Crystallization of High Purity Ammonium Meta -Tungstate for production of Ultrapure Tungsten Metal

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ABSTRACT

The growth mechanism of AMT(Ammonium Meta-Tungstate) crystal was interpreted as two-step model. The contribution of the diffusion step increased with the increase of temperature, crystal size, and supersaturation.

The crystal size distribution from a batch cooling crystallizer was predicted by the numerical solution of a mathematical model which uses the kinetics of nucleation and crystal growth. Temperature control of a batch crystallizer was studied using Learning control algorithm.

The purity of AMT crystal produced in this investigation was above 99.99%

INTRODUCTION

AMT is of commercial significance because of its high solubility in water. This property makes it very desirable starting material for catalysts and producing ultrapure tungsten metal. However, despite the extensive usage of AMT, there is virtually no data concerning on the kinetics of the crystallization of AMT from aqueous solution. Therefore, the present study aims at the development of crystallization process for the production of high purity AMT crystal.

THEORY

Nucleation Kinetics

The semiempirical relationship

$$kn(\Delta C_{max}/C_s)^n = (dC_s/d\theta)b \qquad (1)$$

has frequently been used to relate the mass nucleation rate to the metastable zone

width[1].

Crystal growth Kinetics

Crystal growth from the solution could be analysed by a two-step growth process, that is, crystal growth process consists of two consecutive stages.

(i) Bulk diffusion : $Mg = kdoL^{b1}\exp(-Egd/RgT)(C-C_i)/C_s$ (2)

(ii) Surface reaction : $Mg = kroL^{b2}\exp(-Egr/Rgt)[(C_i-C_s)/C_s]^r$ (3)

Controlled Crystallization

The behavior of a batch crystallizer was predicted from a theory of programmed cooling crystallization based on the moment transformation of the population balance coupled with the material and energy balances.

$$\frac{d\mu_{nj}}{dt} = j\phi\left(\frac{\mu_{n3}(t)}{\mu_{n2}(t)}\right)^{b}\mu_{nj-1} + J_n(t)L_{n0}^{j} \quad (4)$$

$$-\frac{d\Delta C}{dt} = C(\theta,t)\frac{dC_s}{d\theta}(t) + \frac{3W_{so}}{L_{so}^3}L_s^2(t)G_s(L_s,t) + a\rho_c\frac{d\mu_{n3}}{dt} \quad (5)$$

$$\frac{d\theta}{dt} = \frac{-\Delta H}{M_L C_{PL}}\left(\frac{-dC}{dt}\right) - \frac{uA}{M_L C_{PL}}(\theta - T_j) \quad (6)$$

EXPERIMENTAL

AMT manufacturing

AMT solution was prepared from APT slurry and solventing-out method with methanol was used for producing crystalline AMT.

Nucleation measurements

The equilibrium data of AMT in the binary system AMT-water over the experimental range, 10~40℃, were determined by the polythermal method. The solubility was expressed as the relationship

$$C_s = -0.000433899\theta^2 + 0.197532\theta - 0.490991 \quad (7)$$

Crystal shape factors

The surface and volume shape factors for the AMT crystals were determined with the aid of a microscope fitted with a calibrate eyepiece.

Growth experiments

Growth rates of AMT crystals were measured in a fluidized bed crystallizer. The ranges of variables studied are given in Table 1.

Table 1. Range of variables studied in growth experiments

Variables	Range	Units
Relative Supersaturation, $\Delta C/C_s$	0.015 to 0.15	
Temperature, θ	16.5 to 25.5	℃
Seed size	900 to 1700	㎛

Controlled Crystallization

Before each run the solution was maintained at 5℃ above the saturation temperature for 1 hr. The temperature was adjusted to the desired initial value, a weighed quantity of seed crystal was added and the solution was cooled as was programmed.

DISCUSSION OF RESULTS

In order to get the complete conversion of APT crystals to AMT solution, pH values was controlled in the range of 3.5~4.0.

From solventing-out operation with methanol, 92% precipitated fraction based on WO_3 was measured from AMT saturated solution at 21℃. And the purity of AMT crystals was about 99.99%(see Fig.1).

Nucleation Kinetics

Nucleation rate can be described by the expression

$$J_m = 1.6\times10^{39}\exp(-2.81\times10^5/RgT)(\Delta C/C_s)^{3.15} \quad (8)$$

and the surface energy, γ, calculated from nucleation rate measurements was 4.16 erg/cm^2.

Crystal shape factors

The volume and surface shape factors of a crystal(Fig.2), characterized by its characteristic size, La, are given by

$$\text{i) } f_v = -1.08La^5 + 5.14La^4 - 5.19La^3 - 4382.5La^2 - 15.4La + 0.34 \quad (9)$$

$$\text{ii) } f_s = -4.94La^4 + 3.33La^3 - 511341La^2 - 90.4La + 3.37 \quad (10)$$

Crystal Growth Kinetics

The linear growth rate, G, is related to the mass growth rate, Mg, by

$$G = (f_s/3f_v\rho_c)Mg \quad (11)$$

$$= k_G(\Delta C/C_s)^g \quad (12)$$

The exponent g of $\Delta C/C_s$ decreased with increasing temperature. The best estimates of the kinetic parameters in Eqs. 2 and 3 were determined from the experimental data by applying the least-squares multiple regression method and the parameters obtained are shown in Table 2.

Table2. Values of the parameters in Eqs. 2 and 3

kdo	2.298×10^{1}	kro	5.327×10^{4}
bl	-0.281	b2	0.134
Egd	1.840×10^{4}	Egr	2.816×10^{4}
r	1.984		

To determine the effect of surface reaction step on the crystal growth, Garside[3] proposed the concept of the surface reaction effectiveness factor defined as

$$\eta_r = Mg/\ \{kr[(C-C_s)/C_s]^r\} \quad (13)$$

The effectiveness factor, η_r, tends to unity as the surface reaction step increasingly dominates the growth process(see Fig.3).

Controlled Crystallization

Experimental run following programmed cooling curve showed reasonable agreement with the theoretical prediction.

Temperature control of a batch crystallizer was studied using Learning control algorithm. As the result, it was found that Learning control method performed better than the conventional PID algorithm as shown in Fig.4. The final purity of AMT crystal through crystallization was above 99.99%

CONCLUSIONS

It is concluded that the process suggested in this investigation, including

solventing-out, and crystallization unit operations, is the most promising method to manufacture high purity AMT for the prodduction of ultrapure tungsten metal by means of physical metallurgical process.

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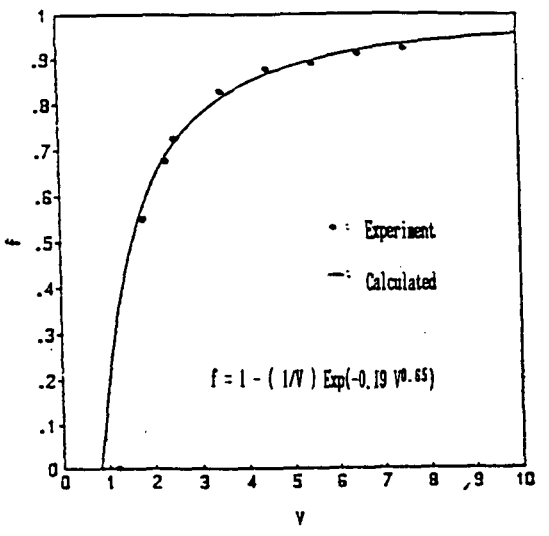

Fig.1 Dependence of the precipitated fraction of AMT on the added volume of Methanol

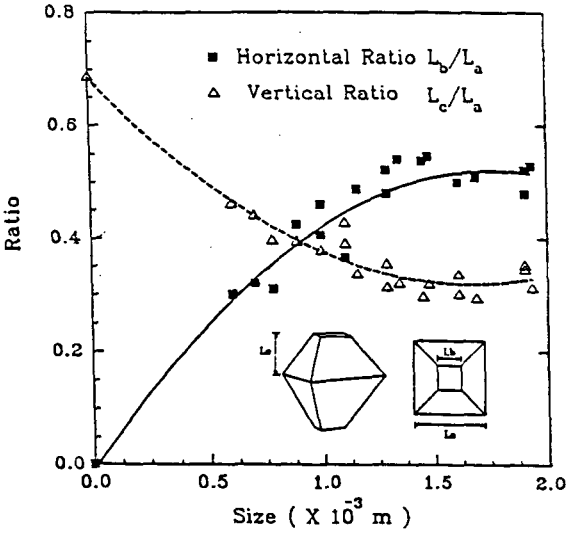

Fig.2 Horizontal ratio and vertical ratio vs. crystal size

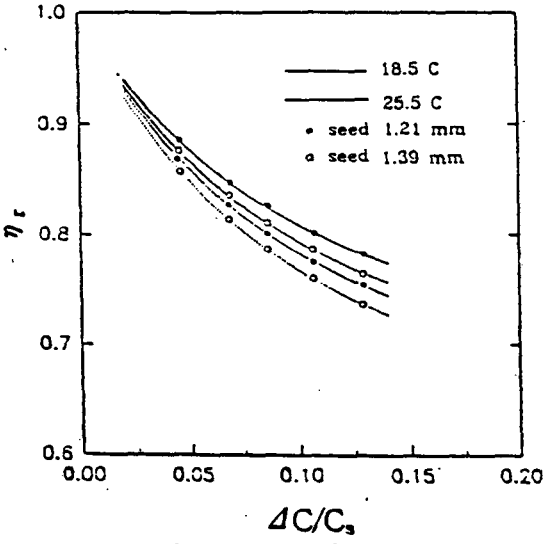

Fig.3 Effectiveness factor vs. relative supersaturation

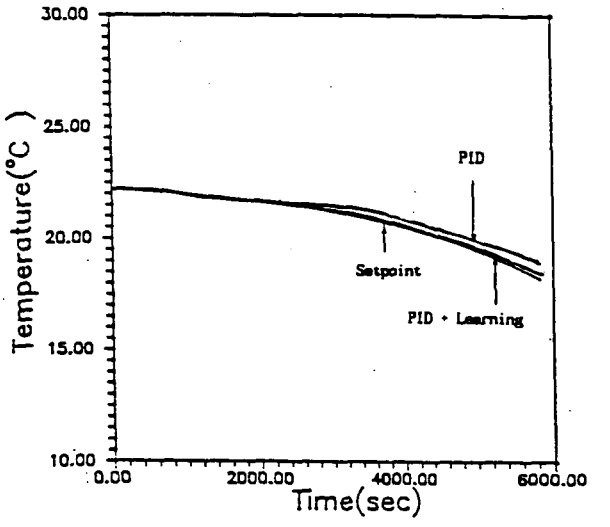

Fig.4 Temperature trajectories during batch operation