Enhancement Mechanism of the Oscillopolarographic Current of Germanium(IV)-Trihydroxybenzoic Acid System and Application

Yuxia ZHANG*, Yongming WU

Central Iron & Steel Research Institute, Beijing 100081, China

In the medium of dilute sulfuric acid germanium(IV)-trihydroxybenzoic acid complex produced an adsorptive current at $-0.62\text{V}(\text{vs.SCE})$, which could produce a parallel catalytic current in the presence of vanadium(IV). After adding EDTA, this current could be further increased. The sensitivity was raised to about 1200-times higher than that in the absence of vanadium(IV) and EDTA in above-mentioned medium. The chemical reaction rate constant(k_1) was calculated to be $14.4 \times 10^6 \text{ L/mol s}^{-1}$. The peak height(second derivative)(i_p'') was proportional to the concentration of germanium(IV)($C_{\text{Ge(IV)}}$) in the range of $0.04\text{--}20 \mu\text{g/L Ge(IV)}$. The correlation coefficient (r) and detection limit (DL) were 0.9996 and $5 \times 10^{-11} \text{ mol/L Ge(IV)}$ respectively. The composition of complex, the apparent stability constant (k) of this complex, the current property, the mechanism of the electrode reaction and the mechanism of the electrochemical response enhanced by EDTA were investigated in detail. Possible interferences were evaluated. The proposed method was applied to determine the trace germanium in alloys with satisfactory results.

Keywords Germanium(IV)-trihydroxybenzoic acid, oscillopolarography, alloy, parallel catalysis

Normally germanium(IV) can not be reduced in acidic media prior to hydrogen evolution, but after forming a complex with reagents of polyhydroxyphenol, or with other complex reagents, a well defined electrochemical response is observed.¹⁻⁵ Although complex polarographic current of Ge(IV)-trihydroxybenzoic acid (THBA) has been reported,⁶ but there was no information about the investigation on the mechanism of the process of electrochemical reaction and on the mechanism of the electrochemical response enhanced by vanadium(IV), especially by EDTA in literatures. In this paper, the optimal condition for determining germanium in Ge(IV)-THBA-V(IV)-EDTA system; coordinating ratio and existing form of the corresponding complex, the mechanism concerned both of chemical reaction and of electrode reaction was studied. This research led to establish a method for the determination of germanium($0.00001\text{--}0.001\%$) in superalloys, which involved separation of interferences by extraction and directly determination for higher concentration of germanium ($>0.001\text{--}0.005\%$) in superalloys without separation.

Experimental

Apparatus and reagents

The polarographic measurements were made with a Model JP-2 Single-sweep oscillopolarograph(with 1st- and 2nd-order derivatives)(Chengdu Instrument Factory, China), coupled with a dropping mercury electrode(DME) as the working electrode, using a saturated calomel electrode(SCE) as the reference electrode, and a platinum wire as an auxiliary electrode. A Model PAR 370-8M Electrochemistry System(EG & G PARC, USA) was used for voltammetry or cyclic voltammetry. The working electrode was a PAR Model 303 static mercury drop electrode and using a three-electrode system: a hanging mercury drop electrode(HMDE) as the working electrode, an Ag/AgCl electrode as the reference electrode, and a platinum wire as the counter electrode.

A Model UV 2201 UV-Vis recording spectrophotometer(Shimadzu, Japan) was used for spectrophotometric experiments.

A stock standard solution of germanium(1 mg/ml) was prepared by dissolving 0.2500 g metal germa-

niun powder(99.99 %) in an appropriate amount of hydrogen peroxide(30 %) and 0.5 g sodium hydroxide, and dropping sulfuric acid to strong acidity, heating to drive out hydrogen peroxide, and diluting to 250 ml in a volumetric flask with water. Transferred an appropriate amount of this stock standard solution to prepare the working standard solution as need. Vanadium(IV) solution (0.1 mol/L) was prepared by dissolving 11.70 g ammonium metavanadate in 300-400 ml of nearly boiling water. Added 50 ml of hydrochloric acid(1+1) and 90 ml of ascorbic acid solution(10 %) at room temperature. After fully dissolved, diluted in 1 L in a volumetric flask with water. Solution of THBA(0.5 %) was stored in a dark-brown bottle, away from the light. Solution of sulfuric acid (0.2 mol/L), EDTA (0.1 mol/L) and ascorbic acid(A.A.)(2 %) were prepared as usual. Only if specified, all chemicals were of analytical-reagent grade. All solutions were prepared with deionized water.

Procedure

An appropriate amount of the working standard solution of Ge(IV) was added to a 25 ml volumetric flask, 1 ml H_2SO_4 (0.2 mol/L), 5 ml THBA(0.5 %), 5ml V(IV)(0.1 mol/L), 2.5 ml EDTA(0.1 mol/L) and 1 ml A.A.(2 %), solutions were then added successively. This solution was diluted to the mark and mixed, and then poured into the cell. A potential scan was performed in the range of -0.40 V to -0.90 V(vs.SCE), observed by oscillograph or recorded by linear voltammetry(including cyclic voltammetry).

Results and discussion

Oscillographic behaviour of germanium(IV) in the different media

The experiments showed that the complex of germanium(IV) with THBA and after adding vanadium(IV) in the media of sulfuric acid or oxalic acid, perchloric acid or acetic acid, or in the buffer solution of chloroacetic acid-sodium acetate, respectively, all these appeared a reductive current at potential in the range of -0.55 V to -0.67 V (vs. SCE)(see Table 1). It can be seen that among the different media investigated for Ge(IV)-THBA system sulfuric acid was the best medium.

Table 1 Oscillographic behaviour of germanium(IV)

Medium	H_2SO_4 (0.008mol/L) (pH~2)	$\text{H}_2\text{C}_2\text{O}_4$ (0.24%)	HAc (0.02mol/L)	buffer solu.
Ge(IV)-THBA-EDTA ¹				
i_p ($\mu\text{A.s}^{-2}$)	0.763	0.046	0.17	0.046
E_p (V)	-0.64	-0.55	-0.67	-0.62
Ge(IV)-THBA-V(IV)-EDTA ²				
i_p ($\mu\text{A.s}^{-2}$)	37	3.95	disappeared	4.78
E_p (V)	-0.61	-0.55	-0.67	-0.64

Notes: ¹ $C_{\text{Ge(IV)}}=0.2 \text{ mg/L}$, ² $C_{\text{Ge(IV)}}=0.02 \text{ mg/L}$

Condition of basic electrolyte

Although the current peak height (i_p) raised with increasing vanadium(IV), but the peak shape became to worse. Therefore the concentration of vanadium was selected to be 0.02 mol/L. The optimal condition of basic electrolyte was H_2SO_4 (0.008 mol/L), THBA (0.1%), vanadium(IV) (0.02 mol/L), ascorbic acid (0.08%) and EDTA (0.01 mol/L) (see Fig.1). The solution was steady for 24h at the same room temperature.

Fig. 1 Effect of the amount of various reagents on the current peak height(i_p) of Ge(IV)-THBA-V(IV)-EDTA Curve: 1.EDTA(0.1mol/L), 2. H_2SO_4 (0.2mol/L), 3. THBA (0.1%), 4. V(IV)(0.1mol/L), 5. AA(2%)

Linear relationship and detection limit

The current peak height (i_p) was measured at -0.61 V (vs.SCE), it was proportional to the concentration of germanium (IV) in the range of 0.04 ~20 $\mu\text{g/L}$. The linear regressive equation was $Y(\mu\text{A.s}^{-2}) = 0.78+85X (\mu\text{g}/25\text{ml})$. The correlation coefficient (r) and detection limit (DL) were 0.9996 and $5 \times 10^{-11} \text{ mol/L Ge (IV)}$, respectively.

Effect of EDTA on the current of Ge(IV)-THBA system and Ge(IV)-THBA-V(IV) system

After adding EDTA, in the medium of dilute sulfuric acid (pH~2) the complex adsorptive current of Ge(IV)-THBA (system A) was split into two waves (see Fig.2, curve 1, 2). The value of ΔE (the difference of E_{p1} and E_{p2}) increased along with the increasing concentration of EDTA, but the values of i_{p1} and i_{p2} did not change remarkably at the same time. Only the distinguishability of the peak currents was improved. This demonstrated that these two peaks of system A were caused by different steps of electrode reaction, not by different complexes.

Fig. 2 Oscillograms of germanium(IV) in different conditions of composition. Curve: 1. H_2SO_4 (0.008 mol/L), THBA (0.1%), AA (0.08%), Ge(IV) (0.04 mg/L), 2. 1+EDTA (0.01 mol/L), 3. V(IV) (0.02 mol/L), Ge(IV) (0.004 mg/L), others as curve 1, 4. 3+EDTA (0.01 mol/L), 5. H_2SO_4 (0.008 mol/L), AA (0.08%), V(IV) (0.02 mol/L), 6. 5+EDTA (0.01 mol/L)

In the presence of vanadium(IV) the current of above system (without EDTA) (system B) became to a sensitive parallel catalytic current, which was further increased about 10 times after adding EDTA. But the value of peak potential remained the same (see Fig.2, curve 3, 4). and about 1200 times higher than that in the absence of vanadium(IV) and EDTA in the same medium. After adding EDTA to system B in the above medium, i_{p1} (E_{p1} -0.60 V) reached to the maximum value, i_{p2} (E_{p2} -0.73 V) appeared, when the molar ratio of V(IV) and EDTA was 1:2. Added EDTA continuously, i_{p1} decreased, and i_{p2} kept the same.

Effect of EDTA on the current of Vanadium(IV)

Vanadium(IV) in the medium of dilute sulfuric acid without EDTA did not produce any peak current,

but after adding EDTA, it appeared a corresponding height of peak current at -0.73 V, which was similar to the i_{p2} in system B (see Fig.2, curve 5 and 6).

Effect of EDTA on the reversibility of electrode process

In the absence of EDTA, from the cyclic voltammogram of Ge(IV)-THBA-V(IV) system, it could be seen the cathodic current was asymmetric, and no corresponding current appeared in the anodic part, the electrode process was irreversible (see Fig.3, curve 1). Addition of EDTA to the solution of Ge(IV) in above medium resulted in the remarkable increase of cathodic current, becoming to well symmetry, meanwhile the corresponding current, but the same direction as cathodic current had, appeared in the anodic part of cyclic voltammogram. The reversibility of the electrode process was improved obviously. These indicated that the electrode reaction of above system was a complex adsorptive parallel catalytic process (see Fig.3, curve 2)

Fig. 3 Cyclic voltammograms of germanium(IV) Curve: 1. H_2SO_4 (0.008 mol/L), THBA (0.1%), V(IV) (0.02 mol/L), Ge(IV) (0.008 mg/L), 2. 1+EDTA (0.01 mol/L)

Formation and molar ratio of Ge(IV)-THBA complex

Only a very small absorbance (0.0064) of THBA in the medium of dilute sulfuric acid was appeared at 750 nm. After adding Ge(IV) or EDTA the absorbance at 750 nm did not change or produce a new absorptive peak at the other wave length. This indicated that the complex of Ge(IV)-THBA did not form in the bulk solution, but formed on the surface of electrode. The molar ratio of Ge(IV)-THBA was estimated to be 1:2 by a polarographic method in which equal molar quantities were successively varied. The apparent stability constant (k) of this

complex was 4.6×10^5 . The short part of the coordinating number for germanium could be completed by H_3Y^- , the first-order dissociation form of $\text{EDTA}(\text{H}_4\text{Y})$ at $\text{pH} \sim 2$. Therefore this complex loaded a negative charge, i.e. $[\text{Ge}(\text{IV})(\text{THBA})_2 \cdot \text{H}_3\text{Y}]^-$, which was also supported by the experiments of electrocapillary curve, initial potential, surfactants, ion-exchange method etc..

Formation and ratio of V(IV)-EDTA complex

It could be seen by eyes that in the medium of dilute sulfuric acid, the colour both of solution $\text{Ge}(\text{IV})$ -THBA-V(IV) system and of the solution in the presence of vanadium(IV) only, was bright blue respectively. Along with the increasing EDTA this colour of solutions turned to darker blue, more and more, which indicated that a new substance produced and increased in the solution.

In the medium of dilute sulfuric acid, the solution of V(IV) appeared a maximum absorption at 590 nm and the solution of THBA appeared a maximum absorption at 750 nm. Addition of 0-5 ml EDTA to these two solutions resulted in the increasing absorbance(A_1) at 590 nm remarkably, but the absorbance(A_2) at 750 nm, changed very little (see Fig. 4), which indicated that a complex of vanadium(IV) and EDTA formed in solution, but THBA did not react with EDTA.

The value of absorbance(A_1) increased with increasing of EDTA presented a S-shape process, at the turning point of this S-shape curve the molar ratio of EDTA and V(IV) was 1:2 (see Fig. 4), i.e. $\text{V}(\text{IV})_2 \cdot \text{H}_3\text{Y}^-$, here the current peak height (i_{p1}) of $\text{Ge}(\text{IV})$ -THBA-V(IV) system reached maximum, which has been mentioned above.

Fig. 4 Influence of the amount of EDTA added on the absorbance of V(IV) and THBA in the medium of dilute H_2SO_4 . Curve A1 Absorbance of V(IV) at 590 nm; Curve A2 Absorbance of THBA at 750 nm.

Character of the complex current

The results of experiments including the relationship between i_p and $C_{\text{Ge}(\text{IV})}$, the temperature coefficient ($\alpha, \%/^\circ\text{C}$) of the peak current [11.9 (5~35 $^\circ\text{C}$), 0.41 (35~55 $^\circ\text{C}$), -2.58 (55~70 $^\circ\text{C}$)], electrocapillary curve, cyclic voltammogram (single- and multi-), effect of deposition time, and scan rate of potential on the peak height of the current (cathodic and anodic), demonstrated that the current of the $[\text{Ge}(\text{IV})(\text{THBA})_2 \cdot \text{H}_3\text{Y}]^-$ complex in the presence of vanadium (IV) has an adsorption (even catalytic) character.

Mechanism of catalytic current of Ge(IV)-THBA-V(IV) system enhanced by EDTA

The above results showed that, the currents $\text{Ge}(\text{IV})$ -THBA system reduced by two steps electrode reaction could be distinguished clearly after adding EDTA. As the $\text{V}(\text{IV})_2 \cdot \text{H}_3\text{Y}^-$ in the medium of dilute sulfuric acid was the effective component of undergoing chemical oxidation, one molecule of $\text{V}(\text{IV})_2 \cdot \text{H}_3\text{Y}^-$ contained two atoms of V(IV), so which strengthened the V(IV) to chemically oxidize $\text{Ge}(\text{II})$ produced by the electroreduction of $\text{Ge}(\text{IV})$ -THBA system. The addition of EDTA also made the electroreduction peak current of $\text{V}(\text{III}) + e \rightarrow \text{V}(\text{II})$ to be distinct. Thus the equilibrium of chemical oxidation shifted to the right direction continuously, the catalytic cycle was accelerated. The complex adsorptive parallel catalytic current (i_p) of system B was increased about 10 times compared with that obtained in the absence of EDTA. The chemical reaction rate constants (k_1) were calculated to be $2.25 \times 10^5 \text{ L mol}^{-1} \text{ s}^{-1}$ [for $\text{Ge}(\text{IV})$ -THBA-V(IV) system] and $1.44 \times 10^7 \text{ L mol}^{-1} \text{ s}^{-1}$ [for $\text{Ge}(\text{IV})$ -THBA-V(IV)-EDTA system], respectively.

Mechanism of electrode reaction of Ge (IV)-THBA-V(IV)-EDTA system

Resersibility, estimation of n and α .

Because of $\gamma = (E_p - E_1)/(E_2 - E_p) = 1.2$, $i_p^+/i_p^- = 1.29$, the electrode reaction of entitled system was a quasi-reversible process. E_1 and E_2 were the potential values at both sides of the half-peak width ($W_{1/2}$); i_p^+ and i_p^- were the left- and right- side of current height, respectively. When $W_{1/2}$ was measured to be 65 mV, room temperature was at 17 $^\circ\text{C}$, assumed α to be 0.5, then according to formula $W_{1/2} = 2.44RT/\alpha nF$, the number (n) of electrons involved in the electrode reaction could be calculated to be 2 and then the electronic transfer coefficient (α) was 0.53.

Parameters concerned adsorption character.

The amount (Γ_s) of the saturated (fully) adsorption was calculated to be 1.47×10^{-9} mol/cm². The coverage (θ) by the adsorptive adsorption species could be obtained from Γ_t/Γ_s , here Γ_t was the amount of the partial of the adsorption. The relationship between $\theta/(1-\theta)$ and $C_{\text{Ge(IV)}}$ was a linear through the zero point, which demonstrated that the adsorption of $[\text{Ge}(\text{THBA})_2\text{H}_3\text{Y}]^-$ on the electrode surface obeyed a Langmuir adsorption isotherm. From the slope of this

linear the adsorption coefficient (β) could be calculated to be $2.73 \times 10^6 \text{ L mol}^{-1}$, then the adsorption free energy (ΔG°) and adsorption equilibrium constant (k_o) were estimated to be $-35.98 \text{ kJ mol}^{-1}$ and $3.7 \times 10^{-5} \text{ mol L}^{-1}$, respectively.

Mechanism of electrode reaction.

According to the above experimental results, a possible reaction mechanism was therefore suggested as follows:

Due to the existence of process(2), the electro-reduction and chemical oxidation in process(1), i.e. the catalytic cycle, could be accelerated.

Analytical application

Interference of coexisting ions.

For 0.05 μ gGe(IV)/25ml in the Ge(IV)-THBA-V(IV)-EDTA system the determination error was less than 5%; the following ions (in times) did not interfere in the determination of Ge (IV): 1×10^6 Na⁺, 2×10^5 As³⁺, 1.6×10^5 Mn²⁺, 1×10^5 Ni²⁺, 6×10^4 Fe³⁺, 5×10^4 Nb(V), Cu²⁺, Cr³⁺, 3×10^4 La³⁺, 2×10^4 Zr(IV), Re(VII), Ga³⁺, K⁺, 1×10^4 Pb²⁺, Be²⁺, Ti⁺, Sn²⁺, Hg²⁺, Sb³⁺, W(VI), Co²⁺, 6×10^3 Cr(VI), 4×10^3 Al³⁺, 2×10^3 V(V), In³⁺, 1.6×10^3 Zn²⁺, 1×10^3 Te⁴⁺, Bi³⁺, Au³⁺, Ag⁺, Mo(VI), Cd²⁺, Ta(V), 6×10^2 Ti⁴⁺, 2×10^2 Se⁴⁺, 2×10^6 ClO₄⁻, NO₃⁻, SO₄²⁻, Cl⁻, 1×10^6 thiourea, Br⁻, 8×10^3 Ac⁻, 4×10^5 SCN⁻, 2×10^5 PO₄³⁻, formate, tartrate, citrate, 8×10^4 oxalate, 4×10^4 F⁻, 2×10^4 I⁻.

All these showed that the proposed method was excellent both in sensitivity and in selectivity. The method has been applied to determine the trace amounts of germanium ($0.00001\text{--}\leq 0.001\%$) after extracting by CCl_4 in the medium of 10 mol/L HCl , which completely eliminated interfering elements as well known and even directly without separation for $>0.001\%$ germanium in superalloys with satisfactory results.

Procedure

The mixed acid of hydrofluoric acid-nitric acid-phosphoric acid on the proportion of 2:2:1 was employed to decompose the appropriate amount of superalloy samples avoiding the loss of germanium.

When the content of germanium was very low ($0.00001\text{--}0.001\%$) germanium chloride(GeCl_4) should be extracted from the medium of hydrochloric acid (10 mol/L) by carbon tetrachloride(CCl_4), back extracted germanium (IV) from the organic phase by water. The extraction rate was more than 98%. The recoverage was 96–102% for $0.1\text{--}0.5\text{ }\mu\text{g Ge(IV)}$. When the content of germanium($>0.001\text{--}0.005\%$) was higher, after dissolving and treating the samples as above, it could be determined directly by the proposed method without separation.

Table 2 Results of the determination of germanium in alloys

Sample	Average value Found (% Ge) (n=4)	RSD %	SP (%Ge)	ICP-MS
10AG	0.00017±0.00007	4.2		0.00016
F1	0.00023±0.000006	2.5	0.00028	
F2	0.00020±0.000012	5.8	0.00021	
C1	0.00012±0.000021	17	0.00011	
C2	0.00013±0.000017	13.3	<0.0001	
S1	0.00024±0.00011	43.3	0.00022	
S2	0.00020±0.000018	9.0	0.00021	
96N-026 Ferroalloy GH169 [*]	0.00031(n=2)			0.00033
1 [#]	0.0014±0.000052	3.7	0.0014	
2 [#]	0.0020±0.000050	2.5	0.0026	
3 [#]	0.0028±0.00017	6.1	0.0039	
4 [#]	0.0052±0.00042	8.1	0.0073	
5 [#]	0.0023±0.00016	7.0	0.0029	

Notes: * determined directly

Results

All results were calculated by the method of standard addition. The results determined by proposed method were summarized in Table 2.

Conclusions

A very sensitive, selective, simple and rapid oscilopolarographic method for determination of germanium in alloys and superalloys has been proposed, and also a basic theoretical study on the mechanism of the parallel catalytic current of Ge(IV)-THBA-V(IV) system enhanced by EDTA in detail by electrochemical and spectrophotometric methods were presented in this paper. The results demonstrated that the current of Ge(IV)-THBA-V(IV)-EDTA system were behaving as an adsorptive complex wave and also as an EC papallel catalytic wave, in which germanium(IV) was a catalytic agent, THBA was a complexing agent, EDTA was an auxilliary agent and V(IV) was a chemical oxidizing agent in the EC process. As vanadium(IV) was existing in form of $V(IV)_2-H_3Y^-$, thus germanium(II), the product of electrode reduction, could be chemically oxidized stronger and the product of it chemical reduction, $V(III)_2-H_3Y^-$, could be expected by the following

electrode reaction: $V(III)_2-H_3Y^- + 2e^- \rightarrow 2V(II) + H_3Y^-$, therefore the reaction equilibrium was shifted to the right direction continuously, which resulted in the catalytic cycle to be accelerated.

Acknowledgements

The authors would like to thank the financial support from the National Natural Science Foundation of China and from the Laboratory of Electroanalytical Chemistry, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences.

References

1. N. S. Odobesky, L. S. Colanckaya *et al.*, *Zh. A. Khim.* **28**, 2171(1973).
2. Ya. I. Tur'yan, L. F. Clina, *et al.* *Zh. A. Khim.* **30**: 1842(1975).
3. J. C. Aguilar, J. de Gyves, *Anal. Chim. Acta*, **306**: 243(1995).
4. Changqing Sun, Qian Gao, Liling Liu, *Talanta*, **42**, 881(1995).
5. Ya. I. Tur'yan, *J. Electroanal. Chem.*, **338**, 1 (1992).
6. C. Schleich and G. Henze, *Fresenius' Z. Anal. Chem.*, **338**, 145(1990).

* Corresponding author

Fax: +86-10-62182584