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OXIDATION OF $TiC_{1-x}N_x$ CERAMIC POWDERS BY MULTIPLE THERMAL ANALYSIS USING A NEWLY DEVELOPED POTENTIOMETRIC CO_2 SENSOR

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ABSTRACT

The oxidation of $TiC_{1-x}N_x$ (x=0-1) ceramic powders has been examined by a multiple technique consisting of thermogravimetry (TG), differential thermal analysis (DTA) and evolved gas analysis (EGA) using a newly developed potentiometric CO_2 sensor. Samples except x =1 are oxidized above 420 K through the substitution of oxygen for carbon and nitrogen at lattice sites and the oxygen dissolution into the interstitial sites at the early stage, forming an amorphous oxide. The oxidation is enhanced by the heat of reaction, which raises the sample temperature, and results in the explosive oxidation at 700-760 K. This process gives an abrupt rise of the sample temperature to about 1150 K and almost completes the oxidation giving rutile. The sample of x=1 is oxidized with the formation of both anatase and rutile at the early stage, and the final product is rutile at the completion.

INTRODUCTION

Materials in the TiC-TiN system have been widely used as coatings for cutting tools because of their high hardness. Recently an attempt has been made to apply TiN to gate electrodes and interconnection in large-scale integrated circuits [1]. The performance of materials for these applications is strictly related to the oxidation resistance. The oxidation process of $TiC_{1-x}N_x$ involves the evolution of gaseous species such as CO_2 and N_2. Furthermore, the dissolution of oxygen into the lattice may be important at the early stage of oxidation [2]. The mass gain in TG is caused by the dissolution of oxygen and the oxidation reaction to TiO_2. Quantitative EGA which is conducted simultaneously with TG and DTA provides a valuable information to the analysis of such a complicated process.

In the present study, the oxidation process of $TiC_{1-x}N_x$ powders was investigated in oxygen by multiple thermal analysis consisting of TG, DTA and EGA with a newly developed potentiometric CO_2 sensor.

EXPERIMENTAL

Powders of $TiC_{1-x}N_x$ (x=0, 0.3, 0.5, 0.7 and 1, grain sizes: 1-2 μm) were provided by Japan New Metals Corp. It was revealed by X-ray diffraction that the crystal structure of $TiC_{1-x}N_x$ was cubic and the spacing of (422) varied linearly from 8.836×10^{-2} (x=0) to 8.666×10^{-2} nm (x=1). This result confirms that each powder is a solid solution in the TiC-TiN system. The oxidation kinetics of the powders were examined by TG, DTA and EGA in oxygen stream whose flow rate of 2.67×10^{-6} m^3s^{-1}. Samples of about 15 mg were weighed and set into the TG-DTA apparatus (SSC/560GH, Seiko Instruments and Electronics Ltd.).

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The complete oxidation of $TiC_{1-x}N_x$ to TiO_2 gives the mass gain:

$$\Delta m/m_o=(20.0-2.0x)/(59.9+2.0x) \quad .....(1)$$

The samples oxidized at various stages were examined by X-ray diffraction. A potentiometric CO_2 sensor was employed for EGA.

The CO_2 sensor was recently develpoped by the present author and his coworkers [3]. The sensor is composed of Na_2CO_3 and NASICON ($Na_3Zr_2Si_2PO_{12}$) which are both sodium ion conductors. Figure 1 shows the schematic illustration of the sensor. When the sensor is placed in an atmosphere containing CO_2, it functions as the following electrochemical cell:

$$Au,\ CO_2,\ O_2\ |\ Na_2CO_3\ ||\ NASICON\ |\ O_2,\ Au$$

The electromotive force (emf: E) is expressed by the Nernst equation:

$$E = E_o -(2.303RT/2F)\log(a_{Na_2O}\ P_{CO_2}/1.01x10^5) \quad .....(2)$$

where E_o is the constant, R the gas constant, T the absolute temperature, F the Faraday constant, a_{Na_2O} the activity of Na_2O in NASICON and P_{CO_2} the partial pressure of CO_2 in pascal. In the case of a fixed activity of Na_2O in NASICON, the partial pressure of CO_2 can be calculated from the measured emf. Figure 2 shows the typical emf characteristic of the sensor. As can be expected from the eqn. (2), the linear relationship is obtained between the emf and $\log(P_{CO_2})$. The details of the construction of the sensor and the derivation of the eqn. (2) were reported elsewhere [3].

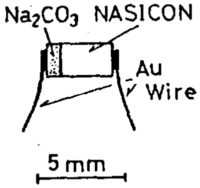


Fig. 1 Schematic illustration of a CO_2 sensor.

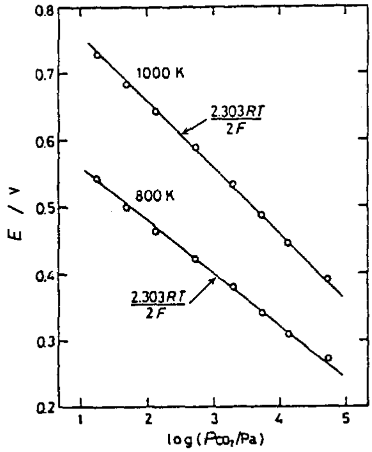


Fig. 2 Emf characteristic of the CO_2 sensor.

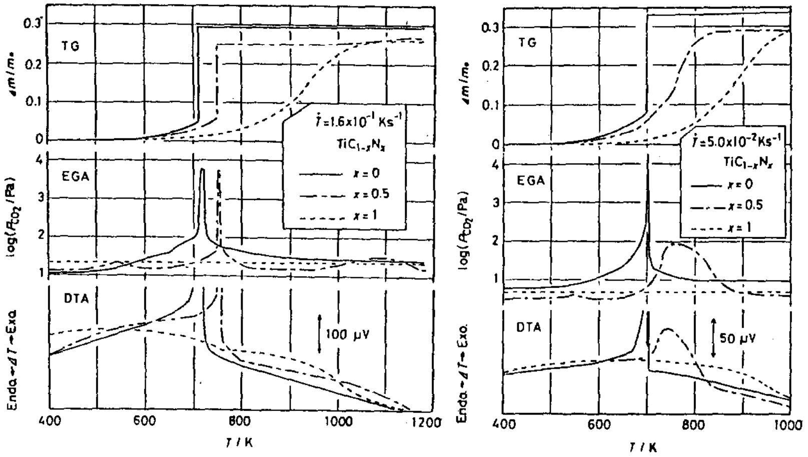
RESULTS

Figure 3 (a) shows typical curves of TG, DTA and EGA at a heating rate of $1.6x10^{-1}Ks^{-1}$. The CO_2 sensor was held at 900 K. For clearness of the figure, only three curves of x=0, 0.5 and 1 are presented. The TG curve of x=0 indicates that the mass gain starts at 520 K. The mass gain is gradually increased to 0.05 up to 710 K, and the explosive oxidation is observed at 710 K to attain the mass gain of 0.295. On the other hand, the EGA curve by the CO_2 sensor shows that the evolution of CO_2 begins at 420 K. The sensor is more sensitive than TG. The explosive oxidation increases the partial pressure of CO_2 to $5.5x10^4$ Pa. The tail of the EGA curve after the explosive oxidation is due to the release of adsorbed CO_2 on the inside of tubes in the gas flow system. The explosive oxidation gives an abrupt rise of the sample temperature to 1150 K. As can be seen in the EGA curve of x=0.5, the evolution of CO_2 begins at 420 K,

Table 1. The temperatures and mass gains at the explosive oxidation. $(T/\mathrm{K})/(\Delta m/m_o)$

	x				
$\dot{T}/\mathrm{Ks}^{-1}$	0	0.3	0.5	0.7	1
1.6x10^{-1}	710/0.05	733/0.07	748/0.06	749/0.06	non
1.0x10^{-1}	713/0.05	738/0.08	758/0.11	741/0.08	non
7.5x10^{-2}	703/0.07	738/0.08	non	non	non
5.0x10^{-2}	700/0.08	non	non	non	non
2.5x10^{-2}	non	non	non	non	non

and a small peak is observed around 540 K. Then, the amount of evolved CO_2 decreases with increasing temperature below 630 K, whereas TG shows a monotonous mass gain below 750 K at which the explosive oxidation occurs. The sample of x=1 provides a smooth TG curve. The CO_2 sensor exhibits no change in emf indicating the excellent selectivity. The DTA shows a broad exothermic peak from 760 K. Figure 3 (b) presents TG, DTA and EGA curves at a heating rate of 5.0x10^{-2} Ks^{-1}. The lowering of the heating rate eliminates the explosive behavior from the sample of x=0.5. Table 1 summerizes the temperatures and mass gains where the explosive oxidation occurs at various heating rates. The sample of higher carbon concentration explodes at lower temperatures and heating rates. However, mass gains remain less than about 0.1. DTA curves showed that the evolved heat decreased with an increase in x. Samples of x=0, 0.5 and 1 were oxidized at a heating rate of 1.0x10^{-1} Ks^{-1} and quenched for X-ray diffraction. In the samples of x=0 and 0.5 quenched before the explosive oxidation ($\Delta m/m_o$=0.06), no newly formed crystalline phase was detected, and the change in the lattice constant of the original phase was negligible. However, the explosive oxidation converted them into rutile. The sample of x=1 yielded small amounts of anatase



(a) $\dot{T}$=1.6x10^{-1} Ks^{-1} (b) $\dot{T}$=5.0x10^{-2} Ks^{-1}

Fig. 3 Typical TG, DTA and EGA curves.

and rutile at mass gain of 0.08, and the anatase had been transformed into rutile until the oxidation was completed.

DISCUSSION

Two processes are probably responsible in the oxidation of $TiC_{1-x}N_x$ (x=1): the dissolution of oxygen into the interstitial sites and the substitution of oxygen for carbon and nitrogen at the lattice sites forming TiO_2. The dissolution process does not require the release of carbon from the lattice, whicn leads to the evolution of CO_2. However, the substitution always accompanies the CO_2 evolution. By assuming that the oxidation proceeds through the following reaction:

$$TiC_{1-x}N_x + (2-x)O_2 \longrightarrow TiO_2 + (1-x)CO_2 + (x/2)N_2 \quad .....(3)$$

the value of P_{CO_2} can be calculated from the observed TG curve and the flow rate of oxygen. The calculated and observed values are compared in Fig. 4 for the cases of x=0 and 0.5 at the heating rate of 1.6×10^{-1} Ks^{-1}. The calculation was performed at the early stage before the explosive oxidation. For x=0, the calculated value agrees roughly with the observed one, but is slightly higher. This fact indicates that the oxidation proceeds mainly through the reaction (3). On the other hand, for x=0.5, a significant difference is recognized between the calculated and observed values, suggesting that the dissolution of oxygen is a probable cause of the mass gain. The products of both samples are amorphous oxides. In this stage, the sample is self-heated because the evolved heat due to oxidation overcomes the effluent heat from the sample holder, and then is explosively oxidized at 700-760 K raising the sample temperature to about 1150 K. The explosive oxidation forms the oxide of rutile. TiN (x=1) is oxidized with the formation of both anatase and rutile at the early stage, and the oxidation is completed giving rutile as the final product.

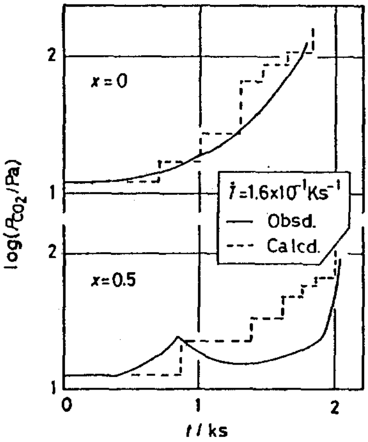


Fig. 4 Comparison of calculated and observed values of P_{CO_2}.

REFERENCES

1. M. Wittmer, J. Noser and H. Melchior, J. Appl. Phys., 1981, 52 6659.
2. V.A. Lavrenko, L.A. Glebov, A.P. Pomitkin, V.G. Chuprina and T.G. Protsenko, Oxid. Met., 1975, 9, 171.
3. Y. Saito, T. Maruyama and S. Sasaki, Report of the Research Laboratory of Engineering Materials, Tokyo Institute of Technology, 1984, 9, 17.