

TEXTURE EVOLUTION DURING CRYSTALLIZATION OF THIN AMORPHOUS FILMS

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ABSTRACT

Stress and energy distributions for crystallization of a thin amorphous film are calculated by means of 3D finite element method. The changes in energy are caused by elastic strain induced by different thermal expansion of the film and the substrate and by different mass densities of the crystal and the surrounding amorphous matrix. The calculations were performed for cubic crystal structure and for disc shaped crystals. Three crystal orientations (001), (011) and (111) were considered. Based on strain energy considerations the (001) orientation of crystals with respect to the film plane is energetically more favorable than (011) and (111) orientations. Interfacial and surface energies are certain to play a part in these effects as well.

INTRODUCTION

Crystallization of amorphous alloys has been studied extensively in the past. However, our understanding about crystallization in thin supported films is still limited. A few studies have suggested that crystallization in thin films differs appreciably from crystallization in thick specimens. Harris and coworkers [1] studied, e.g., crystallization in films of amorphous $\text{Fe}_{75}\text{B}_{25}$ with a thickness of 15 nm and measured a crystallization temperature which is about 200 K lower compared to the crystallization temperature in bulk specimens [2]. Ikari and coworkers [3] studied the crystallization behavior in films of amorphous $\text{Ni}_{81}\text{P}_{19}$ and found a metastable hexagonal phase which generally is not detected in thick specimens with the same composition. The orientation of the c-axis of this phase was found to depend on the film thickness.

While the driving force for crystallization in thick specimens is dominated by the volume energy and by the strain energy induced by the different mass densities of the crystalline phase and of the amorphous phase, the total energy driving the phase transformation in thin films is increasingly affected by the free surface of the film and by the film-substrate interface. Additionally, thin supported films are elastically strained during heating due to the different thermal expansions of film and substrate. The energy driving the phase transformation in thin films is, therefore, affected by the volume energy, by the surface energy, by the interfacial energies and by thermal strain energy. The change in mass density during crystallization also has to be taken into account.

This work presents 3-dimensional finite-element method (3-D FEM) calculations of the influence of grain orientation on the total change in energy during the phase transformation under thermal strain and under strain induced by the different mass density of the crystalline and of the amorphous phase. The crystal structure was assumed to be cubic and the crystals were assumed to have the shape of a disc. It was assumed that the {001}-, the {011}- or the {111} lattice planes of the crystals were parallel to the surface.

METHOD

Calculations were performed using a 3-D FEM. Meshing was done manually. A disc shaped crystal with diameter $d = 20$ nm was chosen for the calculations. The crystals were assumed to be embedded in an amorphous matrix. The film dimensions were 100 nm \times 100 nm \times 20 nm. Due to the symmetry only $\frac{1}{4}$ of the film was actually used for the calculations. Periodic boundary conditions were applied at the side faces. The strain induced in a thin supported film is approximated by a two dimensional strain exerted by a thick SiO_2 substrate. In a first approach, the presence of the substrate is taken into account only to the extent of providing rigid constrain on the lower side of the film, while the upper side is allowed to relax. The thermal expansion coefficients were chosen according to ref. [4] and ref. [5]. The mesh of the undeformed film for a disc shaped crystal geometry is shown in Fig. 1. A cubic crystal structure was assumed. Calculations were performed for (001), (111), and (110) crystal orientation with respect to the film surface. Each orientation was analyzed under the three different conditions:

- (i) Due to different thermal expansion coefficients of the film and of the substrate the film is under tensile or compressive strain. The thermal expansion coefficient of the SiO_2 substrate was chosen as $\beta_s = 2.61 \cdot 10^{-6} \text{ K}^{-1}$ [4] compared to $\beta_f = 1 \cdot 10^{-5} \text{ K}^{-1}$ of amorphous $\text{Ni}_{75}\text{P}_{16}\text{B}_6\text{Al}_3$ [5] (β_s and β_f denote the thermal expansion coefficients of the substrate and of the film, respectively). This results in a 2D compressive strain ϵ of the film which is approximately given by $(\beta_f - \beta_s) \cdot \Delta T$ where ΔT denotes the difference in temperature between room temperature and crystallization temperature. In the present case $\Delta T = 400$ K.
- (ii) During crystallization a change in mass density of about $+1.5 \%$ with respect to the amorphous phase is generally observed. In this paper a relatively large change in mass density of 4.5% is taken into account.
- (iii) A superposition of (i) and (ii) will be calculated.

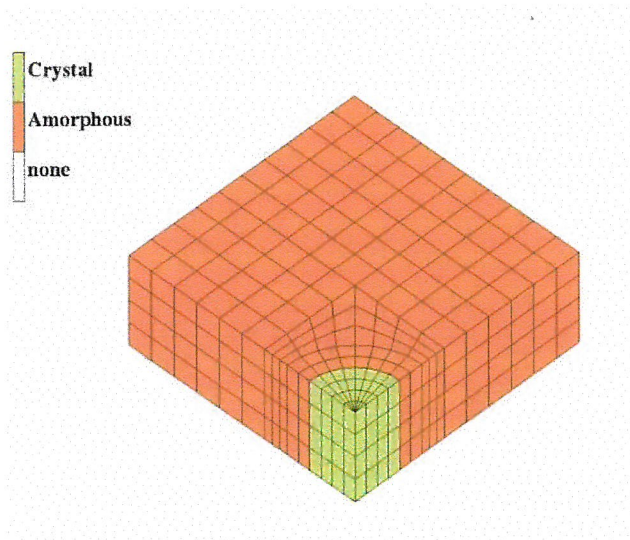


Figure 1 : Crystal and film dimensions used for the 3-dimensional FEM calculations.

The structure of the crystal is assumed to be face centered cubic and for the calculations the elastic constants of nickel $C_{11} = 247$ GPa, $C_{12} = 147$ GPa and $C_{44} = 125$ GPa were used. The elasticity of the amorphous phase was approximated by the isotropic elastic modulus of polycrystalline nickel ($E = 199$ GPa). The Poisson ratio 0.312 of polycrystalline nickel was taken for the amorphous phase.

RESULTS

The elastic strain energy densities from FEM analyses are shown in Fig. 2. The disc-shaped crystal is embedded in the amorphous matrix. We display in Fig. 2a-c the elastic strain energy density distributions due to thermally induced elastic strain. In Fig. 2d-f, their counterparts due to different mass densities of the crystal and the amorphous matrix are shown. In Figs. 2a and 2d, the $\{001\}$ lattice planes are parallel to the the film surface, in Figs. 2b, 2e, the $\{110\}$ planes and in Figs. 2c, 2f, the $\{111\}$ planes.

In Fig. 2a-c, the biaxially strained film can relax in the direction perpendicular to the film surface. For Fig. 2a with (001) parallel to the film surface, from our FEM calculations, the relative softness of the crystal in $\langle 001 \rangle$ results in the crystal bulging higher than the surrounding amorphous matrix. For Fig. 2c, with (111) parallel to the film surface, the FEM results show the reverse. As the (111) plane is denser packed than (001), the elasticity is stiffer in the $\langle 111 \rangle$ direction. On the final relaxed film surface, the crystal surface actually sinks below 20 nm, the height of the film before the application of the biaxial strain. Of course, the compensating relaxation takes place in the surrounding amorphous matrix, i.e., it rises significantly above the crystal surface in the middle.

The two contrasting relaxations seem to result also in contrasting elastic strain energy density distributions. In Fig. 2a, the energy density decreases from the bottom of the film towards the surface, while in Fig. 2c, it increases from the bottom towards the surface.

In a further calculation the upper film surface was kept planar, i.e., relaxation in the direction perpendicular to the film surface was not possible. This calculation resulted in a constant energy density within the crystal in the direction perpendicular to the film surface (see Fig. 3). This calculation supports the above interpretation in terms of surface relaxations.

A comparison of Figs. 2a-c and 2d-f shows that the energy densities caused by thermal strain are larger by about a factor two than those caused by change in mass density. The results of 3D FEM calculations for thermal strain plus change in mass density are therefore dominated by the thermal strain. The results are therefore similar to those shown in Fig. 2d-f and will not be shown in this work. The dominance of the thermal strain is even more pronounced if a more realistic value of 1.5 % for the change in mass density is used. In this case the energy from the change in mass density is smaller by about a factor of 20 compared to the energy caused by the thermal strain (results not shown in this work).

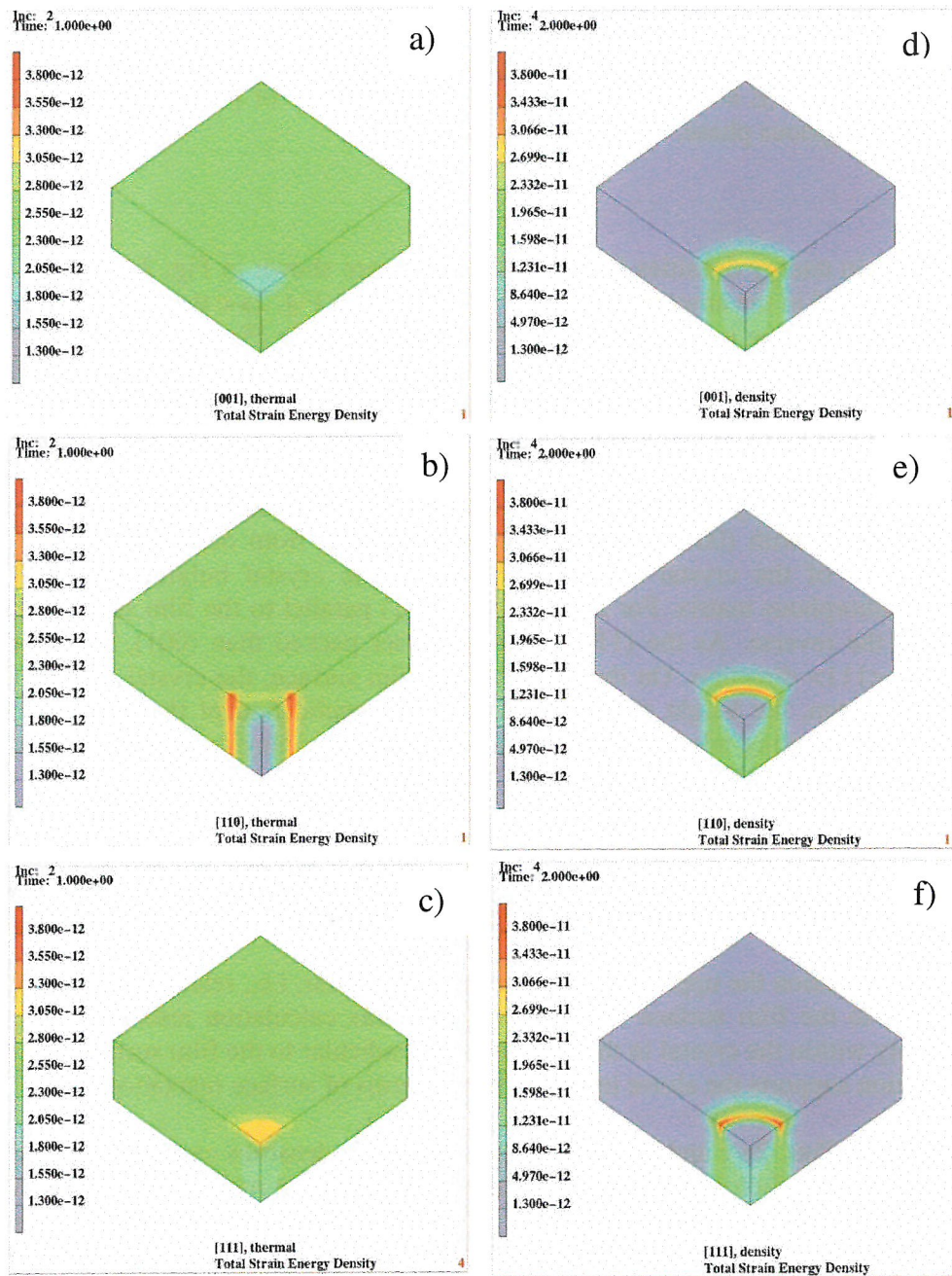


Figure 2: Elastic energy density in units of N/nm^2 of a crystal embedded in an amorphous matrix from FEM analyses. See text for full description.

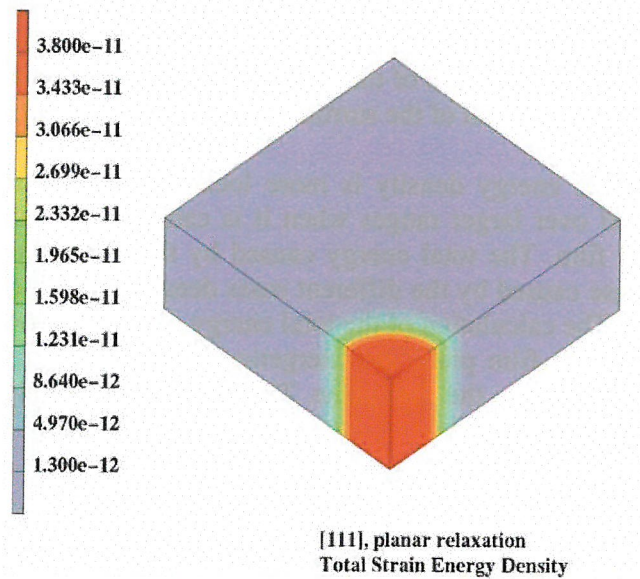


Figure 3: Distribution in energy density without surface relaxation for {111} planes parallel to the surface.

The results of the calculation of the total energy induced by thermal strain and/or by change in mass density during crystallization are listed in Table 1. According to Table 1 the total energy is lowest when the {001} planes of the crystals are parallel to the film plane while the energy is higher if the {111} planes of the crystals are parallel to the film plane. For crystals with {001} planes parallel to the film surface the driving force is larger than for crystals with {111} planes parallel to the surface. Crystals with {001} planes parallel to the surface plane will therefore grow faster in an amorphous matrix than crystals with {111} planes parallel to the surface. This will lead to a {001} - texture in the film.

Table 1: Total change in energy / 10^{-16} Nm

	001	011	111
T	1.292	1.308	1.315
Pt	0.669	0.663	0.659
T+Pt	1.583	1.597	1.600

T: Thermal strain

Pt: Phase transformation

SUMMARY

3D FEM calculations have been performed for fcc crystals of different orientation with respect to the film surface. The crystals were assumed to be completely embedded in an amorphous matrix. The energy density was calculated for (i) the elastic strain caused by the different thermal expansions of the film and of the substrate and (ii) the strain induced by the different mass densities of the crystal and of the surrounding amorphous matrix.

The calculations show that the energy density is more localized for the changes in mass density while it is distributed over larger ranges when it is caused by the different thermal expansions of substrate and film. The total energy caused by thermal strain is appreciably larger than the energy increase caused by the different mass densities of the crystalline phase and of the amorphous phase. The calculation of the total energy of the film shows that crystals with {001} planes parallel to the film plane are energetically favored compared to crystals with {111} planes or {011} parallel to the film plane. The formation of a polycrystalline film with {001}- texture is therefore suggested.

References

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