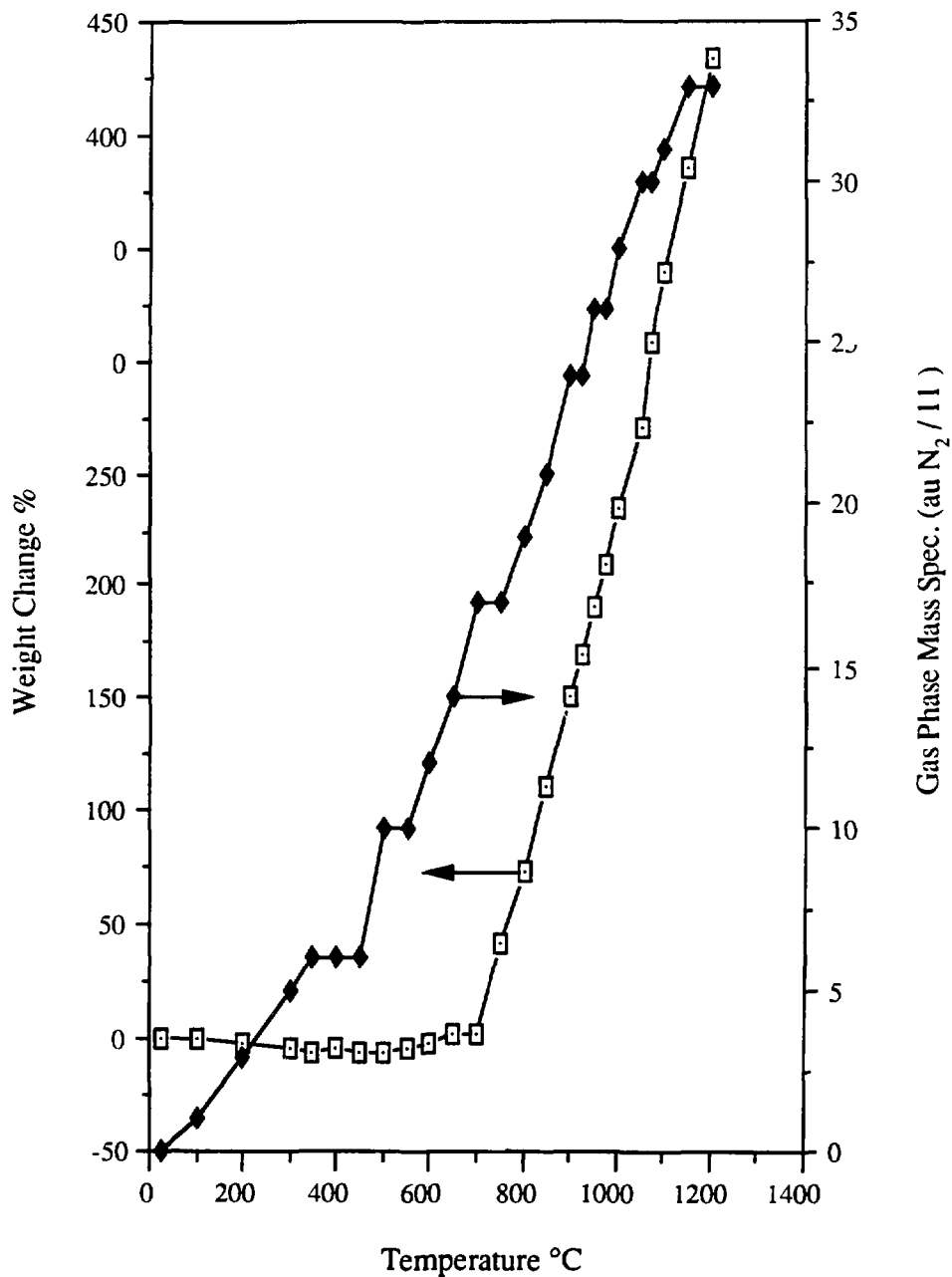


Figure 27: Percentage weight change and N₂ detected in rolled Zr - 2.5% Nb specimen XVIII.3/4 when examined in the thermogravimetric analyzer.

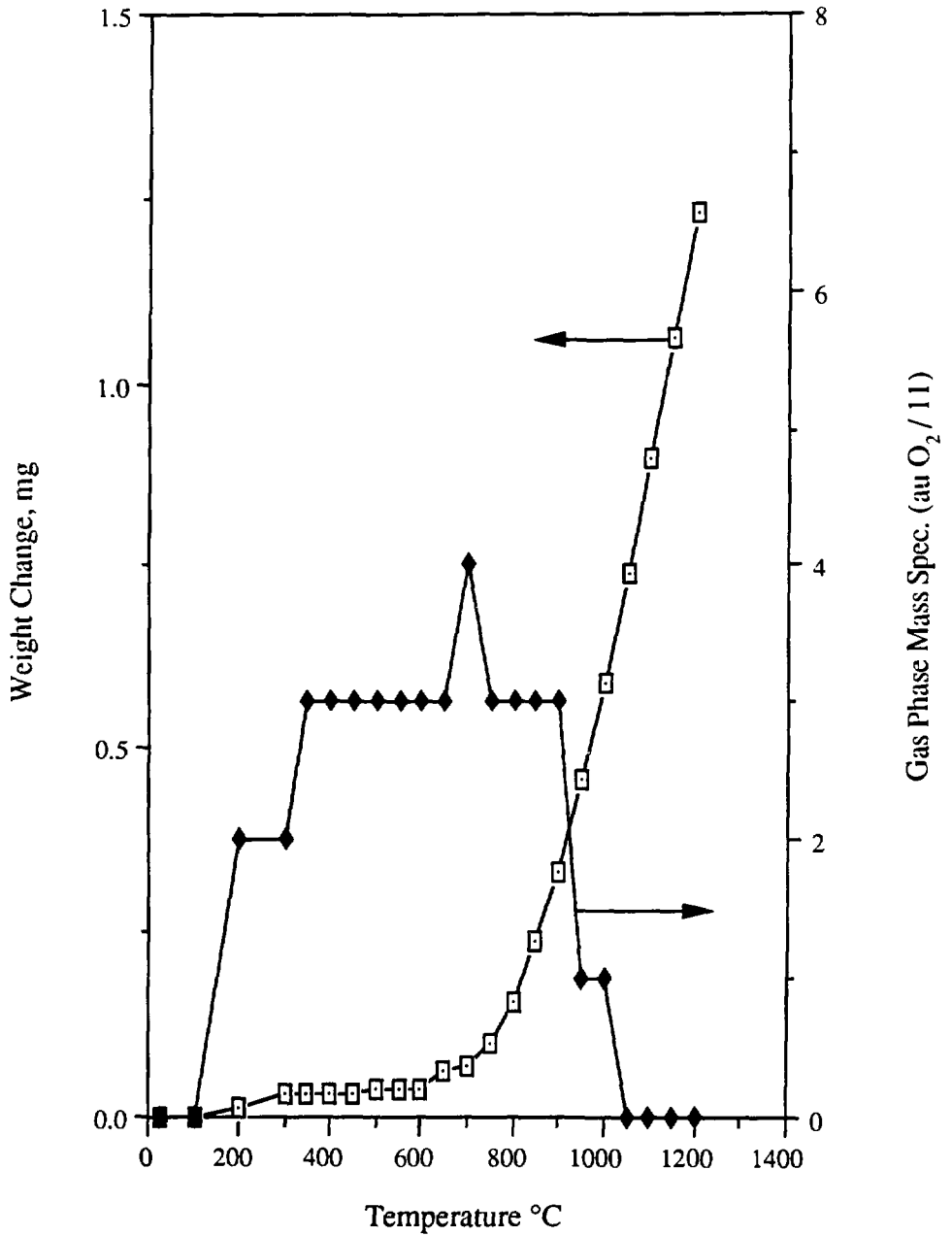


Figure 28: Weight change and O₂ detected in the untreated Zr specimen XXI when examined in the thermogravimetric analyzer.

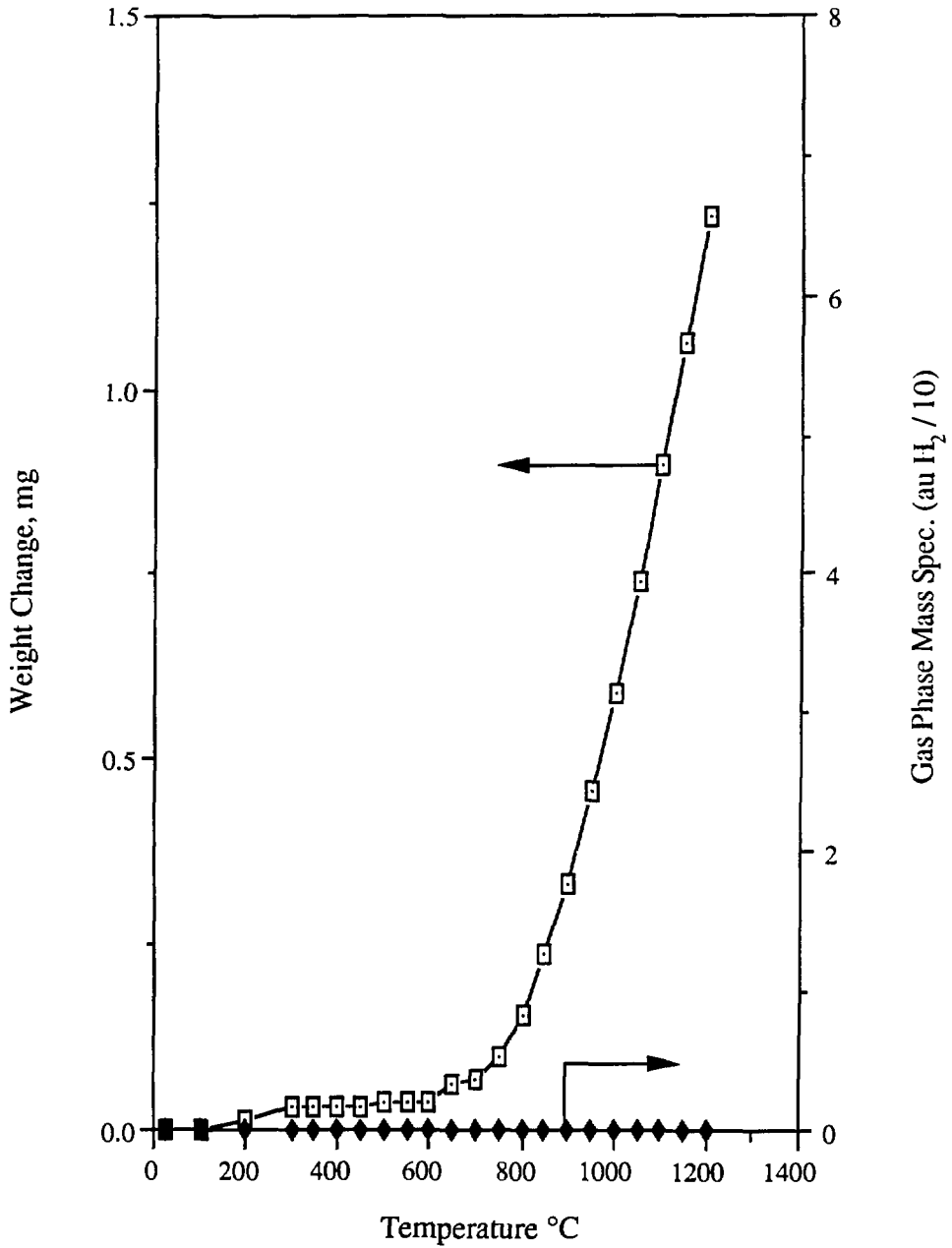


Figure 29: Weight change and H₂ detected in the untreated Zr specimen XXI when examined in the thermogravimetric analyzer.

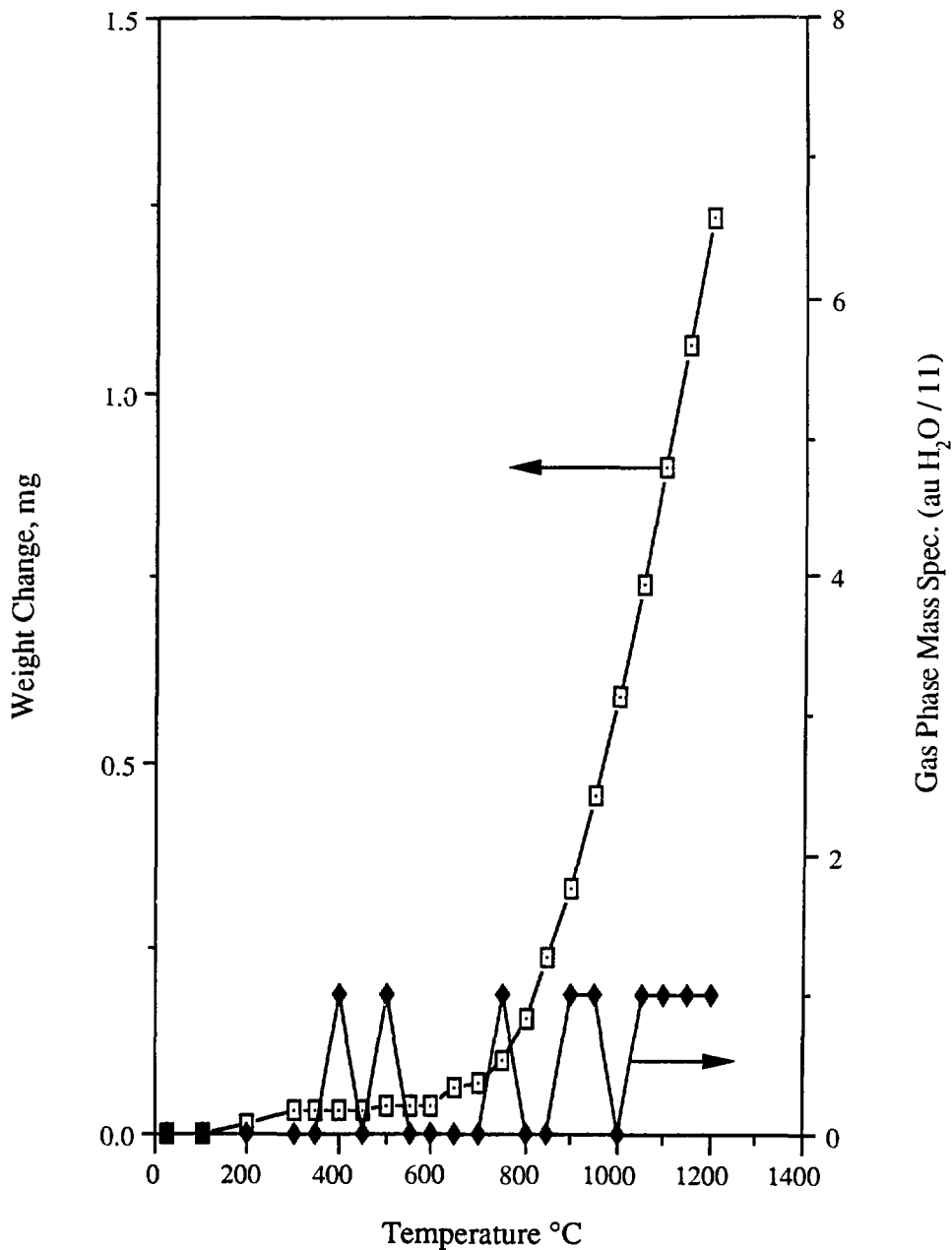


Figure 30: Weight change and H₂O detected in the untreated Zr specimen XXI when examined in the thermogravimetric analyzer.

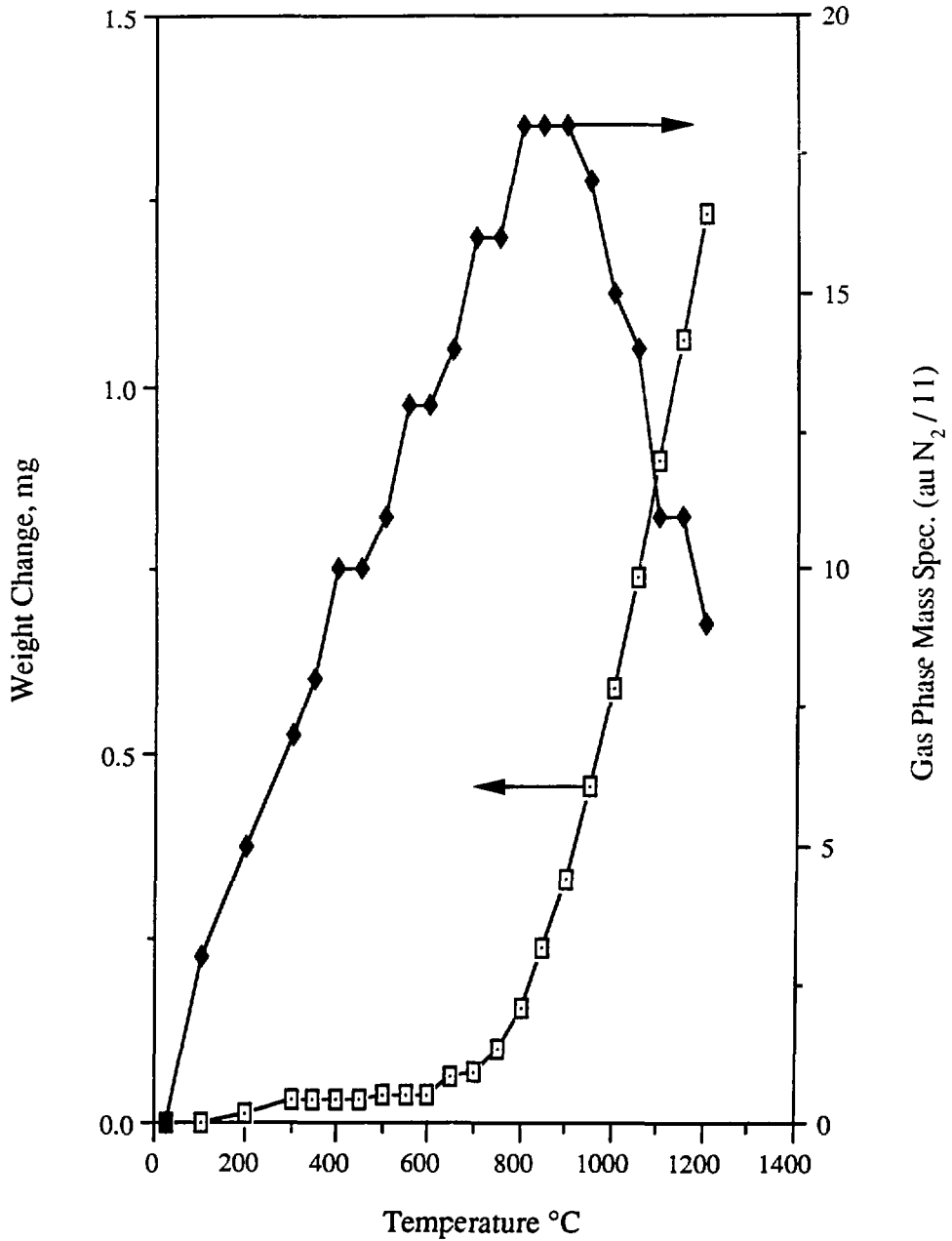


Figure 31: Weight change and N₂ detected in the untreated Zr specimen XXI when examined in the thermogravimetric analyzer.

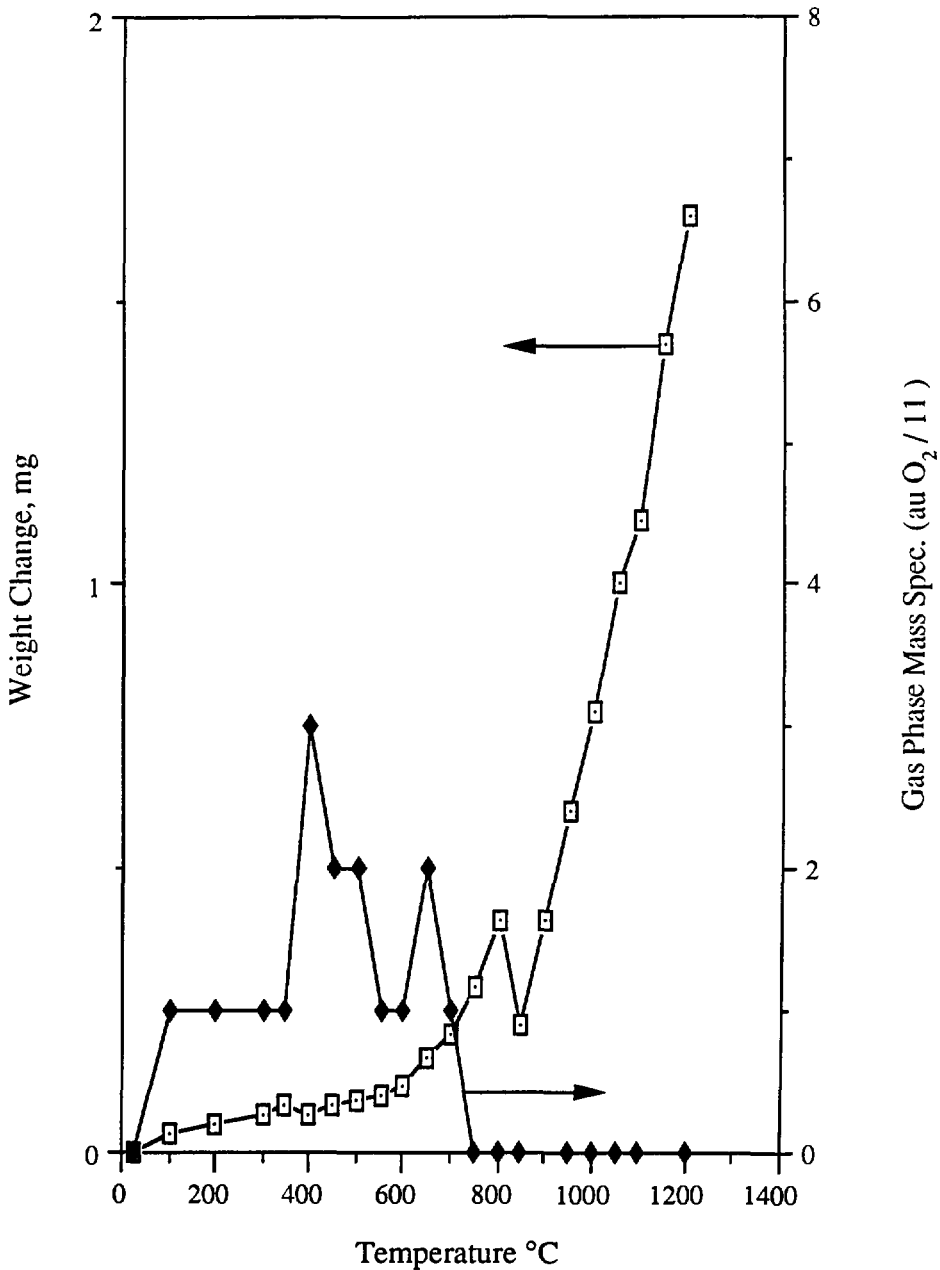


Figure 32: Weight change and O₂ detected in the untreated Zr - 2.5% Nb specimen XX when examined in the thermogravimetric analyzer.

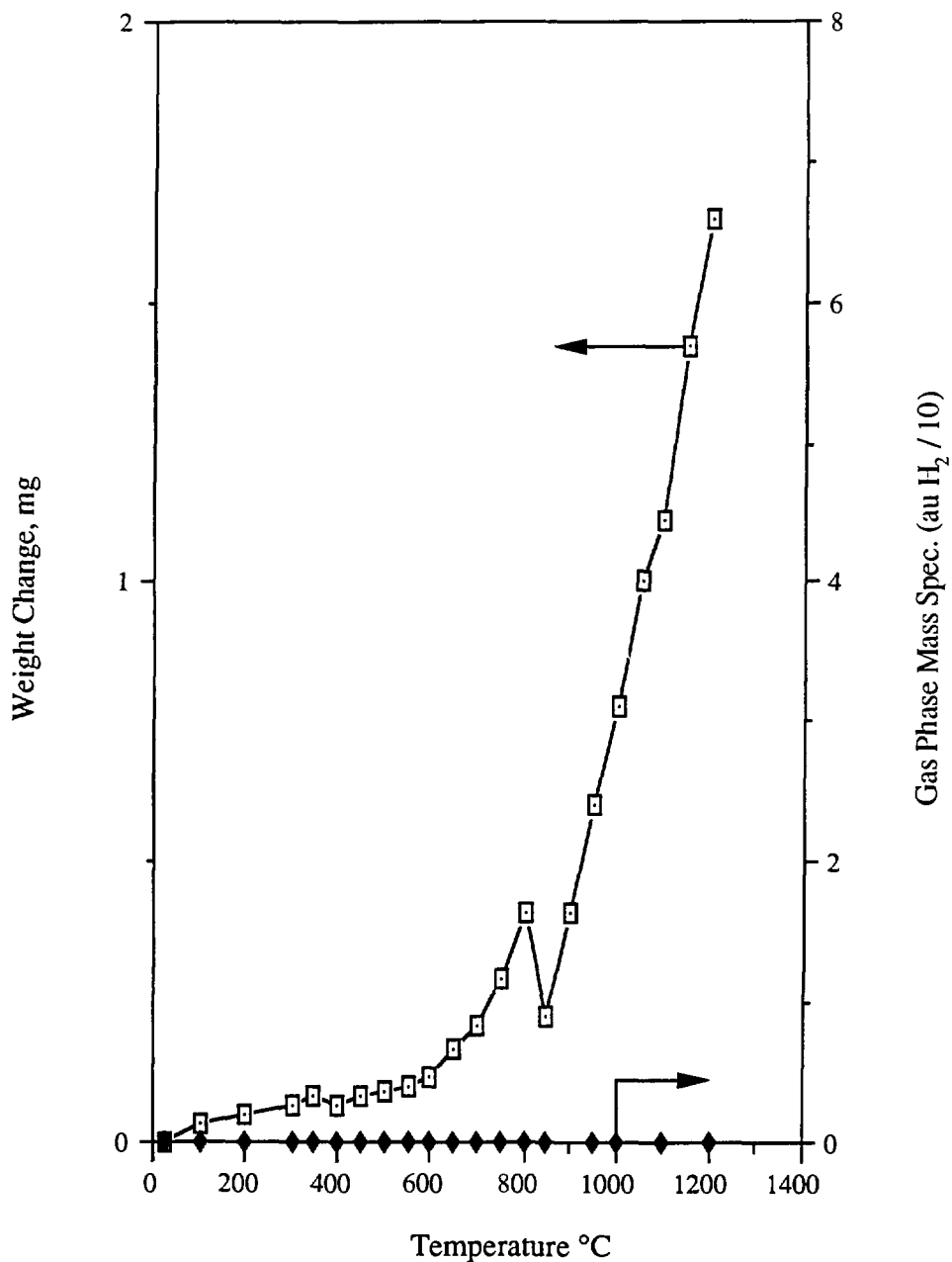


Figure 33: Weight change and H₂ detected in the untreated Zr - 2.5% Nb specimen XX when examined in the thermogravimetric analyzer.

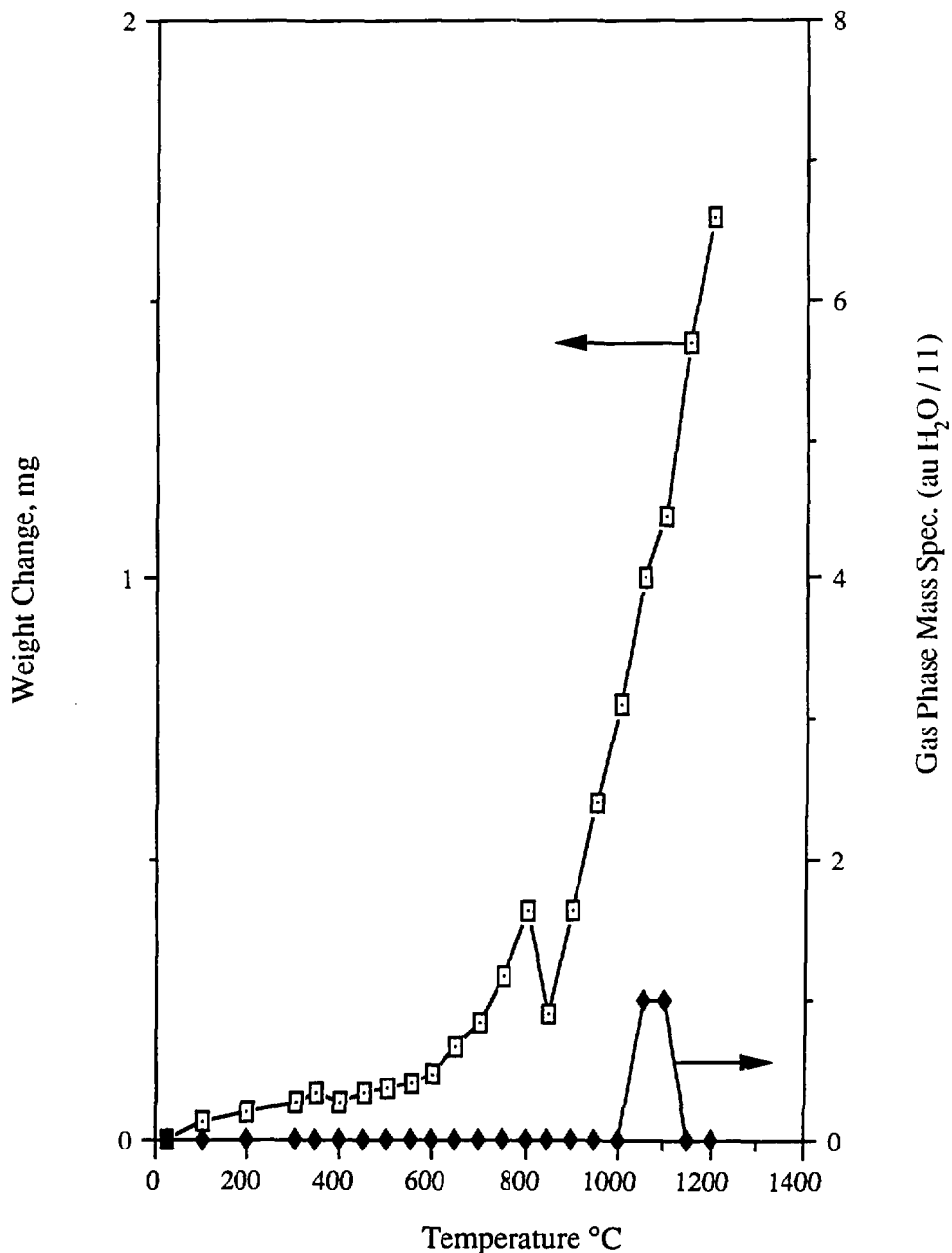


Figure 34: Weight change and H₂O detected in the untreated Zr - 2.5% Nb specimen XX when examined in the thermogravimetric analyzer.

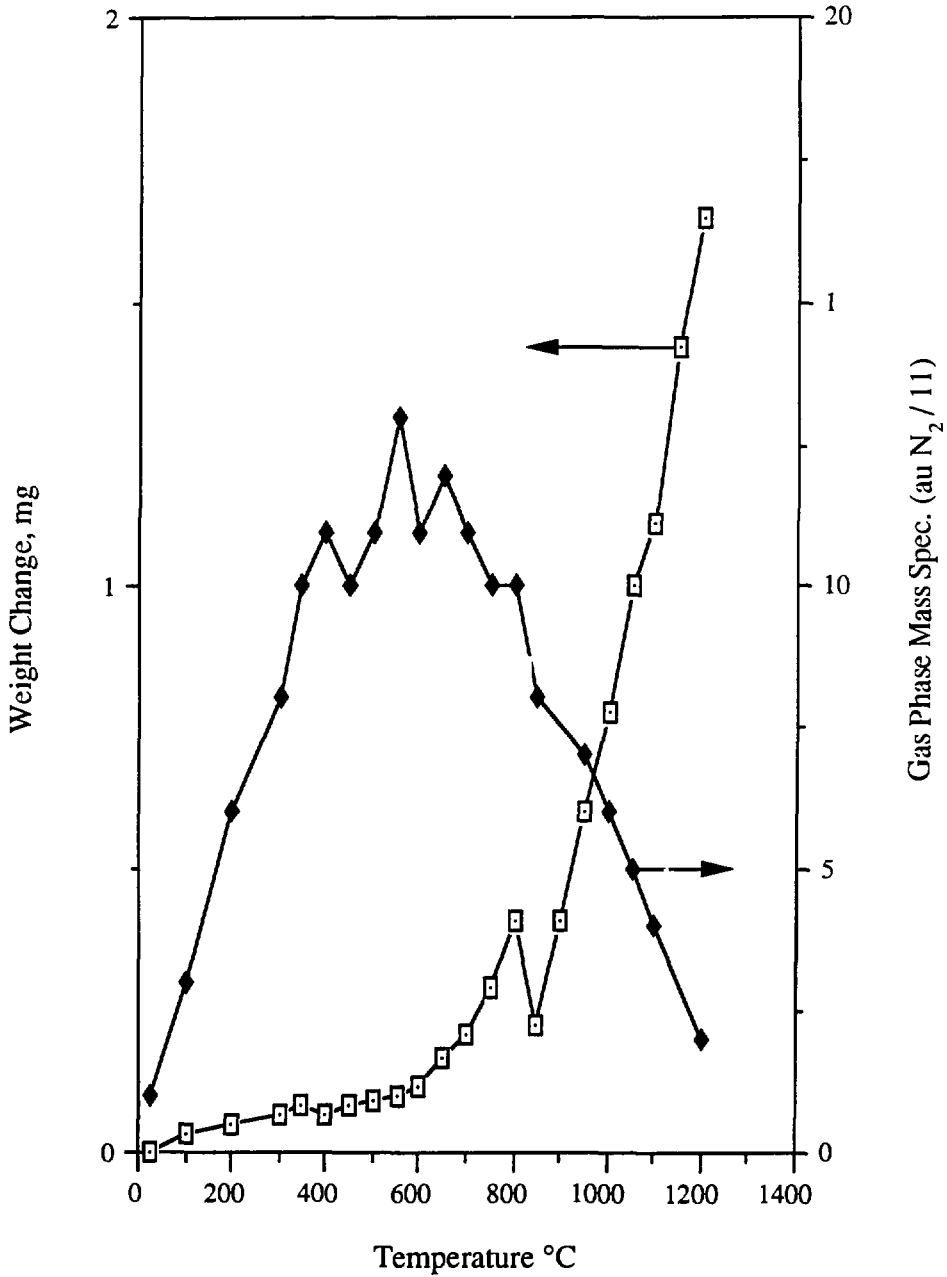


Figure 35: Weight change and N₂ detected in the untreated Zr - 2.5% Nb specimen XX when examined in the thermogravimetric analyzer.

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