THERMAL STRESS ANALYSIS OF TETRAGONAL SINGLE CRYSTAL DURING GROWTH PROCESS : PMO SINGLE CRYSTAL

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ABSTRACT

A three-dimensional finite element computer code was developed to deal with thermal stress analyses of tetragonal single crystals during the growth. They have the crystal anisotropy, so three-dimensional analysis is required for calculation of the thermal stress, even though they have axisymmetrical shapes. A tensor transformation technique was used to obtain the components of elastic constant matrix and thermal strain or thermal expansion coefficient vector corresponding to an arbitrary growth direction. Using this computer code, we performed thermal stress analyses of a lead molybdate ($PbMoO_4$, PMO) bulk single crystal for the various growth directions. The relation between the thermal stress and the crystal quality was discussed.

1 INTRODUCTION

Various single crystals are used as materials of electronic/optical devices. Dislocations generated during crystal growth affect the performance of such devices. Macro-cracking sometimes occurs in single crystals during the growth. Dislocations and macro-cracking would be induced by thermal stress during crystal growth. It is important to clarify thermal stress in a bulk single crystal during the growth from the viewpoint of crystal quality.

Single crystals have anisotropy in elastic constants and thermal expansion coefficients. So three-dimensional finite element analysis must be used for calculation of thermal stress during crystal growth, even if a single crystal has an axisymmerical shape. Miyazaki et al. performed such three-dimensional analyses [1, 2]. They examined the relation between thermal stress and crystal growth directions for trigonal and monoclinic crystals and succeeded in clarifying the relation between the thermal stress and the cracking and quality of a single crystal.

A lead molybdate ($PbMoO_4$, hereafter abbreviated as PMO) single crystal has a tetragonal crystal structure and is used as acousto-optic light detectors and modulators. Its bulk single crystal is usually produced by the CZ growth technique. Subgrains and macro-cracking sometimes occur in a bulk single crystal during the growth due to the thermal stress. Several researches have been performed on the relation between the growth direction of a PMO bulk single crystal and the crystal quality [3 - 8]. There has been no study, in which quality of a PMO single crystal is related to the thermal stress during the crystal growth.

In the present study, we developed a three-dimensional finite element code for thermal stress analysis of tetragonal single crystals during the growth, taking account of the crystal anisotropy. Then we carried out the thermal stress analyses of PMO single crystals for the various growth directions and examined the relation between the thermal stress and the crystal quality.

2 METHOD OF ANALYSIS

Stress-strain relations of a single crystal are given as

$$\sigma_{ij} = C_{ijkl}\varepsilon_{kl} \tag{1}$$

where σ_{ij} and ε_{kl} are the stress tensors and strain tensors, respectively, and C_{ijkl} denote the elastic constant tensors. In a tetragonal single crystal, a right-handed Cartesian coordinate system X_1-X_2-X_3 is taken in such a way that the X_1-, X_2 – and X_3-axes coincide with the crystallographic *a*-axis, *b*-axis and *c*-axis, respectively, as shown in Fig. 1. Then the elastic constant matrix is written as follows, using seven independent elastic constants [9]:

$$\left[C_{ij}\right] = \begin{bmatrix} C_{11} & C_{12} & C_{13} & 0 & 0 & C_{16} \\ & C_{11} & C_{13} & 0 & 0 & -C_{16} \\ & & C_{33} & 0 & 0 & 0 \\ & & & C_{44} & 0 & 0 \\ & sym. & & & C_{44} & 0 \\ & & & & & C_{66} \end{bmatrix} \tag{2}$$

Let us consider a right-handed system X'_1-X'_2-X'_3 shown in Fig. 2, where the X'_3-axis coincides with the growth direction of a crystal, and the X'_1-axis is in the X_1-X_2 plane and normal to the X'_3-axis. By the standard tensor transformation, the elastic tensors C'_{ijkl} associated with the X'_1-X'_2-X'_3 system are related to C_{ijkl} of the X_1-X_2-X_3 system as follows:

$$C'_{ijkl} = a_{im}a_{jn}a_{ko}a_{lp}C_{mnop} \tag{3}$$

where a_{ij} are the direction cosines of the X'_i-axis and X_j-axis..

Thermal strain tensors ε^T_{ij} are given as follows:

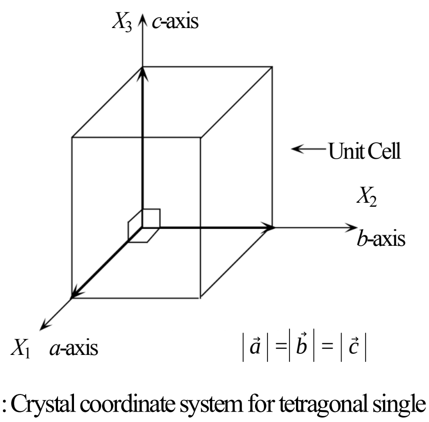


Figure 1 : Crystal coordinate system for tetragonal single crystal

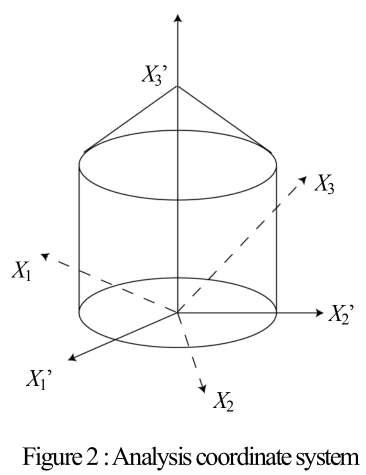


Figure 2 : Analysis coordinate system

$$\varepsilon_{ij}^{T} = \int \alpha_{ij} dT \tag{4}$$

where α_{ij} are the thermal expansion coefficient tensors in the X_1-X_2-X_3 system, and given by two thermal expansion coefficients, that is, $\alpha_{11}=\alpha_{22}=\alpha_1$, $\alpha_{33}=\alpha_3$ and $\alpha_{44}=\alpha_{55}=\alpha_{66}=0$ for a tetragonal single crystal. We obtain the thermal expansion coefficient tensors in the X'_1-X'_2-X'_3 system as follows:

$$\alpha'_{ij} = a_{ik} a_{jl} \alpha_{kl} \tag{5}$$

We can obtain the stress –strain relations and thermal strains in the X'_1-X'_2-X'_3 system, using C'_{ijkl} and α'_{ij} given by Eqs. (3) and (5), respectively. A finite element computer code was developed to perform the thermal stress analysis of a tetragonal single crystal for arbitrary growth directions.

3 RESULTS AND DISCUSSION

Thermal stress analyses of a PMO bulk single crystal of 5cm in diameter and 5cm in height were carried out for the various growth directions. We used the temperature distribution shown in Fig. 3 in the present analyses. The finite element mesh used in the present thermal stress analyses is shown in Fig. 4. The elastic constants C_{ij} and thermal expansion coefficients α_i of a PMO single crystal are quoted from Ref. [10].

At first thermal stress analyses were performed for the *a*-, *b*- and *c*-axis growth directions. The maximum principal stress σ_1 and the Mises equivalent stress $\sqrt{3J'_2}$, where J'_2 is the second invariant of deviatoric stress, were calculated from the results of the thermal stress analyses. The maximum principal stress was adopted as a measure for brittle fracture, and the Mises equivalent stress as a measure governing dislocation generation and multiplication. Figure 5 shows the contours of the maximum principal stress. It is found from the figures that the stress is higher in the peripheral region than in the internal region. This fact conforms to the experimental result obtained by Loiacono et al. [4] showing that subgrain density is maximum at the outer surface of a single crystal. In the case of the *c*-axis growth, thestress distribution is found to be perfectly axisymmetric. This is

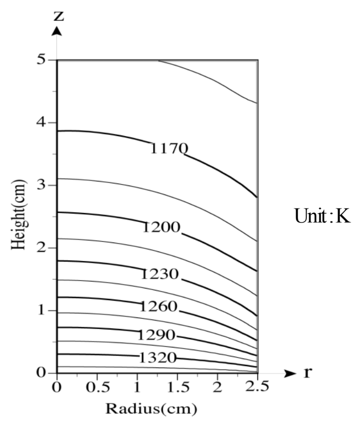


Figure 3 : Temperature profile used in the thermal stress analysis

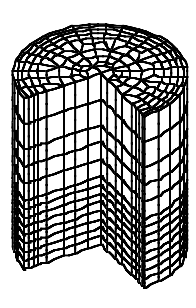
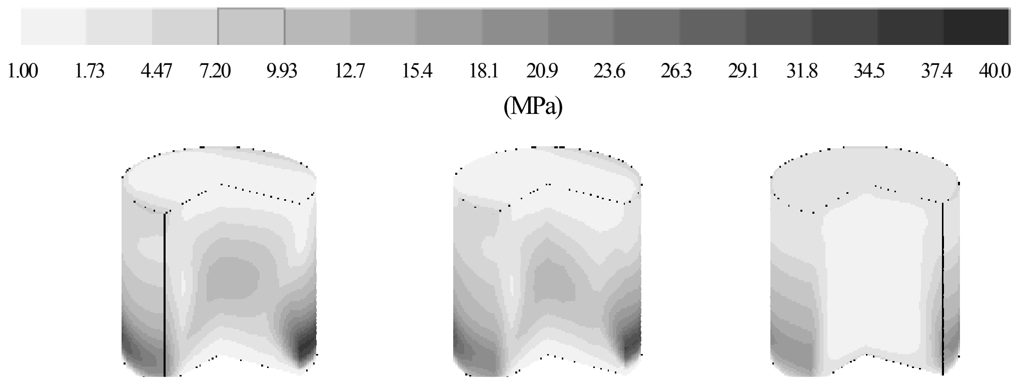


Figure 4 : Finite element mesh ; a quarter part is eliminated to show internal part clearly



(a) *a*-axis growth (b) *b*-axis growth (c) *c*-axis growth

Figure 5 : Distribution of the maximum principal stress, σ_1.

because the *a*-axis and *b*-axis are crystallographically equivalent. The maximum values of the maximum principal stress and Mises equivalent stress for the respective growth directions are summarized in Table 1. Due to the same reason, the results of the *a*-axis growth and *b*-axis growth are completely the same. This table shows that the both the *a*-axis growth and *b*-axis growth provide much larger stress values than the *c*-axis growth. As Bonner and Zydzik [3] pointed out, crystals grown in the *a*-axis or *b*-axis direction are excessively strained as a result of an unequal radial coefficient of thermal expansion in the plane normal to the growth direction, and they often shatter from the heat of hand and in attempts of anneal.

Subgrains are main concern in the quality of PMO bulk single crystals. Followings are experimental results concerning the relation between the crystal quality and the growth direction of a bulk single crystal. Bonner and Zydzik [3] reported that crystals of high quality can be obtained using a growth direction about 30 degrees off the *c*-axis. The study on X-ray characterization of PMO crystals performed by Loiacono et al. [4] shows that the crystal grown in the *a*-axis direction has higher quality than that grown in the *c*-axis direction. According to a series of crystal growth experiments, Takano et al. [5] concluded that the high quality single crystals without subgrains are obtained by using the orientations inclined more than 30 degrees from the *c*-axis in the intermediate planes between the *a*-*c* plane and the *b*-*c* plane. Based on these results, PMO crystals are usually grown either

Table 1 Maximum value of stresses for *a*-, *b*- and *c*-growth direction.

Growth direction	σ_1 [MPa]	$\sqrt{3J_2'}$ [MPa]
a	36.5	41.7
b	36.5	41.7
c	19.7	17.3

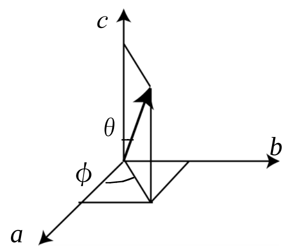


Figure 6 : Notation of angles.

Table 2 Maximum value of stresses for various growth directions.

Growth direction	σ_1 [MPa]	$\sqrt{3J_2'}$ [MPa]
a	36.5	41.7
b	36.5	41.7
c	19.7	17.3
30-0	27.3	28.3
30-30	26.7	26.3
30-60	27.4	28.4
30-90	27.3	28.4
60-0	35.2	38.3
60-30	36.6	42.2
60-60	34.8	37.8
60-90	35.2	38.3
90-30	41.7	53.9
90-60	35.8	40.2

in the *a*-axis direction [6, 7] or in the [110] direction [8], but no definite conclusion has been derived so far on the relation between the crystal quality and the growth directions.

Then thermal stress analyses were performed for various growth directions except for *a*-, *b*- and *c*-axis directions. The growth direction is defined as θ - ϕ by the combination of the angles θ and ϕ shown in Fig. 6. The results are shown in Table 2 for the maximum values of stresses, together with the results of the *a*-, *b*- and *c*-axis growth directions. It is found from the table that the growth direction with the lowest thermal stress is around the *c*-axis. Takano et al. [5] pointed out that the *c*-axis or near the *c*-axis growth directions produce large crack-free crystals. The fact that the growth direction with the lowest thermal stress is around the c-axis validates the Takano et al's comment on crack-free crystals, but does not comply with the experimental results on subgrain distribution in PMO single crystals obtained in the previous studies [3, 5 - 8]. As mentioned before, the same temperature distribution shown in Fig. 3 was utilized for different growth directions in the present thermal stress analyses. This is because the thermal conductivity of a PMO single crystal is isotropic according to the measurement by Coquin et al. [10]. Loiacono et al. [4], however, presumed that the thermal conductivity of the *a*-axis direction is much larger than that of the *c*-axis direction by comparing the quality of an *a*-axis grown crystal and that of a *c*-axis grown crystal. If so, heat can easily transfer along the growth direction in the case of an *a*-axis grown crystal and the temperature gradient in the radial direction becomes small. Consequently thermal stress becomes small for the *a*-axis grown crystal. The Loiacono et al's view does not based on measurement of the thermal conductivity. So it is essentially important to obtain such measurement data at elevated temperatures under the crystal growth condition in order to verify the Loiacono et al's view.

4 CONCLUDING REMARKS

We developed a three-dimensional finite element computer code for thermal stress analysis of tetragonal single crystals that takes account of the crystal anisotropy. Then we performed the thermal stress analyses of PMO single crystals for the various growth directions. The following are conclusions derived from the present study.

(1) Thermal stress during the crystal growth process becomes minimum around the *c*-axis, if the temperature distribution in a bulk single crystal is assumed to be the same irrespective of different growth directions due to the thermal isotropy of the crystal.

(2) The above conclusion validates the experimental result that the *c*-axis or near the *c*-axis growth direction produces crack-free crystals, but the experimental results concerning the relation between subgrain density in a crystal and crystal growth directions are not validated by the conclusion (1). This fact may suggest that a PMO single crystal would have thermal anisotropy at elevated temperatures under crystal growth condition.

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