Study on determination of titanium in Ni-Ti-Nb shape memory alloy by diantipyrylmethane spectrophotometry

Yichun Dai*, Lunfu Tian, Deshuang Zou, Shicao Cao
Institute of Machinery Manufacturing Technology, China Academy of Engineering Physics, Mianyang, 621900, China
*Corresponding author’s e-mail: 1009483998@qq.com or daiweiv@163.com

Abstract: Titanium was one of the main chemical components in Ni-Ti-Nb shape memory alloy. It has high content, narrow range and requires high precision of analytical method. In this study, diantipyrylmethane spectrophotometry was established for the determination of titanium in Ni-Ti-Nb shape memory alloy. The method major interference factors such as dissolve sample, absorption curve and the condition of color reaction were investigated and the analysis conditions of determining titanium were experimentally determined. Beers law was obeyed in the concentration range of 0mg/L ~ 9.0mg/L of Ti. The relative standard deviation of was below 0.3% for the samples (n=6).

1. Introduction
Ni-Ti-Nb shape memory alloy is a new functional material used in the production of special alloys in the aviation, aerospace, military, and biomedical industries. Its analytical technology was still in the exploration research stage. Accurate determination of the chemical composition in the alloy was very important for the development of the material. Titanium was one of the main chemical components of the alloy. The mass fraction of titanium in the nickel-titanium-niobium shape memory alloy was 35%~38%. In the published reports, methods for determination of high content of titanium were titration [1~4], X-ray fluorescence spectrometry [5,6], inductively coupled plasma atomic emission spectrometry [7] and so on. Among of methods, the titration was not suitable for the detection of bulk samples for its cumbersome, long-time, and low working efficiency. X fluorescence spectrum method required grinding powder, tableting and high technology. Inductively coupled plasma atomic emission spectrometry (ICP-AES) had the advantages of wide linear range, high sensitivity, good precision, simultaneous analysis of multiple elements, and high efficiency of analysis while it required expensive equipment. The determination of titanium by diantipyrylmethane spectrophotometry had high sensitivity, good selectivity, simple operation, and accurate results. The application of low titanium content had been studied extensively [8~12] The application of the method to the determination of high titanium content in Ni-Ti-Nb shape memory alloy had not been reported. In this paper, the determination of titanium in Ni-Ti-Nb shape memory alloy was used by diantipyrylmethane spectrophotometry. The method was applied to samples determination. The method had the characteristics of high accuracy, simple operation, fast response, economy and practicality, and the results were satisfactory.
2. Experiment

2.1. Reagents

All reagents used were of analytical grade and all solutions were prepared with deionization water or distilled water or water of considerable purity identified as analytical purity.

The experimental reagents including: 1:1 Sulphuric acid, 1:1 Nitric acid, 1:1 hydrochloric acid, 1:9 hydrochloric acid, 20 g/L of ascorbic acid, 50 g/L of diambirin methane, 1.000 mg/mL of Ti standard solution A, 200 ug/mL of Ti standard solution B, 1.000 mg/mL of Ni standard solution, 1.000 mg/mL of Nb standard solution was used for the experiment.

20 g/L of ascorbic acid was prepared by dissolving 2.0 g of ascorbic acid in water to 100.0 ml. 50 g/L of diantipyrylmethane was prepared by dissolving 5.0 g of diantipyrylmethane in 1:9 hydrochloric acid to 100.0 ml. 1.000 mg/mL of Ti standard solution A was prepared by dissolving 0.1000 g of titanium powder (mass fraction is not less than 99.99 %) in 15 mL of 1:1 sulfuric acid until completely dissolved, then adding 1:1 nitric acid to the solution purple to disappear, and continuing to heat until sulphuric acid smoke for 2minutes, and moving it into 5:95 sulfuric acid to 100.0 ml. 200 ug/mL of Ti standard solution B was prepared by dissolving 20.00 ml of 1.000 mg/mL of Ti standard solution A in 5:95 sulfuric acid to 100.0 ml. 1.000 mg/mL of Ni standard solution was prepared by dissolving 0.1000 g nickel powder (mass score is not less than 99.99 %) in 15 mL of 1:1 sulfuric acid until completely dissolving, cooling to room temperature, moving to 1:1 sulfuric acid to 100.0 ml.

2.2. Apparatus

TU-1900 spectrophotometer was used for the experiment.

2.3. Experiment methods

0.10000 g sample in 250mL beaker with 25 mL of 1:1 sulfuric acid was heated until completely dissolving, then heated to smoke, colded to room temperature, and moved to 1:1 sulfuric acid to 100.0 ml for 1.0000g/L sample solution.

10.00 ml of 1.0000g/L sample solution was added into 250 mL volumetric flask with 10.0 mL of 1:1 hydrochloric acid and 5.0 mL of 20g/L of ascorbic acid. After 5 minutes, 25mL diantipyrroline methane was added into the 6 volumetric flasks and maked up to 100.0 ml with water. The absorbance of the sample solution was determined at 460 nm. The absorbance was obtained from working curve after the sample solution was placed for 15 minutes.

2.4. Work curve production

Working curve was calibrated with the following. 0.00 ml, 1.00 ml, 4.00 mL, 6.00 mL, 7.00 mL and 8.00 mL of 200 ug/mL of Ti standard solution was added into 6 of 200 mL volumetric flasks with 10.0 mL of 1:1 hydrochloric acid and 5.0 mL of 20g/L ascorbic acid, respectively. After 5 minutes, 25mL diantipyrroline methane was added into the 6 volumetric flasks and maked up to 100.0 ml with water. The absorbance of the sample solution was determined at 460 nm. The working curve was calibrated with the mass of titanium as the horizontal coordinate and the absorbance as the vertical coordinate.

2.5. Calculation of results

The result was calculated by % as follow.

\[ W_{Ti} = \frac{m_1 \times V}{m \times V_1 \times 10^6} \times 100 \]

In the formula, Ti concentration from the working curve, 20.00 ml sample volume, the total volume of sample solution and sample mass were denoted by m1, V1, V and m, respectively.
3. Results and Discussion

3.1. Effect of Dissolving Sample Acid and Acidity
Different acid reagents in table 1 were respectively added into the 250.0 mL beaker with 0.1000 g sample, and the sample was dissolved at 250°C on the electric hot plate.

Table 1 Effect of sample dissolution of different acid reagents and its dosage

| Reagent       | Dosage/mL | Sample dissolution                        |
|---------------|-----------|------------------------------------------|
| HCl(1:1)      | 15.0      | Reaction with a slow dilution and incomplete dissolution |
| HNO₃(1:1)     | 15.0      | Almost no reaction                        |
| Aqua regia(1:1)| 15.0      | Reaction with slow dilution and incomplete dissolution |
| H₂SO₄(1:1)    | 20.0      | Reaction with slow dissolution and complete dissolution |
| H₂SO₄(1:1)    | 25.0      | Reaction with fast dissolution and complete dissolution |

The results showed in Table 1 that Ni-Ti-Nb shape memory alloy samples were not dissolved well by HCl, HNO₃ and aqua regia while sample was dissolved well by H₂SO₄. 25.0 mL of 1:1 H₂SO₄ dosage was selected for further work.

3.2. Effect of absorption wavelength
According to the experimental method, the absorbency was measured at different wave lengths from 200 nm to 600 nm using a 1600 ug/200 mL Ti sample. The drawn absorption curve was shown in Figure 1. The result showed that the maximum absorption wavelength of the complex was between 380-400 nm. In practical applications, it was found that the absorbency at 380 nm to 400 nm was not stable for determination of the relatively high concentration Ti samples. After analysis, the method used 460 nm with relatively high sensitivity and stable absorbency as the measurement wavelength.

3.3. Effect of Dosage of hydrochloric acid.
Titanium (IV) and diampirin methane can be formed the soluble yellow complex in the medium of hydrochloric acid, sulfuric acid and the mixture of hydrochloric acid-sulfuric acid. The sensitivity of the yellow complex in hydrochloric acid medium was higher than that in sulfuric acid and the mixture medium. Therefore, hydrochloric acid was selected as the medium in the experiment and the effects of different dosage of 1:1 hydrochloric acid on the determination were investigated. In the test, a 1400ug/200mL of Ti specimen was used to determine the absorption by changing dosage of 1:1 hydrochloric acid. The results showed in Table 2 that the addition of 5 mL ~ 20 mL had little effect on the results. 10 mL of 1:1 hydrochloric acid dosage was selected for further work.

Table 2 Effect of dosage of hydrochloric acid

| Dosage of hydrochloric acid/mL | Absorbance |
|-------------------------------|------------|
| 5.00                          | 0.782      |
| 10.00                         | 0.783      |
| 15.00                         | 0.781      |
| 20.00                         | 0.782      |
3.4. Effect of Dosage of ascorbic acid
In the test, the absorption was measured by changing dosage of 20 g/L of ascorbic acid by using a 1400 ug/200mL of Ti specimen. The results showed in table 3 that 2 ml ~ 10 mL of ascorbic acid had little effect on the measured results. 5mL of 20g/L of ascorbic acid dosage was selected for further work.

Table 3 Effect of dosage of ascorbic acid

| Dosage of ascorbic acid/mL | 2.00 | 5.00 | 8.00 | 10.00 |
|---------------------------|------|------|------|-------|
| Absorbance                | 0.782| 0.783| 0.782| 0.782 |

3.5. Effect of Dosage of diantipyrylmethane
The effect of dosage of 50g/L of diantipyrylmethane on the absorbance was tested by 1400 ug/200 mL of Ti standard solution. The results showed in Figure 2 that the 15 ml ~ 30 mL of diantipyrylmethane had little effect on the absorbance while the absorbance increased with the increase of dosage of diantipyrylmethane with diantipyrylmethane dosage less than 15 ml. 25 mL of 50 g/L of diantipyrylmethanedosage was selected for further work while.

Figure 2 Effect of Dosage of diantipyrylmethane

3.6. Effect of chromogenic time
The effect of chromatic time on the absorbance was tested by 1500 ug/200 mL of Ti standard solution. As showed in Figure 3, the absorbance increased with the increase of chromatic time when chromatic time was below 8 minutes. The absorption was maximum at 8 minutes and the maximum absorption was constant for more than 40 minutes. Therefore, chromatic time of 10 minutes was selected for further work.

Figure 3 Effect of chromogenic time

3.7. Effects of matrix elements
The effect of matrix elements on the absorbance was tested by 1400 ug/200 mL of Ti standard solutions added 0.5 ml of 1.00 mg/ml Nb, 2.0 ml of 1.00 mg/ml Ni and the mix of 0.5 ml of 1.00
mg/ml Nb - 2.0 ml of 1.00 mg/ml Ni, respectively. The results showed in table 4 that the matrix elements had no influence on the determination results.

| Matrix element & Dosage | No matrix element | 0.5ml of 1.00mg/ml Nb | 2.0ml of 1.00mg/ml Ni | Mix of 2.0ml of 1.00mg/ml Ni-0.5ml of 1.00mg/ml Nb |
|------------------------|-------------------|-----------------------|----------------------|-----------------------------------------------|
| Absorbance             | 0.782             | 0.783                 | 0.784                | 0.782                                         |

3.8. Standard curve
According to the experimentale method, standard curve was drawn by different concentration standard solutions of Ti standard solutions. The results showed in Figure 4 that the Ti concentration in the range of 0.0 mg/L to 9.0 mg/L was in accord with Bill's law.

3.9. Sample analysis and determination results
The diantipryl methane spectrophotometry method was used to determine the content of Ti elements in Ni-Ti-Nb shape memory alloys. According to GB/T 6379.6-2009 Accuracy (trueness and precision) of Measurement methods and results- Part 6: Use in practice accuracy values [13], the allowable deviation of the method was 2.8σ at a 95% confidence level. The accuracy test in table 5 was carried out. The relative standard deviation was less than 0.5%(n=6), and the results were consistent with the requirements of laboratory quality analysis.

| Sample        | Determination/% (n=6) [%] | Average/% [%] [%] value | σ | RSD/% |
|---------------|--------------------------|-------------------------|---|------|
| Ni-Ti-Nb-1    | 36.78, 36.75, 36.90, 36.85, 36.90, 36.80 | 36.83 | 0.063 | 0.17 |
| Ni-Ti-Nb-2    | 36.95, 36.94, 36.72, 36.82, 36.73, 36.87 | 36.84 | 0.100 | 0.27 |
| Ni-Ti-Nb-3    | 36.70, 36.69, 36.68, 36.65, 36.73, 36.78 | 36.71 | 0.045 | 0.12 |
4. Conclusion
In this study, the method of determination of titanium in Ni-Ti-Nb alloy by diantipyrylmethane spectrophotometry was established. Precision and accuracy of the method met quality control requirements of laboratory. The method was reliable and applicable for quality control analysis and sample systems analysis.

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