Theoretical study on cracking behavior in two-phase alloys Cr–Cr$_2$X (X = Hf, Nb, Ta, Zr)

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Abstract

To examine the importance of thermal expansion mismatch on cracking in two-phase Cr–Cr$_2$X (X = Hf, Nb, Ta, Zr) alloys, we have calculated the coefficients of thermal expansion (CTEs) of Cr and Laves-phase Cr$_2$X alloys by local-density-functional approach. A Debye model is used to approximate the phonon contribution through the elastic acoustic response. The sound velocities are determined by the calculated elastic constants and associated anharmonicity. The calculations show that the CTE of Cr at high temperatures is notably larger than those of Cr$_2$X. If the difference in CTE between Cr and Cr$_2$X is a primary source of crack initiation, our results fail to explain the experimental observation that, among these four Cr–Cr$_2$X alloy systems, the ingot cracking is present mainly in Cr–Cr$_2$Nb. We suggest that for the cracking to occur, the presence of thermal mismatch stresses are retained by a hard and supersaturated Cr matrix (e.g. due to the relatively high solubility of Nb in Cr in the case of Cr–Cr$_2$Nb). On the other hand, the softer Cr matrix can accommodate thermal misfit dislocations plastically even though the CTE difference between Cr and Cr$_2$X is large. © 2001 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Since single-phase Laves phase alloys are quite brittle, alloy development has been focused on Cr–Cr$_2$X (X = Hf, Nb, Ta or Zr) two-phase alloy [1–5]. The binary Cr–X phase diagrams [6] show a eutectic reaction, making it possible to produce two-phase alloys of the type Cr–Cr$_2$X. In the two-phase region comprising Cr–Cr$_2$X, eutectic composition results in the occurrence of the phases with a fibrous/rod morphology, and in the hypoeutectic alloys the primary phase is Cr solid solution. At temperatures below the eutectic temperature, the Cr solid solution decomposes to provide secondary Cr$_2$X precipitates. The Cr phase provides a soft and ductile matrix, resulting in a strong and tough two-phase alloy.

Recently, Kumar and Liu [4] examined the microstructure of a Cr–Cr$_2$Nb two-phase alloy in the as-cast and annealed conditions using optical and electron microscopy techniques. They found ingot cracking in this system as temperature decreases. Such ingot cracking, however, was not observed in Cr–Hf [3], Cr–Ta [5] and Cr–Zr [5] systems.

In this paper, we investigate if thermal mismatch is a major cause for ingot cracking in these two-phase alloys. To examine the effect of thermal expansion mismatch on cracking, we calculate the coefficients of thermal expansion (CTEs) of Cr and Cr$_2$X. In Section 2, we outline the theory to calculate the CTE of cubic systems. In Section 3, we present the calculated results which also include the second-order and third-order elastic constants of Cr and Cr$_2$X. In Section 4, a discussion on the possible cause of ingot cracking is given in terms of the calculated CTEs. This work is summarized in the final section.

2. Theory: thermal expansion coefficient

The coefficient of thermal expansion $\alpha$ for a cubic crystal is given by [7]

$$\alpha = \frac{1}{T} \left( \frac{\partial l}{\partial T} \right)_p = \frac{1}{3V} \left( \frac{\partial V}{\partial T} \right)_p = \frac{1}{3B} \left( \frac{\partial p}{\partial T} \right)_V,$$  \hspace{0.5cm} (1)

where $p$ is the pressure and $B$ is the bulk modulus.
Nonzero value of CTE results from the anharmonicity of the crystal, i.e. the volume dependence of phonon frequencies. In quasi-harmonic approximation, the free energy \( F \) of the crystal is given by

\[
F(T,V) = E(V) + F_{\text{ph}}(T,V),
\]

where \( E \) is the static contribution to the free energy, and \( F_{\text{ph}} \) is the free energy from phonon modes \( \omega_s(k) \). Here, \( \omega_s(k) \) is the angular frequency of the normal mode with wave vector \( k \) in branch \( s \).

From the pressure, we obtain

\[
\left( \frac{\partial p}{\partial T} \right)_V = -\frac{\partial^2 F_{\text{ph}}}{\partial V \partial T} = \sum_{ks} \gamma_{ks} c_{vs}(k),
\]

where \( \gamma_{ks} \) is the Grüneisen parameter for the normal mode \( (ks) \) given by

\[
\gamma_{ks} = -\frac{\partial (\ln \omega_s(k))}{\partial (\ln V)},
\]

and \( c_{vs}(k) \) is the contribution of the mode \( (ks) \) to the specific heat \( c_v = \sum_{ks} c_{vs}(k) \).

Since the thermal expansion is dominated by low energy excitations, we use a Debye model to describe the vibrating lattice. In the Debye model, the phonon contribution is approximated through the elastic acoustic response. Since all the normal-mode frequencies scale linearly with the cutoff frequency \( \omega_D \) in the Debye model, we can write

\[
\gamma_{ks} \equiv -\frac{\partial (\ln \omega_D)}{\partial (\ln V)} = \gamma.
\]

Also, within the Debye model, \( \left( \frac{\partial^2 P}{\partial T^2} \right)_V \) is equal to \( \gamma c_v \), so \( \alpha \) can be written in a simple form:

\[
\alpha = \frac{\gamma c_v}{3B(T)}.
\]

The temperature dependence of the bulk modulus is obtained from

\[
B(T) = V \left( \frac{\partial^2 F}{\partial V^2} \right)_T.
\]

Using the relation \( k_B \Theta_D = \hbar \omega_D \), Eq. (6) becomes

\[
\gamma = -\frac{\partial (\ln \Theta_D)}{\partial (\ln V)} = -\frac{V}{\Theta_D} \frac{\partial \Theta_D}{\partial V},
\]

where the Debye temperature \( \Theta_D \) is given by

\[
\Theta_D = \frac{\hbar}{k_B} \left( \frac{6\pi^2 N}{V} \right)^{1/3} v_m
\]

Here, \( v_m \) denotes the mean sound velocity of the propagation of elastic waves in the continuum. The propagation velocities \( v_\alpha \) are the solutions of the cubic equation (Christoffel equation) in \( v^2 \) [8,9]:

\[
\left[ k_D^2 - \delta_{ik} v_\alpha^2 \right] = 0
\]

where \( \Gamma_{ik} \) \((i,k = 1,2,3)\) are the Christoffel stiffnesses, subject to the condition \( \Gamma_{ik} = \Gamma_{ki} \). For cubic systems, if \( a_1, a_2, a_3 \) are the direction cosines of the normal to the wave front, the six Christoffel stiffnesses are given in terms of three independent elastic constants \( C_{11}, C_{12}, C_{44} \):

\[
\Gamma_{11} = C_{11} a_1^2 + C_{44} (a_2^2 + a_3^2)
\]

\[
\Gamma_{12} = (C_{12} + C_{44}) a_1 a_2
\]

\[
\Gamma_{13} = (C_{12} + C_{44}) a_1 a_3
\]

\[
\Gamma_{22} = C_{11} a_2^2 + C_{44} (a_1^2 + a_3^2)
\]

\[
\Gamma_{23} = (C_{12} + C_{44}) a_2 a_3
\]

\[
\Gamma_{22} = C_{11} a_3^2 + C_{44} (a_1^2 + a_2^2)
\]

Therefore, the information of elastic constants at several volumes enables us to determine Debye temperature, Grüneisen parameter, bulk modulus, and thus the coefficient of thermal expansion.

3. Results

3.1. Elastic constants

We performed total-energy calculations using the full-potential linearized augmented plane-wave (FLAPW) method within the local-density approximation. The FLAPW method solves the local-density-functional equations without any shape approximation to the potential or charge density. The atomic positions are relaxed by calculating Hellmann–Feynman forces acting on the atoms.

First, we obtained the theoretical equilibrium lattice constants. For bcc Cr, a lattice constant of 2.79 Å was obtained which is in fair agreement with the experimental value of 2.88 Å. The theoretical lattice constants of Laves phases CrX are 6.947 Å (X=Hf), 6.822 Å (X=Nb), 6.809 Å (X=Ta), and 6.990 Å (X=Zr), which are smaller than the experimental lattice constants 7.157 Å.
To determine the Debye temperatures, we evaluated the elastic constants (and from which the sound velocities are obtained by averaging over at least 100 directions). Under elastic strains, the new orthogonal lattice axes \(a_i'\) are related to the original ones \(a_i\) by
\[
a_i' = (1 + \epsilon_{ij})a_j,
\]
where \(\epsilon_{ij}\) are the strain components. The elastic strain energy density \(U\) is given by
\[
U = \frac{1}{2} \sum_{i=1}^{6} \sum_{j=1}^{6} \tilde{C}_{ij} \epsilon_i \epsilon_j,
\]
where \(C_{ij} = \frac{1}{2} \left( \tilde{C}_{ij} + \tilde{C}_{ji} \right)\) and \(\epsilon_i\) are the strain components. The cubic structure has only three independent elastic constants \(C_{11}, C_{12}\), and \(C_{44}\). These elastic constants were determined from three relations (i) \(U = (C_{11} + C_{12}) \epsilon^2\) for \(\epsilon_1 = -\epsilon_2 \equiv \epsilon\), (ii) \(U = (C_{11} + C_{12}) \epsilon^2\) for \(\epsilon_1 = \epsilon_2 \equiv \epsilon\), and (iii) \(U = \frac{1}{2} C_{44} \epsilon^2\) for \(\epsilon_6 = \epsilon\), where the unspecified strain components are zero for each of these cases. The total energy was calculated as a function of strains (up to 3–4%) for each of these deformations. The elastic constants are then obtained from the curvature of total energy-strain curves by fitting the calculated values to third-order polynomials [11].

The second-order elastic constants were calculated at three different lattice constants in the vicinity of the experimental lattice constant. The volume dependence of these second-order elastic constants gives rise to the higher-order elastic constants. The results of elastic constants at experimental volume for Cr and Cr\(_2\) X are given in Table 1.

Note that bulk Cr displays a long-wavelength spin-density wave with a short-range antiferromagnetic ordering below the Neél temperature of \(T_n = 311\) K. Therefore, we calculated the elastic constants of Cr for both antiferromagnetic and paramagnetic cases. The calculated values of antiferromagnetic Cr in Table 1 should be compared with the experimental elastic constants \(C_{11} = 391, C_{12} = 89.6,\) and \(C_{44} = 103\) GPa of Cr measured at 77 K [12].

For Cr\(_2\) X, no single crystal data are available. However, the Hill’s averages [8] of Young’s and shear moduli of Cr\(_2\) X always give smaller values than those of experimental measurements [14]. An independent calculation by Ormeci et al. [15] for Cr\(_2\) Nb also showed a similar trend as found in our result. The reasons for this discrepancy remain unclear. (The calculated elastic constants at the theoretical lattice parameter should be higher than the measured values, since the theoretical lattice parameters are usually 2–3% smaller than the experimental lattice parameters. The present calculations, however, show opposite trend). The calculated elastic constants at different volumes are shown in Figs. 1 and 2. As expected, the elastic constants increase with increasing unit cell volume. Furthermore, all the calculated elastic constants of Cr and Cr\(_2\) X show a linear dependence on volume within the volume range we have considered, which indicates that third-order elastic constants are dominant in the elastic anharmonicity.

By writing the third-order contribution to the elastic energy density \(U\) as
\[
U^{(3)} = \frac{1}{3!} \sum_{\mu \nu \sigma} C_{\mu \nu \sigma} \epsilon_\mu \epsilon_\nu \epsilon_\sigma,
\]
the slopes of lines shown in Figs. 1 and 2 are related to the third-order elastic constants through the following expressions:
\[
C_{11} = (C_{11})_0 + \frac{1}{3} (C_{111} + 2C_{112}) \frac{\delta V}{V},
\]
\[
C_{12} = (C_{12})_0 + \frac{1}{3} (C_{123} + 2C_{112}) \frac{\delta V}{V},
\]
\[
C_{44} = (C_{44})_0 + \frac{1}{3} (C_{144} + 2C_{166}) \frac{\delta V}{V},
\]
where \((C_{11})_0, (C_{12})_0\) and \((C_{44})_0\) are second-order elastic constants at a reference volume, e.g. the experimental volume. Since so far we have considered only three independent deformations, the slopes of lines shown in Figs. 1 and 2 can only give the linear combinations of \(C_{111} + 2C_{112}\) and \(C_{123} + 2C_{112}\), and \(C_{144} + 2C_{166}\). These values are tabulated in Table 2, where the negative values are due to the fact that the elastic constants decrease linearly with increasing lattice parameter. To obtain the third-order elastic constants individually, independent deformations are required. This can be achieved, for example, by setting \(\epsilon_1 = \epsilon\) as the only non-zero strain component in Eq. (18). We then have

\begin{table}[h]
\centering
\begin{tabular}{cccc}
\hline
 & \(C_{11}\) & \(C_{12}\) & \(C_{44}\) \\
\hline
Cr (antiferro) & 373 (391, 350) & 65 (89.6, 57.8) & 81 (103, 101) \\
Cr (para) & 393 & 122 & 68 \\
Cr\(_2\) Hf & 225 & 126 & 58 \\
Cr\(_2\) Nb & 250 & 170 & 58 \\
Cr\(_2\) Ta & 281 & 173 & 73 \\
Cr\(_2\) Zr & 201 & 126 & 46 \\
\hline
\end{tabular}
\caption{Calculated elastic constants (in units of GPa) at experimental volumes for Cr and Cr\(_2\) X (X = Hf, Nb, Ta, Zr)\(^a\)}
\end{table}
For the present purpose, however, the combinations of third-order terms are sufficient for our discussion. We note that, among these Cr$_2$X compounds, the magnitudes of the third-order elastic constants are the lowest for Cr$_2$Zr, indicating a low CTE value for this compound (see next section).

### 3.2. Coefficient of thermal expansion

The solutions of the Christoffel equation give rise to the mean sound velocity, from which the Debye temperature is obtained. Since $\Theta_D$ scales linearly with volume, which is confirmed with a direct calculation, we approximate $\frac{\partial \Theta_D}{\partial V} \approx \frac{\Delta \Theta_D}{\Delta V}$. This enables us to obtain $\gamma$ at given volumes with $\gamma \approx -\frac{\partial \Delta \Theta_D}{\partial \Theta_D}$. The mean sound velocity $v_{sm}$, Debye temperature $\Theta_D$, Gr"uneisen parameter $\gamma$, Bulk modulus $B_0$, and the CTE at high temperatures (e.g. 1000 K) $\alpha^*$ are given for Cr and Cr$_2$X at their experimental volumes in Tables 3 and 4.

The CTE as a function of temperature is shown in Fig. 3. The discontinuity of CTE for Cr shown in Fig. 3 is due to the magnetic phase transition at Néel temperature of 311 K, below which Cr has antiferromagnetic ordering and above which Cr becomes paramagnetic. In this calculation, the magnetic entropy due to the magnetic fluctuations is not included. Even without the
magnetic entropy, the CTE of Cr gives a very good agreement with experimental measurements at low temperatures (< 200 K) and at high temperatures [16]. Since we focus on the high-temperature behaviors in this paper, a further investigation on the effect of magnetic entropy around Néel temperature will be considered elsewhere.

For Cr$_2$X alloys, we found that: (i) the CTE of Cr at high temperatures is notably larger than those of Cr$_2$X; in particular, the CTE of Cr is about twice of that of Cr$_2$Zr, and (ii) the CTEs of Cr$_2$Hf and Cr$_2$Ta are nearly equal and are very close with that of Cr$_2$Nb.

An estimation of CTE from experimental data [4,17] of Cr and Cr$_2$Nb gives 11–12/°C2/10°/K and 8/°C2/10°/K around 1000 K, respectively. For both Cr and Cr$_2$Nb, we found a good agreement between theory and experiment at high temperatures [see Fig. 4(a) for Cr$_2$Nb]. Experimentally [18], the CTE of Cr$_2$Ta is 6–10/°C2/10°/K in going from 300 K to 1500 K. Fig. 4(b) shows the comparison between theory and experiment for Cr$_2$Ta. The theoretical CTE agrees reasonably well with experiment in magnitude.

4. Discussion

Now, we can discuss if thermal mismatch is a major cause for ingot cracking in these Laves two-phase alloys by examining the difference in CTE between Cr and Cr$_2$X. As mentioned already, among these Cr-based two phase alloys Cr–Cr$_2$X (X=Hf, Nb, Ta, Zr), the ingot cracking is present mainly in Cr–Cr$_2$Nb system. If the difference in CTE between Cr and Cr$_2$X is a primary measure on the occurrence of crack, our results fail to explain the experimental observation. This is because the CTE of Cr is notably larger than those of Cr$_2$X considered here, in particular than that of Cr$_2$Zr. Thus, we suggest that the mismatch due to the difference in CTEs is not a major source for ingot cracking in these two-phase alloys; other sources may play important roles in crack initiation.

It was suggested by Kumar and Liu [4], that the presence of appreciable (~6 at.%) Nb solubility in the Cr matrix at the eutectic temperature and the difficulty in precipitating the Nb out as Cr$_2$Nb during cooling can be a source contributing to the cracking. (For the measured solubility of X in the Cr matrix, see Table 5.) In contrast, for Cr–Hf system, there is negligible Hf solubility in the Cr matrix at the eutectic temperature and so matrix supersaturation is not evident, which would render the matrix softer and more tolerant to cracking. Similarly, this is also the case for Cr–Zr system since the Zr solubility in the Cr matrix is negligible (< 0.6%). For the Cr–Ta system, there is a small amount of Ta solubility in the Cr matrix at the eutectic temperature and so matrix supersaturation, if any, will be less dominant than in the Cr–Nb system. On the other hand, the CTE of Cr$_2$Ta is closer to that of Cr than Cr$_2$Nb and Cr$_2$Zr.

In addition to the solid solution hardening contributing to cracking in the case of Cr–Nb system, the presence of appreciable second element in solid solution may also

| Table 2 |
| Calculated third-order elastic constants (in units of GPa) for Cr and Cr$_2$X (X=Hf, Nb, Ta, Zr) |  |
| (C$_{111}$ + 2C$_{112}$)/3 | (C$_{123}$ + 2C$_{112}$)/3 | (C$_{144}$ + 2C$_{166}$)/3 |
| Cr (antiferro) | −1372 | −905 | −237 |
| Cr (para) | −1315 | −395 | −366 |
| Cr$_2$Hf | −724 | −431 | −200 |
| Cr$_2$Nb | −938 | −661 | −186 |
| Cr$_2$Ta | −1052 | −615 | −276 |
| Cr$_2$Zr | −605 | −411 | −90 |

| Table 3 |
| Calculated thermoelastic quantities of Cr at experimental volume: the mean sound velocity ($v_m$), the Debye temperature (θ$_D$), the Grüneisen parameter (γ), the bulk modulus (B); the coefficient of thermal expansion at 1000 K is denoted as α* |
| $v_m$ (m/s) | θ$_D$ (K) | γ | B (GPa) | α* (10$^{-6}$/K) |
| Cr (af) | 4186 | 545 | 1.10 | 168 | – |
| Cr (para) | 3907 | 509 | 2.02 | 212 | 12.26 |

| Table 4 |
| Calculated thermoelastic quantities of Cr$_2$X (X=Hf, Nb, Ta, Zr) at their experimental volumes |
| $v_m$ (m/s) | θ$_D$ (K) | γ | B (GPa) | α* (10$^{-6}$/K) |
| Cr$_2$Hf | 2590 | 311 | 1.39 | 159 | 8.53 |
| Cr$_2$Nb | 2881 | 354 | 1.44 | 197 | 7.66 |
| Cr$_2$Ta | 2713 | 334 | 1.70 | 209 | 8.59 |
| Cr$_2$Zr | 2788 | 332 | 0.91 | 151 | 5.56 |
increase the ductile/brittle transition temperature of the matrix Cr. Thus, due to the presence of Nb, there is not only a decrease in ductility of the Cr matrix but also a larger temperature range over which it has to accommodate the mismatch in a brittle state.

Thus, we suggest that for the crack to occur, the presence of thermal mismatch stresses are retained by a hard and supersaturated Cr matrix (e.g. in the case of Cr–Cr$_2$Nb). On the other hand, a soft Cr matrix can accommodate thermal misfit dislocations plastically even though the CTE difference between Cr and Cr$_2$X is large (e.g. in the case of Cr–Cr$_2$Zr and Cr–Cr$_2$Hf).

5. Summary

The thermoelastic properties of Cr and Laves phases Cr$_2$X (X = Hf, Nb, Ta, Zr) alloys were presented. The calculated results were used to explain the experimental observation that the ingot cracking occurs mainly in the Cr–Cr$_2$Nb two-phase alloy system. The calculated CTEs are in reasonably good agreement with available experiments for Cr$_2$Nb and Cr$_2$Ta. We also found that the CTE of Cr is much higher than those of Cr$_2$X. Therefore, if the difference in CTE between Cr and Cr$_2$X is a primary source of crack initiation, our results failed to explain the experimental fact that, among these Cr–Cr$_2$X alloys, the ingot cracking is present mainly in Cr–Cr$_2$Nb. We suggested that, for the cracks to occur, the presence of thermal mismatch stresses are retained by a hard and supersaturated Cr matrix as in the case of Cr–Cr$_2$Nb. On the other hand, the softer Cr matrix can accommodate thermal misfit dislocations plastically even though the CTE difference between Cr and Cr$_2$X is large.

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