Determination of Oxygen and Nitrogen in Zr-Based Amorphous Alloy by Inert Gas Fusion-Infrared Absorption/Thermal Conductivity Method

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Abstract. A Method was studied for determination of oxygen and nitrogen in Zr-based amorphous alloy by inert gas fusion-infrared absorption/thermal conductivity method, the optimum conditions were determined by experiments on the parameters such as crucible, sample weight and analysis power. When zirconium-based amorphous alloy is melted by heated crucible, the sample weight ranges between 0.07 g~0.08 g, with analysis power is 6.0 KW; results will be stable and reliable. The relative standard deviation of the accuracy was between 1.13% and 3.47%, the relative standard deviation of the precision was between 0.67% and 4.92%. This method is quick and convenient, and the results are accurate and reliable, it can guarantee the quantitative determination of oxygen and nitrogen element in Zr-based amorphous alloy and guide the scientific research and production activities.

Keywords: Inert Gas Fusion-Infrared Absorption Method, Thermal Conductivity Method, Zr-Based Amorphous Alloy, Oxygen, Nitrogen

1. Introduction
Zirconium-based amorphous alloy is used in armor-piercing projectile core widely, energetic fragment and liner due to its high strength and low modulus. The development of Zirconium-based amorphous alloy combines metal, glass and related disciplines, therefore it can represent the research forward position of materials scienc [1-2]. Oxygen and Nitrogen are the main nonmetallic impurities in zirconium-based amorphous materials, which often exist in the form of interstitial solid solution, the content of these two elements have remarkable effect upon physical and mechanical properties of alloy material [3].

Researchers show that the concentration of oxygen impurity has influence on the glass forming ability, critical cooling rate and chemical stability of zirconium-based amorphous alloy greatly [4]. Addition of a small amount of oxygen also has an impact on the formation of phase in amorphous composite and the thermal stability of amorphous phase [5]. Nitrogen is easy to form dispersed and stable nitride in zirconium-based amorphous alloy, which can improve the corrosion resistance, hardness and strength of the material. However, "blue brittleness" wills appears when the nitrogen content exceeds limit while heating up, which can reduce the plasticity of the material [6]. Some
oxygen and nitrogen will enter the alloy when preparing zirconium-based amorphous bulk alloy due to the limitation of raw material purity or under the action of smelting high temperature atmosphere [7]. Therefore, accurate detection of oxygen and nitrogen content is the key in the development process, product evaluation and quality control of zirconium-based amorphous alloy. The quantitative analysis of gas impurity elements is of great significance for the precise preparation, performance change and cost control of alloy material.

The determination methods of oxygen in metals include inert gas fusion infrared method and coulometric method. The determination methods of nitrogen include traditional distillation-titration method and distillation-colorimetric method, inert gas fusion-thermal conductivity method and inert gas fusion-time of flight Instrumental mass spectrometry methods and so on [8-9]. The development of single element to multi-element simultaneous detection gradually with the continuous grow of gas analysis technology and new materials. For example, the contents of oxygen and nitrogen in materials such as vanadium-aluminum alloy [10] and high beryllium-aluminum alloy are determined by inert gas melting-infrared/thermal conductivity detection method [11]. This paper discusses the simultaneous determination of oxygen and nitrogen in Zr-based amorphous alloy by inert gas melting infrared absorption method and thermal conductivity method, which can have quantitative analysis of oxygen and nitrogen content quickly, efficiently and accurately.

2. Experiment

2.1 Instrument and Reagent
LECO-TC600 Oxygen and nitrogen analyzer; Mettler toledo XS104 electronic balance; High purity helium, purity is more than 99.9%; nitrogen, purity is more than 99.5%; Alkali asbestos, 550um-830um, LECO;Anhydron,830um-2360um,LECO;Rare earth copper oxide; Graphite inner and outer crucible(SP);Nickel basket(UP).

2.2 Experimental Principle and Method
LECO-TC600 oxygen and nitrogen analyzer uses independent electrode furnace for melting. Oxygen is detected by infrared method in the form of CO and CO\textsubscript{2} in the external red pool, CO\textsubscript{2} has a strong absorption band at 4.26um, and the solid-state infrared sensor can determine the oxygen content of the tested sample by measuring the light intensity change after gas absorption indirectly, the percentage content of CO\textsubscript{2} gas concentration is then analyze. Nitrogen is detected by thermal conductivity method in the thermal conductivity cell, and the percentage content of nitrogen can be detected through different heat, which taken away by nitrogen and helium on different bridge arms of thermal conductivity detector.

Turn on power of the instrument, supply power gas (pressure set at 0.25Mpa) and carrier gas (pressure set at 0.15Mpa), open the software, select the channel and flux, test the standard substance for coefficient correction, raise the lower electrode, add the weighed sample and flux, then press the analysis key to run the analysis program.

2.3 Working Conditions of the Instrument
Degassing power: 6 500 W; Analysis power: 6 000 W; Flow rate: 450 mL/min; Degassing time: 20s; he shortest analysis time: 30 s; Comparator level: 1.00%.

3. Results and Discussions

3.1 Crucible
Crucibles for oxygen and nitrogen analysis include heated crucibles and high-temperature crucibles. Heated crucible consists of a standard graphite outer crucible and an inner crucible. The outer crucible heats the inner crucible through electrode current uniformly and can be used for 5-8 times. The inner crucible must be replaced after each analysis. High-temperature crucible is used for super alloy,
insoluble metal or other raw materials. When using high-temperature crucible, clean the electrode and replace the crucible after each analysis.

The temperature required for the release of oxygen and nitrogen is high, due to the high melting point of Zr-based amorphous alloy. It is necessary to select a high-temperature crucible or a heated crucible for test to separate oxygen or nitrogen from zirconium completely. Experimental results show that samples often overflow when melted in a high-temperature crucible, and a small crack appears at the bottom of the crucible, so the heated crucible is chosen. When zirconium-based amorphous alloy is melted by heated crucible, the melt temperature in the crucible is uniform, which will form a stable temperature field. It is beneficial to release gas elements evenly, so as to obtain stable and reliable test results.

3.2 Sample Weight
The stability and accuracy of the measured value of sample is determined by sample weight for gas elements. Less sample weight and poor representativeness of samples will lead to low precision of measured values. Due to the limitation of crucible volume, excessive sample weight results in the release of oxygen and nitrogen in the sample is incomplete, and peak tail is serious, therefore, the measured value is lower. Zirconium-based amorphous alloys are mostly irregular large blocks, and the uniformity of block samples is poor. If ground into powder, it is easy to adsorb gas and lead to surface oxidation, so the processing granularity of samples should be appropriate. In this method, preparation equipment is used to process samples into granular with size less than 5mm, and weight is controlled below 0.10g.

Ultra-pure nickel basket with weight about 1.00 g after pickling was used in the experiment, Control the weight of samples between 0.04 g~0.10 g to measure 7 times continuously, then plot the relationship between the measured values of oxygen and nitrogen and weight respectively. Results in Figure 1 and Figure 2 show that the analytical precision of oxygen and nitrogen elements in zirconium-based amorphous alloy samples is better when the sample weight ranges between 0.07 g~0.08 g.

![Figure 1. Relationship between different samples and Oxygen measurements](image-url)
3.3 Analytical Power
After a large number of experiments, we use heated crucibles, with the analysis power as 4.0 kW, 4.5 kW, 5.0 kW, 5.5 kW, 6.0 kW, respectively, the results are found in Table 1.

When the analytical power is 5.5kW-6.0kW, the measurement values of oxygen and nitrogen in the sample are more consistent. When the analytical power is 4.0kW-5.0kW, the measurement values of oxygen and nitrogen in the sample are relatively low, which may be due to the low heating power and incomplete release of oxygen and nitrogen in niobium-based amorphous alloys. The analytical power used in the experiment is 6.0kW to ensure the full release of oxygen and nitrogen.

| analysis power/kW | Oxygen measurements □/% | Nitrogen measure □/% |
|-------------------|-------------------------|---------------------|
| 4.0               | 0.131                   | 0.0032              |
| 4.5               | 0.135                   | 0.0038              |
| 5.0               | 0.144                   | 0.0042              |
| 5.5               | 0.151                   | 0.0045              |
| 6.0               | 0.152                   | 0.0045              |

3.4 Accuracy Test
Under the working conditions of the instrument and the experimental conditions of the method, BCR-276 zirconium alloy columnar reference material was selected for accuracy test, the results are shown in Table 2.

| Sample   | element | Found     | Average | standard    | SD   | RSD |
|----------|---------|-----------|---------|-------------|------|-----|
| BCR-276  | O       | 0.154,    | 0.156   | 0.154±0.008 | 0.0018 | 1.13 |

Figure 2. Relationship between different samples and Nitrogen measurements
0.154, 0.157, 0.158

N
0.0042, 0.0044, 0.0044, 0.0041, 0.0045, 0.0044
0.0043
0.0041±0.0009
0.0015
3.47

3.5 Precision Test
Under the working conditions of the instrument and the experimental conditions of the method, two groups of zirconium-based amorphous alloy samples were selected for precision test, the results are shown in Table 3.

| sample | element | Found          | Average | SD   | RSD   |
|--------|---------|----------------|---------|------|-------|
| 1      | O       | 0.031, 0.032, 0.032, 0.034, 0.030 | 0.031 | 0.0012 | 3.93 |
| 2      | N       | 0.0050, 0.0048, 0.0049, 0.0051, 0.0047, 0.0052 | 0.0049 | 0.0002 | 3.44 |
|        | O       | 0.143, 0.145, 0.144, 0.142, 0.143, 0.144 | 0.143 | 0.0010 | 0.67 |
|        | N       | 0.016, 0.017, 0.015, 0.017, 0.016, 0.016 | 0.016 | 0.0008 | 4.92 |

4. Conclusions
Coating the sample with nickel blue, choosing a heated crucible, melting the zirconium-based amorphous sample at 6.0kW power, it can decompose the oxides and nitrides in the sample completely. The method is rapid, accurate and easy to operate, and can meet the requirements of quantitative analysis of oxygen and nitrogen content in zirconium-based amorphous alloy samples produced by scientific research in large quantities.
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