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Thermodynamic analysis of production of high purity titanium by thermal decomposition of titanium iodide

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Abstract: High purity titanium was prepared by thermal decomposition of titanium iodide. The feasible synthetic route and optimum decompositon temperaure were obtained by thermodynamic analysis in the process of thermal decomposition of titanium iodide and nucleation growth theory. The temperature for the formation of titanium iodide is in the range of 800−900 K, at which a large amount of titanium iodide vapour can be obtained. The decomposition temperature of titanium iodide is in the range of 1 300−1 500 K, at which a favourable decomposition rate can be achieved. The experiment results show that the purity of the produced titanium is more than 99.995%.

Key words: high purity titanium; titanium iodide; thermal decomposition

1 Introduction

The high purity titanium was currently used as sputtering target materials in the preparation of control electrode of large-scale integrated circuits, diffusion impervious layer and wiring materials due to its excellent specific strength, workability and corrosion resistance. The impurities in the titanium will result in performance reduction of the materials, so it is necessary to remove the impurities in the titanium used as sputtering target materials[1−4]. The preparation of high purity titanium has been deeply researched in USA and Japan[5−9], but there are few reports on this field in China. The methods to prepare high purity titanium involve Kroll process, iodization process and molten salt electrolysis process [10−13].

A conventional method for obtaining high purity titanium is the iodide thermal decomposition process (also known as the iodization process). In the process, the titanium tetra-iodide(TiI_4) is synthesized firstly in a closed container at 500−700 K by using sponge titanium and iodine as raw materials, and then the synthesized TiI_4 is heated to 1 600−1 800 K on the titanium wire at the center of the reactor to deposit high purity titanium. The iodine produced as a by-product by the thermal decomposition reaction can be cyclically used in the synthesis of titanium iodide. The reactions in the process can be written as:

Synthesis reaction

$$Ti(crude)+2I_2 \rightarrow TiI_4;$$

Thermal decomposition reaction

$$TiI_4 \rightarrow 2I_2+Ti\ (high\ purity)$$

During the synthesis of titanium iodide, there exist two kinds of compounds, TiI_2 and TiI_4. The synthesis of higher-valent iodide(TiI_4) can be completed at lower temperature (500−700 K), but it must be decomposed at higher temperature (1 600−1 800 K). While the synthesis of lower-valent iodide(TiI_2) must be performed at higher temperature(1 000−1 200 K), but it can be decomposed at relatively low temperature (1 300−1 500 K)[14−15]. Accordingly, the thermal decomposition of the metal impurities contained in the lower valent titanium iodides used as the gas source for depositing titanium is hindered, thereby eliminating the possibility that any metal impurities might be deposited on the titanium[16−18]. Under optimal process conditions, higher synthesis rate and decomposition rate of titanium iodides can be

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obtained, while that of impurities in the raw titanium can be controlled at a low level. So the impurities cannot deposit on the titanium and a high purity titanium is produced.

In this work, high purity titanium is obtained using sponge titanium and iodine as raw materials with the self-made apparatus. Based on the thermodynamic analysis on the process of thermal decomposition of titanium iodides and nucleation growth theory, the optimum conditions of preparing high purity titanium are obtained.

2 Thermodynamic analysis

2.1 Thermodynamic analysis of titanium iodide reactions

Assuming there are equilibriums in the iodization process and the thermal decomposition process, the relationships between Gibbs free energies and equilibrium constants of the reactions (1) and (2) can be determined based on the thermodynamic data of iodine, titanium and titanium iodide as shown in Table 1.

$$2I_2(g)+Ti(s)\leftrightarrow TiI_4(g) \quad (1)$$

$$TiI_4(g)+Ti(s)\leftrightarrow 2TiI_2(g) \quad (2)$$

The relationship between Gibbs free energy ΔG^{Θ} and reaction temperature T can be determined by the following equation:

$$\Delta G_1^{\Theta}=-415.36+0.391T-11.046\times10^{-3}T\ln T+5.69\times10^{-6}T^2+1.061\times10^{2}T^{-1} \quad (3)$$

Also, the Gibbs free energy of the reactions (2) can be determined by the following equation approximately:

$$\Delta G_2^{\Theta}=170.43-0.384T+5.53\times10^{-3}T\ln T+5.142\times10^{-6}T^2-0.115\times10^{2}T^{-1} \quad (4)$$

According to the classical thermodynamic theory, the relationship between the equilibrium constant K_p and ΔG^{Θ} can be determined by the following equation:

$$\lg K_p=-\Delta G^{\Theta}/2.303RT \quad (5)$$

Based on Eq.(5), the reaction temperature T can be calculated with K_p and ΔG^{Θ}.

The reactions (1) and (2) are expected to proceed to right to form much amounts of iodides including TiI_4 and TiI_2 in the iodide source area. However, it is expected to deposit titanium as much as possible on the substrate in the deposition area, where a low concentration of TiI_4 is needed. If the temperature of the iodide area is T_2 and the temperature of the deposition area is T_1, the difference $\Delta T=|T_2-T_1|$ should be low enough to ensure the reversibility of the reactions (1) and (2) changing with the operating temperature, i.e. $\lg K_p\approx0$.

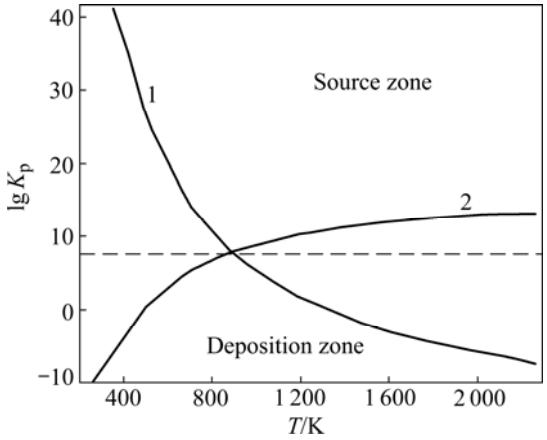

Fig.1 Relationship between lgK_p and T

The temperature can be calculated according to Eq.(5) when lg K_p=0. Then, the temperature T_2 in the case of lg K_p>0 is beneficial for synthesizing iodides in the iodide source area; in contrary, in the case of lg K_p< 0, the decomposition reaction in the deposition area is preferential.

By plotting the equilibrium constants (K_p) against the reaction temperatures T, two curves are obtained as shown in Fig.1.

As shown in Fig.1, curve 1 and curve 2 cross at lg K_p=8 (marked by a dashed line). In the upside of the dashed line , $K_{p1}>K_{p2}$ (K_{p1} and K_{p2} are the equilibrium constants of reactions (1) and (2) respectively), the reaction (1) moves right to produce more TiI_4 and thus more TiI_2; in the downside of the dashed line, $K_{p1}<K_{p2}$, reaction (2) proceeds to the left, thus TiI_2 decomposes to deposit titanium on the deposition substrate. So, the downside zone of the dashed line is the favorable deposition area, and the upside zone of the dashed line is the favorable iodide area.

2.2 Thermodynamic analysis of nucleation

The thermal decomposition process of iodides can

Table 1 Thermodynamic parameters of some matters[16]

Matter	$c_p=a+bT+cT^{-2}$ (kJ/(mol·K))			ΔH_{298}/(kJ·mol^{-1})	S_{298}/(J·mol^{-1}·K^{-1})
	a	b	c		
I_2(g)	37.405×10^{-3}	0.569×10^{-6}	-0.619×10^{-2}	62.42	260.57
TiI_4(g)	108.010×10^{-3}	0.042×10^{-6}	-3.360×10^{-2}	−287.02	432.96
Ti(s)	22.158×10^{-3}	10.280×10^{-6}	−	0	30.65
TiI_2(g)	62.321×10^{-3}	0.021×10^{-6}	-1.565×10^{-2}	−57.74	329.32

be expressed by the following reactions:

$$2TiI_2(g) \rightarrow Ti(g)+TiI_4(g) \quad (6)$$

$$Ti(g, p) \rightarrow Ti(s, p^0) \quad (7)$$

According to the classical nucleation theory, under the condition of homogeneous nucleation and spherical nucleus, the activation energy of nucleation process may be defined as:

$$\Delta G^* = \frac{16\pi\gamma^3 V^2}{3R^2T^2\ln^2(p/p^0)} \quad (8)$$

where V is the molar volume of titanium; γ is the surface tension of titanium; T is the temperature; p is the partial pressure of gaseous titanium; p^0 is the vapour pressure of solid titanium; p/p^0 is the vapour supersaturation[19−20]. So, under steady state, the nucleation speed and the critical nucleation diameter can be determined by the following equations:

$$I = Ze^{\frac{-\Delta G^*}{RT}} \quad (9)$$

$$D = \frac{4\gamma V}{RT\ln(p/p^0)} \quad (10)$$

where Z and R are constants. As for titanium, the molar volume V is 10.64×10^{-6} m^3/mol, and the surface tension γ is 1.588 J/m^2. When the diameter of nucleation is smaller than the critical diameter, the newly formed nucleation is unstable which can be dissolved again; when the diameter of nucleation is larger than the critical diameter, the nucleation can grow.

For reaction (6), p can be calculated by the following equations:

$$\Delta G=170.43-0.984T+5.53T\ln T\times10^{-3}+5.142T^2\times10^{-6}-11.5T^{-1} \quad (11)$$

$$\ln K_p = -\frac{\Delta G}{RT} \quad (12)$$

$$K_p = \frac{p^2}{(1-2p)^2} \quad (13)$$

p^0 can be calculated by the following equation:

$$\lg(p^0/\text{Pa})=141.8-3.23\times10^5T^{-1}-0.0306T \quad (1\ 200-2\ 000\text{K}) \quad (14)$$

Fig.2 shows the relationship between the nucleation speed I and the vapour supersaturation p/p^0, and Fig.3 shows the relationship between critical nucleation diameter D and vapour supersaturation p/p^0.

As shown in Fig.2 and Fig.3, in the temperature range of 1 200−1 500 K, the faster nucleation speed I and smaller critical nucleation diameter D can be obtained simultaneously at proper vapor supersaturation, which verifies that a fast deposition rate can be guaranteed under this operating condition.

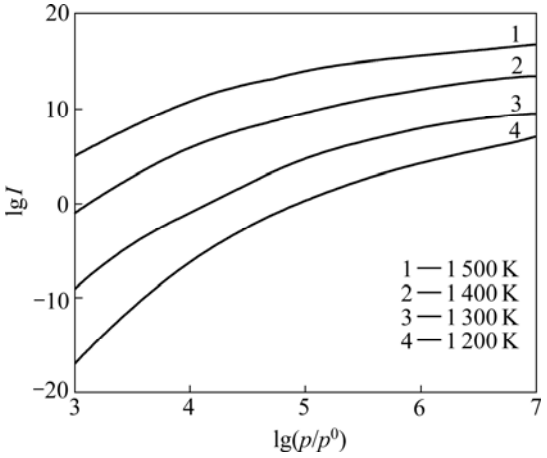

Fig.2 Relationship between nucleation speed and vapour supersaturation

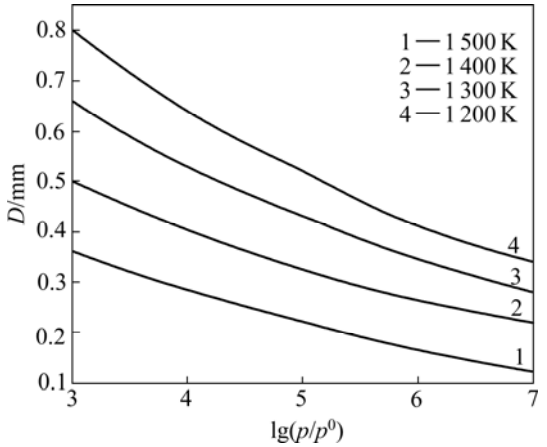

Fig.3 Relationship between critical nucleation diameter and vapour supersaturation

3 Results and discussion

During the preparation process of high purity titanium, the reaction (1) of crude titanium with iodine to form TiI_4 can begin at temperatures of 500−600 K in the iodide source area, and the reaction (2) of titanium with titanium tetra-iodide to form TiI_2 can occur at 700−900 K. In the experiments, the temperatures of iodide source area was controlled at 800−900 K, at which the iodides can be kept in gaseous form. The reaction (6) of TiI_2 thermal decomposition initiated at 1 300−1 500 K, by which high purity titanium deposited on the substrate in the deposition area. The iodine and iodide produced by the thermal decomposition reaction were then recycled for reaction with crude titanium[8−9].

Fig.4 shows the SEM images of sectional morphology of high purity titanium as-prepared. Fig.4(a) displays the junction between the deposition substrate and columnar crystals. There is a cluster of columnar crystals, which is the typical phenomenon in the crystallization of pure metals. These compact columnar

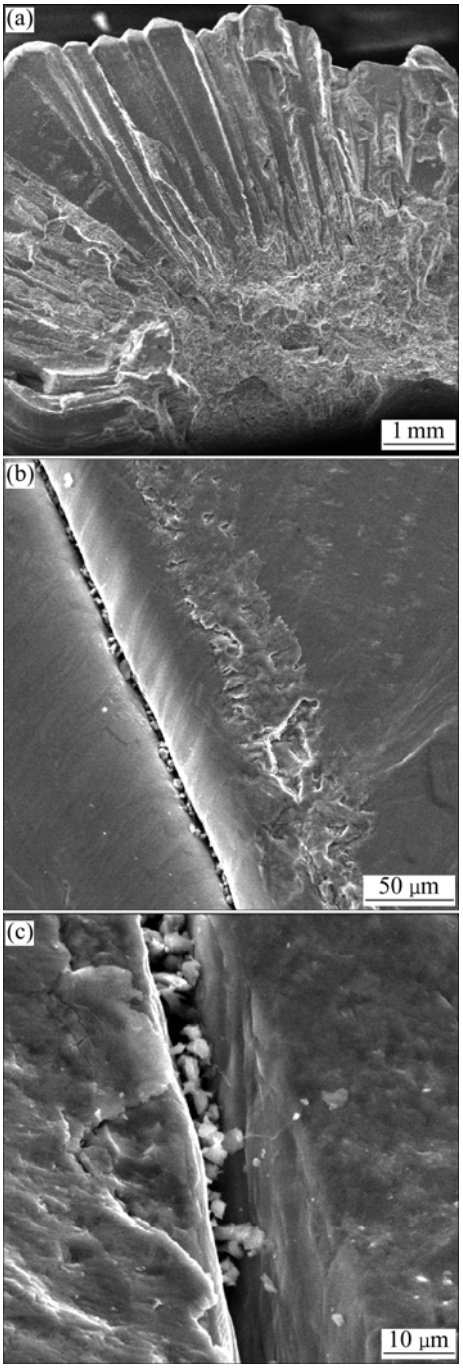

Fig.4 SEM images of sectional morphology of high purity titanium as prepared

crystals radially grow in the axial direction.

Figs.4(b) and (c) show the gap between two columnar crystals. The impurities in the gap can be seen clearly, which is the main factor affecting the purity of titanium.

Fig.5 shows the chemical ingredients of the impurities in the gap between columnar crystals by EDS. And the analysis data of the impurities are listed in Table 2.

As shown in Fig.5 and Table 2, there are elements

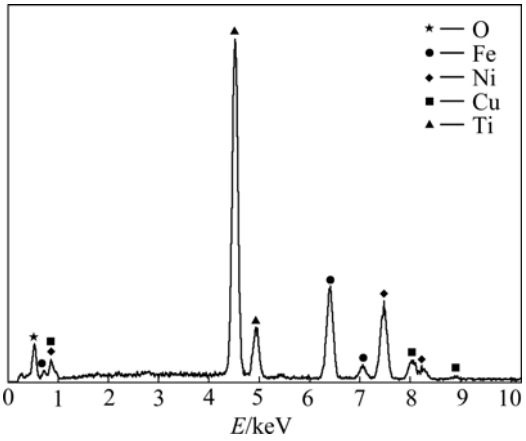

Fig.5 EDS spectrum of impurities in gap between columnar crystals

Table 2 Chemical composition of gap between columnar crystals analysed by EDS

Element	Mass fraction/%
O	12.20
Ti	42.26
Fe	18.96
Ni	20.60
Cu	5.99

of O, Fe, Ni, Cu and Ti existing in the gap. The high purity titanium produced by the thermal decomposition of titanium iodides is mainly composed of columnar crystals. In the columnar crystals, there is almost no impurities. When the crystal grains grow in different directions intersect, at the boundary there exist impurities, which mainly come from the crude titanium by iodide reaction of impurities. Table 3 lists the average chemical compositions of the produced high purity titanium by GDMS analyses. Table 4 lists the standard impurities contents of 4N5 titanium abroad.

From Table 3, the total impurities content in the product is 42.2×10^{-6}. Except for the elements of Fe, Ni and Mn, the rest are in accordance with the standard of 4N5 titanium abroad. These impurities of Fe, Ni and Mn mainly come from the etching of equipment, including the reactor and the vacuum pipeline, which can be readily eliminated by electron beam smelting in the following process.

4 Conclusions

1) Based on the analyses of the thermodynamics and nucleation theories, the optimum temperature ranges of synthesis and decomposition reaction for preparing

Table 3 Chemical compositions of produced high purity titanium by GDMS analyses

Element	Ag	Al	Au	Cd	Cl	Co	Cr
Content/10^{-6}	＜0.02	3.5	＜0.05	＜0.05	0.22	0.31	3.00
Element	Cu	Fe	K	B	Bi	Ca	Na
Content/10^{-6}	5.00	20.00	＜0.01	0.73	＜0.01	＜0.2	＜0.01
Element	Ni	P	Si	Sn	Th	U	Li
Content/10^{-6}	2.30	1.00	2.00	＜0.05	＜0.000 1	＜0.000 1	＜0.005
Element	Mg	Mn	Mo	V	W	Zn	Zr
Content/10^{-6}	0.21	1.30	＜0.05	0.35	0.76	＜0.02	1.00

Table 4 Standard impurity contents of 4N5 titanium abroad

Element	Fe	Ni	Cr	Mn	Al	Si
Content/10^{-6}	15	10	5	5	5	5
Element	Sn	Cu	Na	K	O	C
Content/10^{-6}	5	5	0.05	0.05	500	50

highly pure titanium by iodization process were obtained.

2) The temperature for synthesizing titanium iodides should be controlled at higher level such as 800−900 K, which can ensure the iodide gas formation rate and thus accelerate the iodide process. The thermal decomposition of titanium iodides in the deposition area should be controlled at a lower temperature in order to get faster decomposition rates. The suitable temperature should be at 1 300−1 500 K. Under this temperature, a faster nuclei forming rates of titanium can be obtained.

3) The high purity titanium with a purity of 99.995% was obtained by the thermal decomposition process of titanium iodide.

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