

What Determines the Martensitic Transition Temperature in Alloys?

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The intriguing puzzle is addressed concerning the dramatic dependence generally observed of the Martensitic transition temperature on the composition of alloys. Based on one of the simplest possible systems, the Ti_cZr_{1-c} alloy system, a theory is developed including the effect of a disorder scattering of the phonons due to a mass difference between the elements. The depression of the Martensitic transition temperature, ΔM_s , is shown to depend parabolically on concentration c , as $c(1-c)$, for small depressions. For larger ΔM_s an enhancement at intermediate c is predicted. This gives rise to a more triangular dependence as a function of c . The theory contains only one phenomenological parameter. Comments are given relevant for other more complicated alloy systems.

1. INTRODUCTION

In practically interesting Martensitic materials the transition temperature is often close to room temperature. It is surprisingly easy to obtain a large range of transition temperatures, M_s in the complicated alloys of three or more components. The question is why the transition temperature is so dramatically dependent on the alloy composition? The effect is much larger than conceivable from estimated consequences of changes in the electronic effects, in the inter atomic forces, in atomic radii or as a result of atomic ordering. In the complicated alloys, as for example Ni_xTi_{1-x} [1] and Cu_3AlBe_ϵ [2] a dramatic change in M_s is observed for $x \approx 0.5$ and $\epsilon \approx 0$. In these interesting systems probably all the mentioned effects play a role, but still it is hard to understand the strong influence on M_s . A model including electronic effects was proposed [3] for the ternary $NiTi$ -based alloys providing an interpolation formula between two elements of the type $NiTi$ and $MxTi$, where Mx is an element which forms the B2 structure with Ti . It was possible to account for a small downward deviation from a linear interpolation of M_s between the two pure systems, using two essentially free parameters (and including temperature influence on the electrons). However, in that model one totally neglects the thermal nature of the Martensitic transformation; and in most cases it is a high temperature transformation compared to the natural energy scale, the Debye temperature.

In order to get a deeper understanding let us turn to the simplest possible model systems, the pure group-IV elements, which have been intensively studied both experimentally and theoretically. For Zr it was demonstrated that an accurate first principles band structure calculation [4] gives the *hcp* structure as the stable structure at $T = 0$, i.e. from purely electronic considerations. It was

also demonstrated that the inclusion of anharmonic effects was necessary, and sufficient to stabilize the *bcc* structure at high temperatures. No similar calculations have been made for pure *Ti*, but detailed neutron scattering measurements have been made for both *Ti* [5] and *Zr* [6]. The phonon spectra for the *bcc* phase at the same temperature are identical apart from a scale factor which is square root of the ratio of the masses (m^{Zr}/m^{Ti})^{1/2}. Since the phonon frequency is proportional to $(f_\nu/m)^{1/2}$ it shows that the force constants, f_ν , i.e. the inter atomic forces for the two metals are identical. However, the masses are different by a factor of ≈ 2 , since $m^{Ti} = 47.90$ and $m^{Zr} = 91.22$. The metals are very close in chemical respect and consequently they form ideal mixtures for all concentrations and all temperatures. This means that if there is a tendency to form stoichiometric, ordered alloys the ordering energy is small. Thus the ordering temperature is so low that the diffusion kinetics is too slow for ordered structures to form. The alloy system is also well documented [1] and shows that the melting temperatures are almost independent of concentration: $T_{melting}^{Ti} = 1860^\circ C$ and $T_{melting}^{Zr} = 1720^\circ C$, interpolating almost linearly in the alloys with a small depression of only about $100^\circ C$, or by only 5%. The Martensitic transition temperatures are also almost identical: $M_s^{Ti} = 882^\circ C$ and $M_s^{Zr} = 865^\circ C$, differing by only 1.5%. One could then, based on the above mentioned electronic effects, expect that M_s in the alloy would follow a linear interpolation and fall within $882 - 865^\circ C$. On the contrary M_s decreases by about a factor of two at the 50-50% concentration to $M_s = 500^\circ C$. The intriguing data for M_s in the *Ti - Zr* alloy system [1] are shown in Fig.1.

In the next section we will seek an explanation for the paradox of the remarkable dependence of M_s on alloying. The suggested mechanism is most probably also of relevance for the more complicated situations in ternary alloys or binary alloys of very different metals.

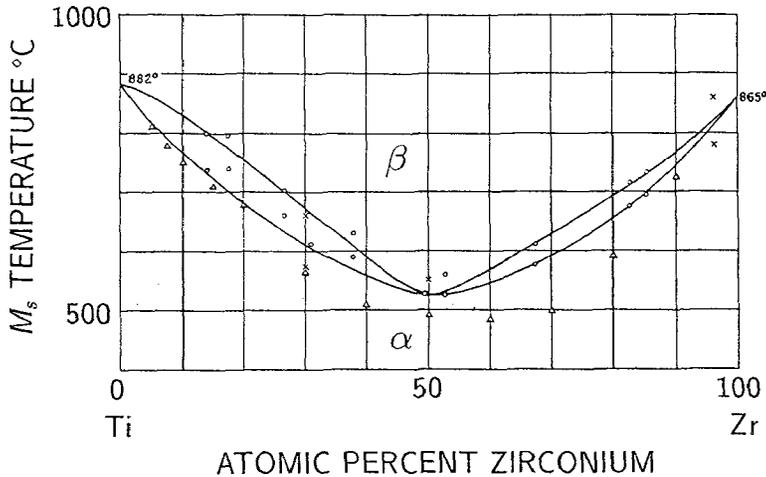


Fig.1. Martensitic transition temperature for the *Ti - Zr* alloy system [1].

2. DISORDER MODEL FOR DEPRESSION OF M_s IN ALLOYS

The *Ti - Zr* alloy system represents a perfect example of a model of an alloy between two identical elements with the same M_s^{pure} , only differing in the atomic masses by a factor of two. Such models have been considered by perturbation theory for small concentrations c [7] to first order in c . No rigorous results exist for large c , however Ziman [8] rationalizes the physically appealing result, that the phonon damping must be proportional to $c(1 - c)$, which is symmetric in the alloy elements. For both *Ti* and *Zr* there is already a considerable anharmonic frequency shift Δ_q and damping Γ_q at

$T = M_s$ [4]. We remark that $M_s = 1138^{Zr} - 1155^{Ti} K$ is large compared to the Debye temperatures for both the *bcc* and the *hcp* phases, which for *Ti* are [5] $\Theta_D^{hcp} = 360K$ and $\Theta_D^{bcc} = 290K$. Thus in our case we have $M_s^{pure} = 3.4 \Theta_D$. The anharmonic scattering of phonons is due to the lattice distortions created by other phonons being present, while a studied phonon is propagating through the lattice. The large wave length phonons tend to see only the average structure and are therefore not much influenced by small scale distortions of the neighbor distances. On the other hand the small wave length (or zone boundary q -vector) phonons are strongly effected, since the distortions are on the same length scale. Effectively, the distortions change the inter atomic forces seen by the small wave length phonons. The mass-disorder scattering behaves in a similar way with respect to the wave length. The only essential difference is that the mass-disorder is quenched (fixed), whereas the anharmonic disorder is temperature induced.

We shall now analyze the effect of additional mass-disorder scattering of the phonons. Let us assume it gives rise to an additional shift $\Delta_q \rightarrow \Delta_q + \delta_q$ and damping $\Gamma_q \rightarrow \Gamma_q + \gamma_q$ [9]. The imaginary part of the phonon Greens function [10] can then be written, expanding the denominator to first order in δ_q and γ_q

$$ImG_q^{alloy}(\omega) = \frac{1}{\pi} \frac{2\omega_q(\Gamma_q + \gamma_q)}{(\omega_q^2 - \omega^2)^2 + 4\omega^2\Gamma_q^2 + 4\omega_q[(\omega_q^2 - \omega^2)\delta_q + 2\omega_q\Gamma_q\gamma_q]} \approx \left(1 - \frac{\gamma_q}{\Gamma_q}\right) ImG_q(\omega), \quad (1)$$

where $\omega_q = \omega_q^0 + \Delta_q$ includes the anharmonic shift, and the last expression is obtained by expanding near the resonance $\omega = \omega_q$. The anharmonic damping is of the form [10]

$$\Gamma_q = \frac{18\pi}{\hbar^2} \sum_{k,k'} |V_3(q, k, k')|^2 \{(n_k + n_{k'} + 1)\delta(energy) + (n_k - n_{k'})\delta(energy)\}, \quad (2)$$

where V_3 is the third derivative of the anharmonic potential and $n_q = [e^{\beta\hbar\omega_q} - 1]^{-1}$ is the phonon population factor, $\beta = 1/(k_B T)$; the δ -functions conserve the energy in the scattering processes (for simplicity of notation we set $\hbar = 1$ in the following). For large temperature $T \gg \Theta_D$ the phonon population is large $n_q \gg 1$ and $n_q \approx 1/(\beta\omega_q)$. For *Zr* the Debye temperature is $\Theta_D^{Zr} = 210K$ and at $T = M_s$ the population of the highest frequency phonons is $n \approx 5$. The population is even higher, $n \sim 20$, in the low frequency 'valley' along the [112] wave vector direction, which always seem to exist in the elastically highly anisotropic Martensitic materials. On the other hand the mass-disorder induced damping is independent of temperature and proportional to $c(1 - c)$ [8] and the mass difference $\Delta m = m^{Zr} - m^{Ti}$ squared. Accordingly, displaying only the most important features

$$\frac{\gamma_q}{\Gamma_q} = \beta c(1 - c) |f_q|^2. \quad (3)$$

This correction is largest in the phase where the anharmonic damping is small, i.e. in the *hcp* phase. We have introduced a q -dependent ratio $|f_q|^2$ of the mass-disorder and the anharmonic scattering, which is difficult to calculate. Since the scattering mechanisms treat the long and short wave length phonons similarly, we expect that $|f_q|^2$ is not very strongly q -dependent and is proportional to Δm^2 . The free energy F can be calculated from the internal energy $\langle \mathcal{H} \rangle$ by integrating the exact relation

$$\frac{d}{d\beta}(\beta F) = \langle \mathcal{H} \rangle_\beta. \quad (4)$$

The average of the Hamiltonian $\langle \mathcal{H} \rangle = \sum_q \omega_q (n_q + \frac{1}{2})$ is related to $ImG_q(\omega)$ [11]. The mass-disorder correction to the internal energy is from eq.(1) and eq.(3) then found to be of the form

$$\Delta \langle \mathcal{H} \rangle = -c(1 - c) \sum_q |f_q|^2 \int_{-\infty}^{\infty} \frac{1}{e^{\beta\omega} - 1} \beta \omega^2 ImG_q(\omega) / \omega d\omega \approx c(1 - c) \frac{1}{2} \beta \sum_q |f_q|^2 \langle \omega_q^2 \rangle, \quad (5)$$

where we have made a high temperature expansion and introduced the second moment of the phonon spectrum $\langle \omega_q^2 \rangle$ (assuming that odd moments are zero, no other terms exist). In the presence of anharmonicity $\langle \omega_q^2 \rangle$ might be significantly larger than $(k_B \Theta_D)^2$. The coefficient to $c(1 - c)$ in eq.(5) is

therefore quite large at $T = M_s^{alloy}$ corresponding to a few Θ_D . We can now from eq.(4) calculate the free energy difference between the *hcp* and the *bcc* phases in the presence of the mass-disorder scattering. It has the following simple form, reflecting the ratio between the disorder and the anharmonic scattering power

$$F_{hcp} - F_{bcc} = c(1-c) \frac{a}{T} \Big|_{disorder} = (M_s^{pure} - T) \Delta S_{pure}. \quad (6)$$

In the last equation we have equated the disorder induced free energy difference to the temperature dependent free energy difference between the pure phases. This temperature dependence is assumed to be given by the entropy term $T \Delta S_{pure} = T(S_{bcc} - S_{hcp})$. The Martensitic temperature for the alloy M_s^{alloy} is obtained as the solution for T to eq.(6). In the case of a small depression we can insert $T = M_s^{pure}$ on the left hand side and we simply find

$$\Delta M_s = M_s^{pure} - M_s^{alloy} \propto c(1-c) M_s^{pure}. \quad (7)$$

This gives a parabolic depression, as may be expected intuitively. However, when the depression is large, i.e. T gets smaller, there is an enhancement effect of the left hand side, as is clear from eq.(6). This enhances the large depression regions even further. Thus one gets a more 'triangular' dependence on the concentration. This is in fact observed as seen in Fig.1. This remarkable behavior is here explained by eq.(6) in terms of just one phenomenological parameter $p = a/\Delta S_{pure}$.

3. DISCUSSION

The characteristic features of the behavior of M_s , Fig.1., can thus be understood as a mass-disorder effect. However, we can go a step further and understand that asymmetries will arise in the concentration dependence if the anharmonic damping is different in the two pure materials [9]. The depression is smallest when there is already a large anharmonic scattering. According to Petry *et al* [5, 6] the damping is larger in *Ti* than in *Zr* at $T \sim M_s$. We therefore expect a slight enhancement of the depression for the *Zr* rich alloys. Fig.1. shows the expected shift of the minimum toward *Zr*.

In the above arguments we have assumed the same M_s^{pure} for both elements *A, B*. The result can easily be generalized to the case of different M_s values. This is for example the case in systems like the *NiT_i* and *MxTi* ternary alloys, mentioned in the introduction. Clearly electronic effects, giving rise to different atomic force constants, must now be included. In the simplest approximation, for iso-structural alloys, it would just give rise to a linear interpolation between the different pure temperatures M_s^A and M_s^B . The disorder scattering effect (in which we can now include both mass-disorder and force-constant-disorder) will generally produce a parabolic-like depression, which may be asymmetric in the concentrations. This is in fact the general feature observed in the mentioned alloys. The present theory is able to qualitatively account for all the observations with *Mx=Pd, Pt, Au*, giving a large depression, probably mainly due to the large mass difference $\Delta m = m^{Mx} - m^{Ti}$. Also the observed asymmetry is as predicted, since presumably the anharmonicity is larger for the high M_s compounds, thus shifting the maximum of the depression toward the low M_s compound. The electronic model [3] is able only to account satisfactorily for the *NiT_i - PdTi* ternary alloy system. It is clear that both the disorder and the electronic effects may have to be taken into account.

For alloys of chemically very different elements, which form different stoichiometric, ordered structures, for example *Ni_xTi_{1-x}* and *Cu₃AlBe_e*, the situation is much more complicated. Here, the electronic properties, in particular the electronic densities of states, change rapidly for different ordered phases. However, in addition, the above discussed disorder effect, which is even enhanced due to atomic disorder relative to the preferred order, must be taken into account. In *Cu₃AlBe_e* the disorder element *Be* has a very small mass compared to the other elements: $m^{Be} = 9$, $m^{Al} = 27$ and $m^{Cu} = 63.5$. Therefore Δm is large and already the mass-disorder effect is large, in addition

Be is chemically very different (divalent) from *Al* and *Cu*. Consequently, our theory may contribute substantially to the explanation for *Be* being such an effective agent with which to depress M_s in Cu_3Al [9].

In this paper we have demonstrated that the disorder scattering of phonons play a large role for determining the Martensitic transition temperature M_s , resulting in a general depression of M_s for intermediate concentrations. The disorder essentially weakens the potentially stable *hcp* phase, whereas it probably stiffens the *bcc* lattice since $\Delta_q + \delta_q$ increases. Notice the shift δ_q does not enter into our argument. Experimental measurements of a *TiZr* alloy would be quite interesting. In fact there exists an early neutron scattering measurement [12] of $Ti_{67}Zr_{33}$ which seem to indicate that the energy $\omega_N \approx 7.8meV$ of the potentially soft N -point T_1 phonon [4, 5] (or soft 'valley') is not softer in the alloy with $M_s^{alloy} \sim 773K$ than that in the pure systems, $\omega_N^{Ti} = 8.5meV$ and $\omega_N^{Zr} = 5meV$ at $T = M_s = 1155K$. In particular it would be interesting to observe damping effects and quasi-elastic scattering in the *hcp* and the *bcc* phases. Physically we expect that in the depressed regions, for temperatures below M_s^{pure} the *hcp* structure will be replaced by short range order of *hcp* phase, located around concentration fluctuations toward a concentration favoring the *hcp* phase. In a scattering experiment it would probably give rise only to *quasi*-elastic scattering, since it is probable that the short range ordered regions are not completely stable with time. These regions, of course, would correspond to the well known tweed phenomena [15] often observed in alloys, but not in pure materials. One may consider that such a short range ordered phase is equivalent to the spin-glass phase, much discussed in magnetism. Damping effects are observed[13] for the excitations (spin waves) in spin-glasses in the quasi long-ranged-ordered high temperature (ferromagnetic) phase, which probably corresponds to the high temperature *bcc* phase in the Martensitic case for the alloys. The interesting analogy between the Martensitic and the spin-glass problems was recently pointed out by Kartha *et al*[14], although in a slightly different form and context.

4. CONCLUSION

We have introduced a simple disorder-scattering theory and shown that it can account for the observed large depression of the Martensitic transition temperature in the *TiZr* alloy system. General comments have been given to the effect that the mechanism does contribute also in other, more complicated cases to a significant dependence of the Martensitic temperature on the alloy concentration. The effect will be largest when the additional alloy element has a very different mass or is chemically very different from the other elements.

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