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On the thermodynamics of the β-phase in Cr–Ti

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Abstract

The possibility of amorphization of the β-phase in the Cr–Ti system is considered using free energy calculations based on the Miedema method. The results of this calculation are also compared with those obtained by other workers using phase diagram fitting and the cluster variation method. These calculations do not suggest any possibility of amorphization, called spontaneous vitrification, as has been reported in the literature. It is also found that strain energy can make only a negligible contribution to the overall free energy and thus cannot destabilize the β-phase. The possibility of spinodal decomposition of the β-phase is also considered.

1. Introduction

For the past few years there has been considerable interest in the phase transformation behaviour of the b.c.c. β-phase of binary Cr–Ti alloys. Blatter and von Allmen [1] reported that laser-quenched thin films of β-$Cr_{30}Ti_{70}$ can be amorphized by annealing at 873 K. They termed this transformation spontaneous vitrification. Later, Blatter *et al.* [2] reported that a similar transformation is also possible for bulk samples. Although amorphization in the solid state is well known by other methods (see, for example, ref. 3) this is apparently the only example of a polymorphous crystal-to-amorphous transformation. We have previously reported our failure to observe this transformation both in thin films and bulk alloys [4]. Mizutani [5] and Sinkler and Luzzi [6] have also reported similar failures.

Despite our failure to observe amorphization, we did observe several indications of the instability of the β-phase: (i) broad peaks in X-ray diffraction patterns [4], (ii) copious diffuse scattering in the electron diffraction patterns [4], and (iii) a step in the specific heat C_p as observed in differential scanning calorimetry [7].

These results have led us to consider the thermodynamics of the β-phase. We have calculated free energies of the β and amorphous phases by the well known semi-empirical Miedema method [8]. We correct an earlier calculation presented by Gallego *et al.* [9].

We also compare the results obtained by the Miedema method with those obtained by the cluster variation method (CVM) and phase diagram fitting of other workers. On the basis of such a comparison we have proposed an interpolation scheme which can give better estimates of the free energies of the various phases. Even these interpolations do not suggest any amorphization.

It has been suggested by various researchers that defects can play an important role in making the β-phase unstable with respect to the amorphous phase. We therefore made an attempt to estimate the inhomogeneous strain in our samples using X-ray measurements. The results and implications of these measurements are described.

Another point of interest in the thermodynamic behaviour of β-Cr-Ti is spinodal decomposition which could be an alternative to amorphization. Menon and Aaronson [10] have calculated the coherent spinodal temperatures of β-Cr–Ti. However, Ikematsu *et al.* [11] have observed spinodal decomposition at temperatures much above those predicted by Menon and Aaronson. In this light we have re-evaluated the calculation of Menon and Aaronson [10] and found that their calculation is in error. A new corrected version of the calculation is presented and discussed.

2. Free energies based on Miedema's model

2.1. The Miedema model

Miedema and coworkers developed a semi-empirical approach to the estimation of heat of mixing of binary alloys. An outline of the method is presented here for the purpose of describing the present calculations.

The heat of formation ΔH of a binary crystalline solid solution $A_{1-x}B_x$ is taken to be

$$\Delta H = \Delta H^{\mathrm{chem}} + \Delta H^{\mathrm{elas}} + \Delta H^{\mathrm{struc}} \qquad (1)$$

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where ΔH^{chem}, ΔH^{elas}, and ΔH^{struc} are respectively the chemical, elastic and structural contributions. The chemical component ΔH^{chem} is given by

$$\Delta H^{\text{chem}} = x_A x_B [x_B \Delta h^{\text{chem}}(\text{A in B}) + x_A \Delta h^{\text{chem}}(\text{B in A})] \tag{2}$$

where x_A, x_B are atom fractions of components A and B and Δh^{chem} (A in B) are listed for various binary systems in Tables V-4.02 to V-4.26 in de Boer *et al.* [8]. The elastic component is given by

$$\Delta H^{\text{elas}} = x_A x_B [x_B \Delta h^{\text{elas}}(\text{A in B}) + x_A \Delta h^{\text{elas}}(\text{B in A})] \tag{3}$$

where Δh^{elas} (i in j) is given by

$$\Delta h^{\text{elas}}(i \text{ in } j) = \frac{2K_i \mu_j (V_i^* - V_j^*)}{3K_i V_j^* + 4\mu_j V_i^*} \tag{4}$$

where K_i is the bulk modulus of solute i (*i.e.* A or B), μ_j is the shear modulus of the matrix j, and V_i^* and V_j^* are the molar volumes of A and B corrected for charge transfer effects. The structural component ΔH^{struc} is given by

$$\Delta H^{\text{struc}} = E_{\text{alloy}}(Z_{\text{alloy}}) - [x_A E_A(Z_A) - x_B E_B(Z_B)] \tag{5}$$

where $E_{\text{alloy}}(Z_{\text{alloy}})$, $E_A(Z_A)$ and $E_B(Z_B)$ are the lattice stabilities of the alloy, element A and element B, evaluated at the respective values of their average number of valence electrons (*i.e.* number of d+s electrons) Z_{alloy}, Z_A and Z_B per atom. Values of the lattice stability parameter for the three main crystalline forms (b.c.c. h.c.p. and f.c.c.) of the transition metal elements have been estimated as a function of the number of valence electrons per atom by Miedema and coworkers and are available in de Boer *et al.* [8].

The heat of formation of an amorphous binary alloy is considered to be simply the chemical component described above, it being assumed that the elastic and structural components are negligible.

To calculate the mixing free energy ΔG of various phases, the entropy of mixing ΔS is also required, and in the Miedema approach is assumed to be ideal:

$$\Delta S = -R(x_A \ln x_A + x_B \ln x_B) \tag{6}$$

where R is the gas constant.

Apart from the mixing terms described above, we also need to estimate the free energy difference between amorphous and crystalline phases for the unmixed pure components A and B. Miedema proposes a simplified approximation for the free energy difference ΔG_i between the crystalline and amorphous phases of pure component i as

$$\Delta G_i = \alpha(T_i^{\text{m}} - T) \tag{7}$$

where T_i^{m} is the melting point of component i, T is the temperature and α is an empirical parameter set equal to 3.5 J mol^{-1} K^{-1}.

2.2. *Existing calculation for Cr–Ti*

Gallego *et al.* [9] calculated the free energies of β and amorphous phases in the Cr–Ti system. Here we correct a mistake in their calculation and evaluate the free energies at 873 K, which is the temperature of interest for spontaneous vitrification.

Equation (7) for the free energy difference between crystalline and amorphous phases can be used for chromium and β-Ti at a temperature $T = 77$ K with $T_{\text{Cr}}^{\text{m}} = 2130$ K and $T_{\beta>\text{-Ti}}^{\text{m}} = 1943$ K [12] yielding

$$\Delta G_{\text{Cr}} = 7.2 \text{ kJ mol}^{-1} \text{ (at 77 K)}$$

$$\Delta G_{\beta\text{-Ti}} = 6.5 \text{ kJ mol}^{-1} \text{ (at 77 K)}$$

Although Gallego *et al.* [9] have shown the difference between amorphous and crystalline chromium correctly, the difference between amorphous and β-Ti is shown only as 2.2 kJ mol^{-1} (our measurement from their plot) instead of 6.5 kJ mol^{-1} as calculated above. The difference between free energies of α-Ti and amorphous titanium phases in their figure comes close to 6.5 kJ mol^{-1}. Thus Gallego *et al.* [9] have set the free energy difference between the amorphous phase and α-Ti equal to the difference between the amorphous phase and β-Ti. (Note that eqn. (7) could be used to calculate $\Delta G_{\alpha\text{-Ti}}$ if the metastable melting point of α-Ti were known.) When the correct $\Delta G_{\beta\text{-Ti}}$ is used, the free energy curve for the β-phase always lies below that for the amorphous phase, never intersecting it in the manner shown by Gallego *et al.* [9]. Thus spontaneous vitrification for the β-phase is not predicted even at 77 K, at variance with their claim.

To calculate Δh^{elas} (A in B) defined in eqn. (4) and required for calculation of the elastic component of the enthalpy of mixing in eqn. (3), Gallego *et al.* [9] used the bulk and shear moduli of α-Ti. Since clearly the moduli of β-Ti should be used, this could introduce significant error in the calculations.

2.3. *New calculation for Cr–Ti*

In the present work only the free energies relevant for the amorphization of the β-phase are considered. The temperature of most interest for the calculation is that corresponding to the suggested spontaneous vitrification, *i.e.* 873 K.

Following the procedure outline in Section 2.1, the chemical, elastic and structural components of the enthalpy of mixing are evaluated. The chemical component is obtained from eqn. (2) using the parameters from Table V-4.04 of de Boer *et al.* [8]:

$\Delta h^{\mathrm{chem}}(\mathrm{Cr\ in\ Ti}) = -27\ \mathrm{kJ\ mol^{-1}}$

$\Delta h^{\mathrm{chem}}(\mathrm{Ti\ in\ Cr}) = -33\ \mathrm{kJ\ mol^{-1}}$

To calculate the elastic component using eqns. (3) and (4) we need the bulk and shear moduli of chromium and β-Ti at the temperature of interest. For chromium, single-crystal elastic moduli data are available from Bolef and de Klerk [13] from 80 K to 500 K. The values at 873 K were estimated by extrapolating their data, as shown in Fig. 1. For β-Ti there are no data available below 1150 K, where it is no longer a stable phase (perhaps explaining why Gallego *et al.* [9] used the moduli of α-Ti in place of those for β-Ti). However, Fisher and Dever [14, 15] have measured the single-crystal elastic constants in the β-phase in Cr–Ti alloys with 28.37, 13.81, 9.36 and 6.98 at.% chromium at 298 K and 1273 K. The composition dependence of the moduli is, except for C_{12}, to a good approximation parabolic, permitting straightforward extrapolation to pure β-Ti (see Fig. 2(a) for 298 K and Fig. 2(b) for 1273 K; fitting parameters in Table 1). Fisher and Dever [14] show that the variation of the moduli between these temperatures is linear. To obtain the polycrystalline bulk and shear moduli from these single-crystal data, the well known Voigt and Reuss averaging methods were used (see, for example, ref. 16) to obtain respectively the upper and lower limiting values. For the present calculations we employed the mean of the upper and lower bounds.

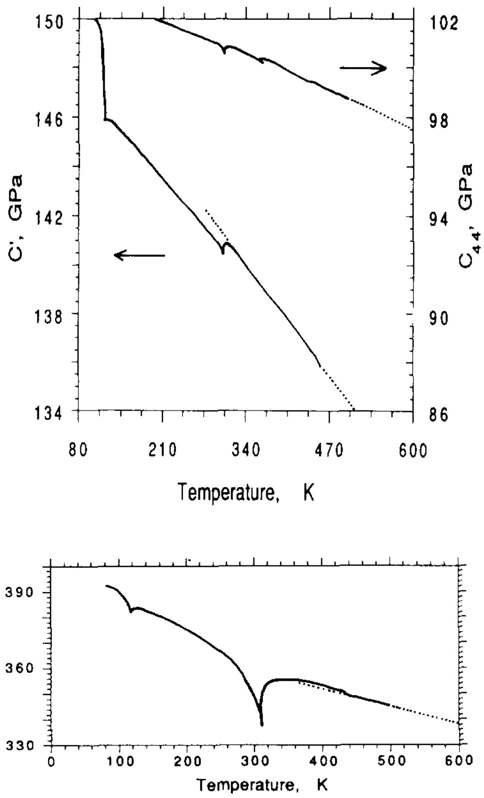

Fig. 1. Elastic stiffness constants, C_{11}, C_{44} and C' ($C' = (C_{11} - C_{12})/2$) for pure chromium as measured by Bolef and de Klerk [13]. The dotted lines indicate the linear fits used in the present work to extrapolate to higher temperatures.

In using eqn. (4), one also needs to correct the molar volumes of pure titanium and chromium for charge-transfer effects, as described in de Boer *et al.* [8].

For the structural component of the enthalpy of mixing of the β-phase we use eqn. (5) with $Z_{\mathrm{Cr}} = 6$, $Z_{\mathrm{Ti}} = 4$ and $Z_{\mathrm{alloy}} = x_{\mathrm{Cr}} Z_{\mathrm{Cr}} + X_{\mathrm{Ti}} Z_{\mathrm{Ti}}$. From the data given by de Boer *et al.* [8] we have:

$E_{\mathrm{Cr}}(Z_{\mathrm{Cr}}) = E_{\mathrm{bcc}}(6) = -12.0\ \mathrm{kJ\ mol^{-1}}$

$E_{\mathrm{Ti}}(Z_{\mathrm{Ti}}) = E_{\mathrm{bcc}}(4) = +2.0\ \mathrm{kJ\ mol^{-1}}$

For the b.c.c. solid solution we need to know $E_{\mathrm{bcc}}(Z_{\mathrm{alloy}})$ between $Z_{\mathrm{alloy}} = 4$ to 6. From ref. 8 we have $E_{\mathrm{bcc}}(4) = +2.0$, $E_{\mathrm{bcc}}(5) = -9.5$, $E_{\mathrm{bcc}}(5.5) = -14.5$ and $E_{\mathrm{bcc}}(6) = -12.0$ (all values in kJ mol^{-1}). Between these points, E_{bcc} is evaluated by a linear interpolation. Note that in the present calculation for the structural term, b.c.c. β-Ti is being used as the reference state for the pure titanium. Gallego *et al.* [9] used α-Ti as the reference state. Although this will change the actual values of the free energy of the solid solution phase, it will not affect the relative positions of the free energies of solid solution and amorphous phases.

The results of the calculation for 873 K, which corresponds to the spontaneous vitrification temperature, are shown in Fig. 3. It is found that the curve for the amorphous phase is still above that for the β-phase at all compositions, showing no possibility of spontaneous vitrification. For Ti–40 at.%Cr the difference in the free energies of the amorphous and the β-phases is about 4.1 kJ mol^{-1}.

It is of interest to compare the Miedema method with other methods of estimating free energies. Sluiter and Turchi [17] calculated the Helmholtz free energy of β-Cr–Ti by the cluster variation method (CVM) in the tetrahedron approximation. Their result for 400 K is shown in Fig. 4. For comparison, the free energy of the β-phase calculated using the Miedema method is also shown. It is found that although the two curves differ in detail, there is very good general agreement between the values calculated by the two methods. However, the free energy formula of Murray [18] gives a very different value both in magnitude and sign. As Murray's formula was obtained by fitting the high temperature part of the Cr–Ti phase diagram, it is quite likely that it is not accurate at low temperatures. However, near the melting point, Murray's formula should be applicable as it is able to predict the phase diagram accurately. Figure 5 compares the values obtained by the Miedema method and Murray's fitting at the melting point. It is found that near the melting

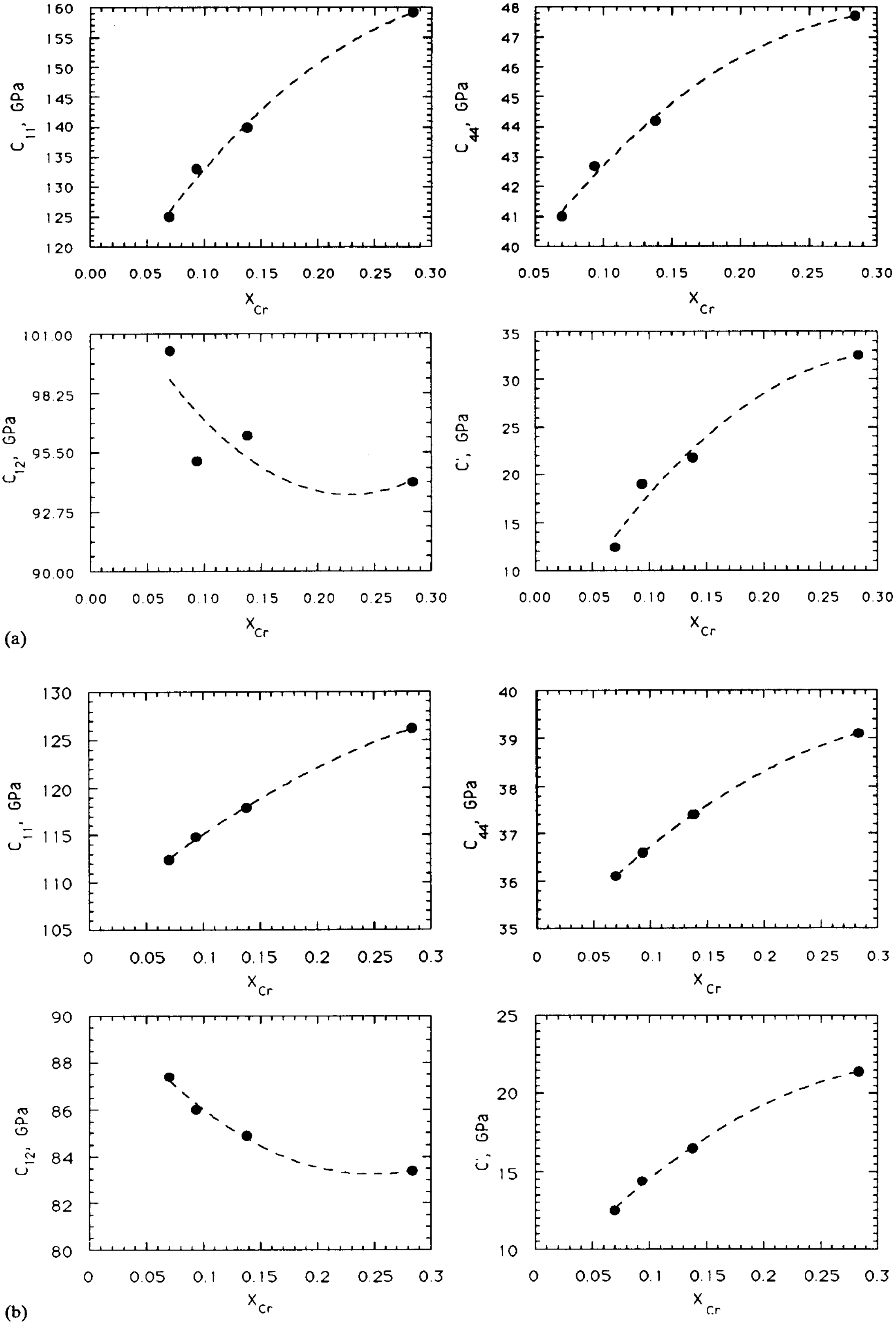

Fig. 2. The elastic stiffness constants C_{11}, C_{12}, C_{44} and C' of four Cr–Ti alloys at (a) 298 K and (b) 1273 K as measured by Fisher and Dever [14, 15]. The dashed line shows the parabolas that best fit the data, which were used to estimate the values for pure titanium by extrapolation. The fitting parameters of the parabolas are given in Table 1.

TABLE 1. The composition dependence of the elastic constants in Cr–Ti alloys is found to be parabolic of the form: (elastic constant, in GPa) $=A+Bx+Cx^2$, where x is the mole fraction of chromium; the values are given of A, B and C used in fitting the data for 298 K and 1273 K, illustrated in Fig. 2.

Elastic constant	298 K			1273 K		
	A	*B*	*C*	A	B	C
C_{11}	106.91	301.51	−414.98	105.87	103.31	−111.68
C_{44}	36.90	68.93	−108.86	34.44	26.18	−34.45
C_{12}	104.62	−97.19	212.81	90.98	−62.08	124.82
C'	1.14	199.35	−313.90	7.45	82.70	−118.25

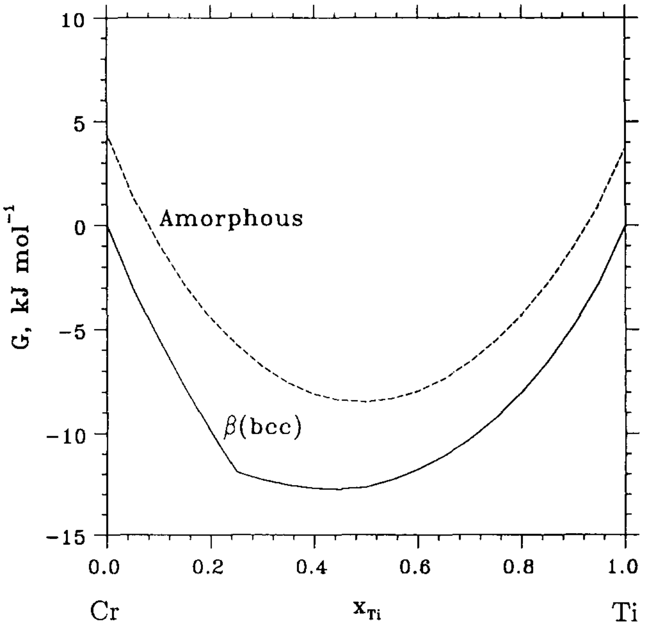

Fig. 3. The free energies of the β and amorphous phases of Cr–Ti at 873 K (the temperature of spontaneous vitrification according to ref. 1), calculated using the Miedema model. The reference states for the elements are the b.c.c. phases chromium and β-Ti.

temperature the Miedema method gives a rather poor approximation to the free energy of the β-CrTi. It can be concluded then that Miedema's method is a good approximation at lower temperatures (400 K) whereas Murray's function is accurate near the melting point (1673 K).

We describe below an *ad hoc* attempt to interpolate between these two methods in the hope of obtaining reasonable value of free energies at intermediate temperatures, in particular 873 K of interest for spontaneous vitrification. in this discussion we restrict ourselves to $Cr_{40}Ti_{60}$. Wirz *et al.* [19] have shown that there is a step in the specific heat of the β-phase at about 723 K, an observation also verified by us [7]. The specific heat below 723 K is close to the Dulong and Petit value, but above 723 K it is significantly in excess of this value. Extrapolation of Murray's function to lower temperature does not take this step into account. It is possible, then, to speculate that the difference between the values for the β-phase predicted by the two methods can be attributed to an excess specific heat on the high temperature side of this step. A step of 19.5 J mol⁻¹ K⁻¹ at 723 K in the specific heat can bring down the

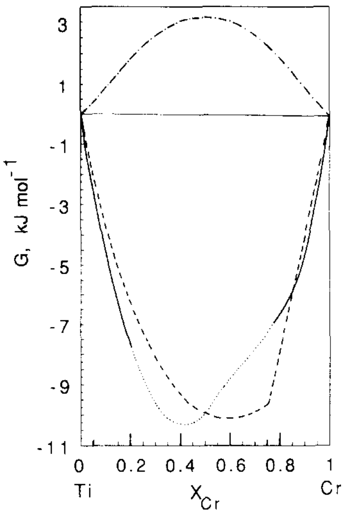

Fig. 4. Comparison of the free energy of β-Cr-Ti at 400 K calculated by various methods: the solid line shows results from the cluster variation method of Sluiter and Turchi [17], the dotted extension representing the ordered B2 structure; the dashed line shows the values calculated in the present work based on the Miedema model; the dot-dashed line shows the fitting function of Murray [18].

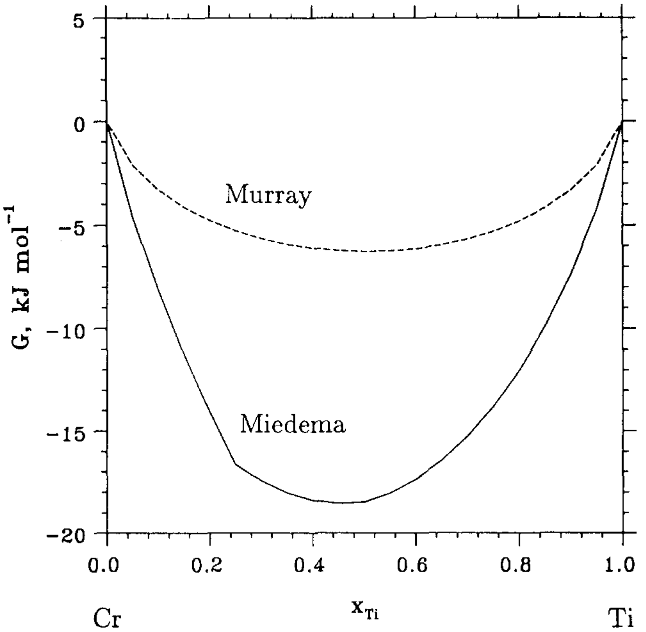

Fig. 5. Comparison of the free energy of β-Cr-Ti at 1673 K (close to the melting point) as calculated on the basis of the Miedema model (present work) and of the fitting function of Murray [18].

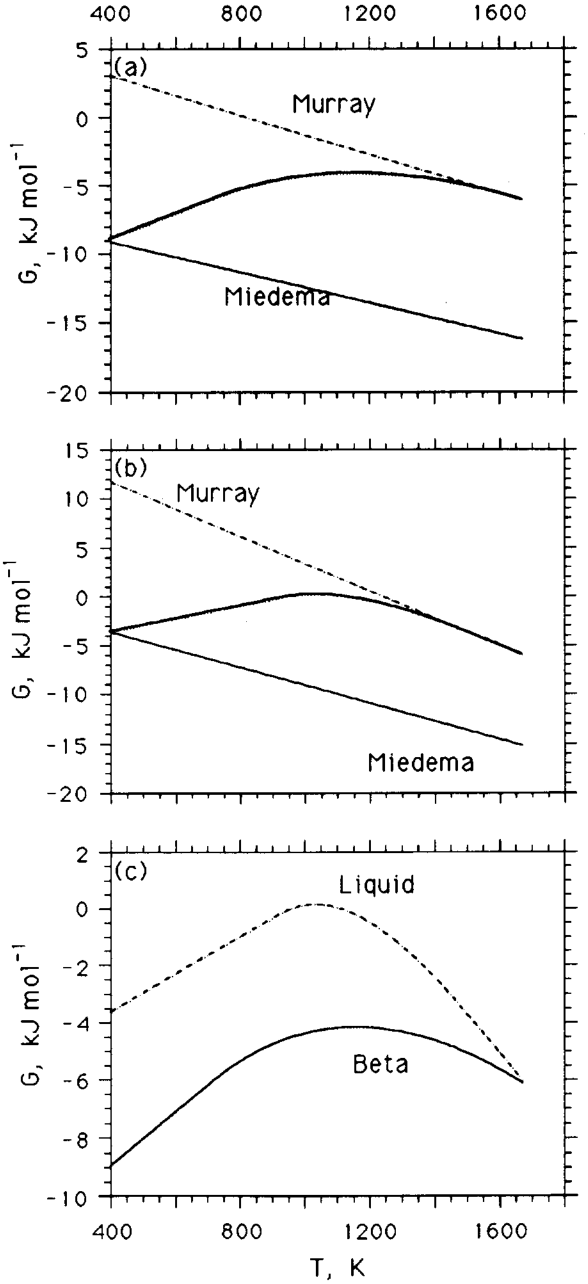

Fig. 6. Free energy of β and amorphous phases of $Cr_{40}Ti_{60}$ as functions of temperature and composition: (a) β phase, (b) amorphous–liquid phase. The heavy unmarked curves in (a) and (b) represent the interpolations suggested in the text. In (c) the interpolated values for the β and amorphous phases are compared.

free energy of the β-phase at 400 K from 3 kJ mol^{-1}, predicted by Murray's fitting, to the -9.2 kJ mol^{-1} of the Miedema method. Although large compared with the experimentally determined step in the specific heat of about 6 J mol^{-1} K^{-1}, it is of the same order of magnitude. The difference could perhaps arise if the specific heat gradually increases after the step rather than staying constant. The free energy of the β-$Cr_{40}Ti_{60}$ as a function of temperature calculated by the methods of Miedema and Murray and by the interpolation scheme outlined above is shown in Fig. 6(a).

Let us now consider the liquid or amorphous phase. Arguments similar to that presented for the β-phase indicate that Murray's fitting is reliable near the melting point whereas Miedema's method is expected to be a good approximation at lower temperatures. It is well known that the specific heat of a glass-forming system rises continuously from the melting point to the glass-transition temperature. We assume similar behaviour for liquid-$Cr_{40}Ti_{60}$, with an assumed glass-transition temperature T_g of 923 K and an excess specific heat, for $T_m > T > T_g$, given by

$$\Delta C_{p,liq}^{xs} = -E(T - T_m) \tag{8}$$

where E is an adjustable parameter. With E taking the value 8.37 J mol^{-1} K^{-2}, the free energy difference between the liquid of Murray and the glass of Miedema can be accounted for. The free energy of the liquid–amorphous phase predicted by the methods of Miedema and Murray and the suggested interpolation is shown in Fig. 6(b). In Fig. 6(c) the interpolated values of the free energies of the β and amorphous phases have been redrawn for comparison. As the curves never interest below the melting point, no spontaneous vitrification is suggested.

3. X-ray diffraction measurement of strain in β-Cr–Ti

It is found that the X-ray diffraction peaks from the β-phase are unusually broad. Blatter *et al.* [20] reported a correlation between peak width and amorphizability: the β-phase in water-quenched bulk samples and laser-quenched thin films has broader peaks and undergoes spontaneous vitrification, whereas melt-spun ribbons with narrower peaks do not amorphize. Blatter *et al.* [20] expressed these results in terms of coherence length (related to the peak width through the well known Scherrer formula; see for example ref. 21, but peak broadening can have contributions both from low coherence length and high inhomogeneous strain. Indeed, Von Allmen and Blatter [22] have considered strain energy as the driving force for spontaneous vitrification. In the present work we attempt a quantitative separation of coherence length and inhomogeneous strain contributions to the peak width in our β-phase samples. The samples were made by arc-melting on a water-cooled copper hearth in an argon atmosphere. The samples were remelted three or four times to ensure homogeneity. In the as-cast form the samples showed X-ray peaks only from the β-phase without further heat treatment being necessary.

According to Klug and Alexander [23], theoretical considerations and experimental results show that in most cases the peak profile due to size broadening is approximately Cauchy, whereas that due to strain is approximately Gaussian. In this situation they have shown that the following equation is satisfied:

$$\left(\frac{\delta s}{s}\right)^2=\frac{1}{L}\left(\frac{\delta s}{s^2}\right)+\frac{25}{4}\epsilon_{\mathrm{rms}}^2 \tag{9}$$

Here, $s=2\sin\theta/\lambda$ and $\delta s=\beta_{\mathrm{p}}\cos\theta/\lambda$ with θ the Bragg angle of the peak maximum, λ the wavelength and β_{p} the physical (after separation of machine contributions) integral breadth of the peak, L is the coherence length and ϵ_{rms} the root mean square strain perpendicular to the reflecting planes. Thus, a plot of $(\delta s/s)^2$ against $\delta s/s^2$ is a straight line with its intercept proportional to the square of the r.m.s. strain and its gradient proportional to the reciprocal of the coherence length.

Samples of as-cast β-phase were examined in a θ–2θ vertical diffractometer using Cu Kα radiation. In order to apply the above analysis, the peaks of the β-phase were scanned with a step size of 0.02° 2θ, allowing 20 s per step. A divergence slit of width ½° and a receiving slit of 0.2 mm were used, together with a graphite monochromator. The observed peak widths β_{o} were extracted using a fitting procedure [24] which includes Cauchy and Gaussian contributions in the peak shape.

An estimate of the machine contribution to the peak width β_{m} was made by running well annealed quartz crystals under identical conditions. The machine contribution was then separated from the observed peak width β_{o} to obtain the physical width β_{p} of the peaks using the parabolic correction [23]:

$$\beta_{\mathrm{p}}=\beta_{\mathrm{o}}\left[1-\left(\frac{\beta_{\mathrm{m}}}{\beta_{\mathrm{o}}}\right)^2\right] \tag{10}$$

A plot of $(\delta s/s)^2$ *vs.* $\delta s/s^2$ is shown in Fig. 7. All the points do not seem to fall on a straight line, and this may indicate different coherence lengths and strains in different crystallographic directions.

Even in the case of such anisotropy, two or more orders of reflections from the same set of planes can be used to separate the size and strain contributions. For the present data this is possible only for the 110 and 220 reflections, and the line joining these two points is indicated in Fig. 7. The negative slope would indicate an impossible negative coherence length. It seems that within experimental error the slope may be taken as zero, corresponding to a very large coherence length. This fact is consistent with the very large grains seen in optical micrographs and absence of any sub-grains in transmission electron micrographs [7]. In the case of very large coherence length, the size contribution to the width of a peak is negligible. The r.m.s. inhomogeneous strain which will give the observed peak-breadth is 5.5×10^{-3}. This strain value is comparable with that found in cold-worked metals and alloys. It can thus be concluded that the inhomogeneous strain content of the as-cast CrTi samples is rather high. Using an isotropic modulus of 100 GPa gives an estimate of strain energy as 1.5×10^6 J m^{-3}. With a molar volume of 10^{-5} m^3 mol^{-1} this is equivalent to 15 J mol^{-1}. This would correspond to a very high defect density in the as-cast β-phase. Blatter and von Allmen suggest that such defects can destabilize the crystalline β-phase leading to vitrification. However, the energy involved is still small and would barely affect the equilibrium shown in Figs. 3 or 6.

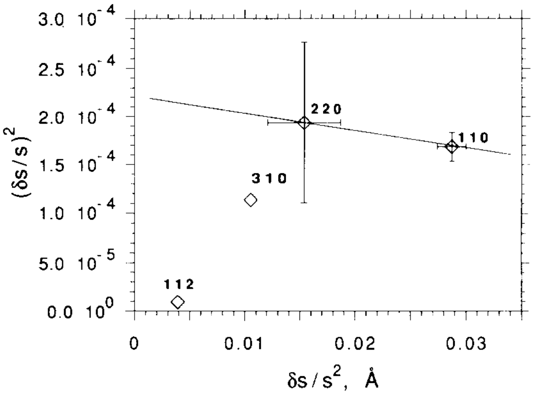

Fig. 7. A plot of $(\delta s/s)^2$ *vs.* $\delta s/s^2$ to separate size and strain contributions to the width of the X-ray peaks of as-cast β-$\mathrm{Cr_{40}Ti_{60}}$ based on an assumption of Cauchy size broadening and Gaussian strain broadening. Here $s=2\sin\theta/\lambda$ and $\delta s=\beta\cos\theta/\lambda$ with θ the Bragg angle, λ the wavelength and β the integral peak-width. The negative slope indicated is not physically possible; taking the slope within experimental error to be zero, the peak broadening is entirely due to strain.

The large grain size of the samples leads to problems in the present X-ray diffraction analysis. Each peak in a diffractometer trace comes from a different subset of grains (except when they are different orders of the same reflection), where each subset includes a rather small numbers of grains (expected from grain size and penetration depth to be 10–50). Thus the size and strain broadening of a peak arise from imperfect averaging and may not yield a good fit by the above procedures. Methods to obtain a smaller grain size (*e.g.* grinding) would risk affecting the strain to be measured.

4. Coherent spinodal temperatures of β-Cr–Ti

If the β-phase of Cr–Ti unstable, an alternative to amorphization may be spinodal decomposition. In this section we consider this possibility.

According to Cahn [25], in the regime of coherent spinodal of a cubic crystal

$$\frac{\partial^2 G}{\partial x^2}+2\eta^2 Y_{uvw}V_{\mathrm{m}}\leqslant 0 \tag{11}$$

where G is the chemical free energy, x the atom fraction (of chromium in the present case), $\eta = \partial \ln a/\partial x$ and V_m is the molar volume of the alloy. Y_{uvw} is an effective modulus defined in terms of the three elastic moduli C_{11}, C_{44} and C_{12} of a cubic crystal as follows:

$$Y_{uvw} = \frac{1}{2}(C_{11} + 2C_{12}) \times \left[3 - \frac{C_{11} + 2C_{12}}{C_{11} + 2(2C_{44} - C_{11} + C_{12})(l^2m^2 + m^2n^2 + n^2l^2)}\right] \tag{12}$$

Here, l, m and n are the direction cosines of the direction (uvw). The equality in eqn. (11) defines the coherent spinodal temperature for instability against a composition wave in the direction (uvw).

4.1. Parameters for Cr–Ti

A discussion follows of the available values of the parameters G, η, Y_{uvw} for the β-phase, all of which are functions of composition x and temperature T.

4.1.1. Chemical free energy G^β

The molar chemical free energy G^β of the β-phase used for this calculation is the value obtained by Murray [18], from phase diagram fitting. Differentiating Murray's expression and substituting the fitted parameter values we obtain:

$$\frac{\partial^2 G^\beta}{\partial x^2} = T\left[\frac{R}{x(1-x)} + 13.34\right] - 3600x - 47534 \tag{13}$$

where R is the gas constant, T the absolute temperature and x the atom fraction of chromium.

4.1.2. Fractional linear expansion due to composition change η

For the β-phase, η is defined as

$$\eta = \frac{1}{a_\beta}\left(\frac{\partial a_\beta}{\partial x_{Cr}}\right) \tag{14}$$

where a_β is the lattice parameter. To obtain η as a function of composition and temperature we need to know the composition and temperature dependences of a_β. Cuff *et al.* [26] have shown that a_β follows Vegard's law at room temperature, *i.e.* varies linearly with composition. Using the measured linear thermal expansion coefficients α of chromium and β-Ti, η can be expressed as a function of x and T. Taking $a_{Cr} = 0.28847$ nm at $T = 298$ K [27], $a_{\beta\text{-Ti}} = 0.33162$ nm at $T = 1323$ K [28], $\alpha_{Cr} = 9.4 \times 10^{-6}$ K^{-1} at $T = 973$ K [29], $\alpha_{\beta\text{-Ti}} = 13.6 \times 10^{-6}$ K^{-1} at $T > 1173$ K [28] we obtain the lattice parameter in nanometres:

$$a_\beta = 0.33162[1 + 13.6 \times 10^{-6}(T - 1323)](1 - x) + 0.28847[1 + 9.4 \times 10^{-6}(T - 298)]x \tag{15}$$

from which $\eta(x, T)$ is easily derived. It should be noted that since η occurs as a square in eqn. (11), the calculated values of coherent spinodal temperatures are rather sensitive to its value.

4.1.3. Molar volume, V_m

The molar volume V_m of the b.c.c. β-phase can be found simply from its lattice parameter a_β and the Avogadro number N_A.

4.1.4. Effective modulus Y_{uvw}

Y_{uvw} (eqn. (12)) depends upon the three elastic moduli C_{11}, C_{12} and C_{44} of the cubic crystal. Y_{uvw} is needed as a function of temperature and composition but the data available in the literature for C_{11}, C_{12} and C_{44} for β-Cr–Ti are very limited. The Fisher and Dever [14, 15] data outlined above are for C_{11}, C_{44} and $C'[C' = (C_{11} - C_{12})/2]$ for four alloys with chromium fraction $x = 0.0698$, 0.0936, 0.1381, 0.2837 at 298 K and 1273 K. Some of these data points are extrapolated rather than measured values, and overall their data are insufficient to establish the elastic moduli as a function of composition and temperature over the entire range required for the present calculation. Most importantly, the composition of interest for spontaneous vitrification, 30 and 40 at.% chromium ($x = 0.3$ and 0.4), fall outside the range of the data. Fisher and Dever [14] state that the temperature variation of the elastic moduli can be taken to be linear. As a first step, the coherent spinodal temperatures only for the four compositions for which the data are known are calculated in the present work, assuming a linear variation of moduli with temperature at these compositions.

4.2. Existing calculation

In their study of "black plate" formation in Cr–Ti alloys, Menon and Aaronson [10] presented a calculation of the coherent spinodal temperatures. Consider an alloy with $x = 0.2837$ atom fraction chromium at room temperature $T = 298$ K. Whether this point (x, T) lies in the (100) coherent spinodal regime or not will depend on eqn. (11). Equation (13) gives the first term of this function as $(\partial^2 G/\partial x^2) = -3.2 \times 10^4$. The negative sign assures us that the point lies within the chemical spinodal. The value of $2\eta^2 Y_{100} V_m$ is calculated to be 4.15×10^4 J mol^{-1}. Thus the value of the left-hand side of eqn. (11) is 9.5×10^3, a large positive value clearly showing that the point lies much above the coherent spinodal and not within it. Calculations shows that the coherent spinodal temperature for this composition is just 132 K. These facts stand in contrast to what can be concluded from the calculation of Menon and Aaronson [10] which shows the coherent spinodal temperature for this composition as 791 K (measurement from their figure).

Although Menon and Aaronson [10] used the Fisher and Dever [14] data for the elastic moduli, they indicate neither the manner in which these data were extrapolated to calculate the coherent spinodal temperatures in the range $x=0.25$ to $x=0.75$, nor the assumed temperature variation of the moduli.

4.3. New calculation

As all the terms in eqn. (11) are dependent on temperature, it is necessary to use a numerical routine to solve for the temperature at which the equality is satisfied. The equation was solved using a bisection method. To be able to calculate the coherent spinodal temperatures for the entire range of composition, it is essential to assume a functional dependence of the moduli on composition. In addition to the data of Fisher and Dever [14, 15], modulus data for chromium are available in Bolef and de Klerk [13]. Although a parabolic fit was used in the previous section (see Fig. 2(a),(b)) to extend the measurement for four titanium-rich alloys to estimate the elastic constants for pure titanium, it is not reasonable to expect this to be a good fit over the entire composition range. Owing to the small number of data points and lack of any theoretical ground to assume otherwise, a linear fit was assumed to represent the elastic constants over the entire range of composition. The temperature dependence was assumed, as previously, to be linear. Based on these assumptions, the calculated (100) coherent spinodal temperature curve is shown in Fig. 8. Note that not only are the coherent spinodal temperatures suppressed below room temperature, but also the critical composition (of about 11 at.% chromium) is shifted much towards the titanium. Although, owing to the extrapolations and uncertainties in the data, these temperatures may not be very precise, the calculation shows that the coherent spinodal lies much below room temperature.

In a recent transmission electron microscopy study of the Cr–Ti system, Ikematsu *et al.* [11] studied 30, 40 and 50 at.% chromium alloys. They found that alloys quenched to room temperature after annealing in the β-phase field show spinodal-like contrast in their microstructure and satellite spots around the 200 reflection. This can be taken as an indication of spinodal decomposition. According to this study the ⟨100⟩ modulated structure, resulting from spinodal decomposition is seen at temperatures as high as 1100 K. This fact is not in agreement with the calculation in the present work. Furthermore, the experimentally observed temperatures are not only above the coherent spinodal temperature but even higher than the chemical spinodal temperature.

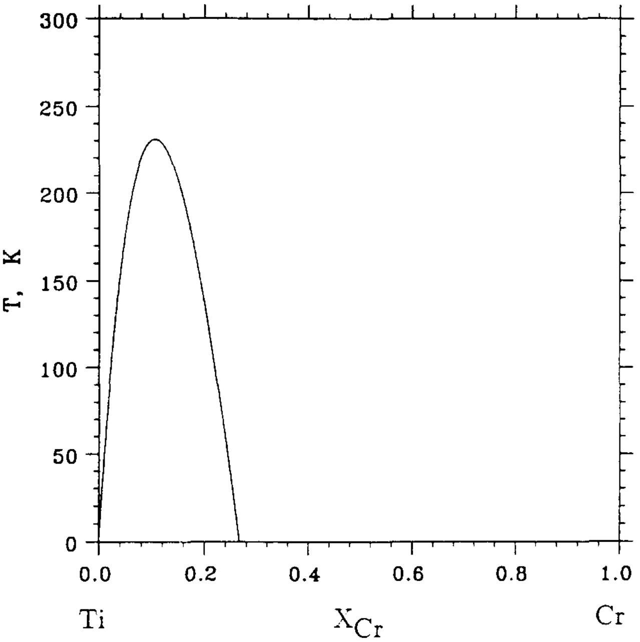

Fig. 8. The coherent spinodal curve of β-Cr–Ti as calculated in the present work. The spinodal curve is at much lower temperatures than in the calculation by Menon and Aaronson [10].

A problem with the calculations is the use of the free energy function of Murray [18] which was obtained by fitting phase diagram and is expected to be correct in the temperature range 1473 to 1773 K. In the present calculation this free energy function is used down to 0 K, although as already shown in Fig. 4, extrapolation from high temperature data seems to be inappropriate even at 400 K. However, it is expected from Fig. 4, that the true free energy functions may actually predict chemical and coherent spinodal lines that are even lower than those predicted by Murray's function. Thus, the values calculated on the basis of the free energy function of Murray can be considered to be an upper bound on the chemical and coherent spinodal temperatures.

We consider the CVM estimate of the free energy of the β-phase at 400 K by Sluiter and Turchi [17]. As this shows a negative curvature at a composition of 0.6 atom fraction chromium (Fig. 4), the point $x=0.6$, $T=400$ K lies within the chemical spinodal. The value of $(\partial^2G/\partial x^2)_{x=0.6}$ estimated from the diagram is -16.8 kJ mol^{-1}. The estimated value of $2\eta^2Y_{100}V_m$ at this temperature and composition is 76.5 kJ mol^{-1}. Thus eqn. (11) is not satisfied, indicating that the coherent spinodal temperature is much below 400 K. Therefore the results of Ikematsu *et al.* [11] still cannot be explained on the basis of the free energy as estimated by the CVM.

There are, however, problems in experimental identification of spinodal decomposition as well. For example, Khachaturyan [30] has shown that modulated structures giving rise to satellite reflections can also form owing to strain-induced coarsening during a nucleation and growth process.

5. Conclusions

We find that the Miedema method does not predict spontaneous vitrification of β-Cr–Ti. It is shown that the free energy of the β-phase predicted by the Miedema method is incompatible with the high temperature phase diagram data, but at 400 K its predictions are in agreement with that of the CVM calculation. However, the free energy function derived from the phase diagram fitting at high temperature cannot be extrapolated to low temperature without introducing inaccuracies and this can be attributed to an excess specific heat appearing in the β-phase above 723 K. At 873 K, the temperature of spontaneous vitrification, neither the Miedema method nor extrapolation from phase diagram fitting is expected to give very accurate values. An attempt was made to estimate the free energies of the β and amorphous phases by interpolating between the two methods. This estimate also does not suggest any spontaneous vitrification.

Measurement using X-rays shows that there is a large inhomogeneous strain of 5.5×10^{-3} in our samples of the β-phase. Its contribution to the overall free energy, however, is rather insignificant.

Our calculation shows that, based on the free energy derived from the high temperature phase diagram fitting, the coherent spinodal of β-Cr-Ti is suppressed below room temperature. Although extrapolation to low temperature of the free energy function derived at high temperature is not reliable, it is expected to give upper bounds on the chemical and coherent spinodal temperatures. An estimation based on the CVM calculation of other workers shows that the coherent spinodal temperature is at least below 400 K. The apparent disagreement with observations of decomposition has not been resolved.

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