"Cold Melting" of Invar Alloys

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Abstract

An anomalously strong volume magnetostriction in Invars may lead to a situation when at low temperatures the dislocation free energy becomes negative and a multiple generation of dislocations becomes possible. This generation induces a first order phase transition from the FCC crystalline to an amorphous state, and may be called "cold melting". The possibility of the cold melting in Invars is connected with the fact that the exchange energy contribution into the dislocation self energy in Invars is strongly enhanced, as compared to conventional ferromagnetics, due to anomalously strong volume magnetostriction. The possible candidate, where this effect can be observed, is a FePt disordered Invar alloy in which the volume magnetostriction is especially large.
I. INTRODUCTION

Among various approaches to the theory of crystal melting (see review [1]) the dislocation model (see [2–8] and references therein) occupies the leading position, describing the relevant physical phenomena in the most adequate way. According to the simplest version of the model [3], one should consider the change of the crystal free energy $\Delta F = W - T\Delta S$, caused by a single dislocation, calculated per its unit length. Here $W$ is the internal energy change, and $\Delta S$ is the corresponding entropy change. At elevated temperatures the free energy $\Delta F$ may become negative, so that a spontaneous multiple generation of dislocations becomes thermodynamically favorable. This generation destroys the long range order of the crystal and leads to its amorphization and melting. A reasonable assumption is that both the energy $W$ and the entropy $\Delta S$ are related only to the elastic strains induced by the dislocation and, hence, they hardly depend on temperature. It means that the melting temperature can be determined by the equation

$$T_{m}^{\text{hot}} = \beta W_{el}a,$$

with $a$ being the interatomic spacing. Here $\beta$ is a proportionality coefficient, which is $\beta = 1/(a\Delta S)$ in the simplest case [3]. Generally, the coefficient $\beta$ may have a more complicated shape, since it should additionally incorporates such effects, as interactions between the dislocations, entropy due to various dislocation configurations and so on (see discussion in [5] and in the most recent paper [8]). The notation $W_{el}$ in equation (1) emphasizes connection of the dislocation self energy to the elastic strains.

When considering ferromagnetic crystals, whose internal energy incorporates also the exchange interaction energy, one may think about an additional contribution due to the variation of this exchange interaction in the field of the elastic strains around the dislocations. In typical ferromagnetics, say, Fe or Ni, the exchange interaction contribution makes at best several tenths of one percent of the elastic energy and can be disregarded. However, a very strong volume magnetostriction typical of the Invar alloys, as demonstrated, e.g., in [9], may result in an enormous enhancement of the dislocation exchange self energy and become comparable with the elastic one. Our recent paper [10] discusses the influence of this enhancement on the interaction between dislocations and solute atoms in Invar alloys with the aim to explain some features of plastic deformation of Invars.

The exchange self energy of a dislocation is negative and its absolute value grows in the ferromagnetic phase with decreasing temperature. It will be demonstrated in this paper that at low enough temperatures ($T < T_{C}$, $T_{C}$ is the Curie temperature) the total dislocation energy, which is now the sum of the elastic and exchange contributions, decreases significantly with decreasing temperature, and in some Invar alloys may even change its sign. It means that the criterion (1) can be met not only at elevated temperatures but also at a low temperature. It may lead to a situation when spontaneous multiple generation of dislocations and crystal amorphization may become thermodynamically favorable below a certain critical temperature.

This phenomenon may be called "cold melting". We plan to discuss here the conditions of the cold melting and find the temperature below which it becomes possible. We have no intentions to address here in detail the problem of what is the state of the crystal below the transition temperature and what the order of the transition is. We may only mention
that we do not currently see reasons why the analysis of, say, Edwards and Warner [5] is not applicable in our case as well. They have demonstrated for the usual hot melting that the dislocation mechanism results in a first order phase transition. We expect that a similar first order transition may lead to an amorphized glassy-like state at low temperatures.

In order to find the temperature of the cold melting we need to calculate the dislocation self energy. First, the elastic energy of a unit length of an edge dislocation is determined by the equation [11]

$$W_{el} = \frac{\mu b^2}{4\pi(1-\nu)} \ln \frac{R}{r_0}. \quad (2)$$

Here $b$ is the magnitude of the dislocation Burgers vector, $\mu$ is the shear modulus, $\nu$ is the Poisson coefficient. When calculating the energy (2), the integral of the dislocation induced strain field is cut both at small distances $r_0$, of the order of the interatomic spacing, and at large distances $R$, of the order of the average distance between the dislocations.

The volume magnetostriction results in a variation of the exchange energy of a ferromagnetic in the strain field in the vicinity of a dislocation. In order to calculate the corresponding energy change we consider the density of the exchange energy of the ferromagnetic in the molecular field approximation (see, e.g., [12])

$$W_{ex} = -\frac{\omega M^2}{2} \quad (3)$$

where $M$ is the local magnetization, and

$$\omega = \frac{3k_B T_C}{np_{eff}^2 \mu_B^2} \quad (4)$$

is the constant of the molecular field. Here $n$ is the atomic density, $p_{eff}$ is the effective number of the Bohr magnetons $\mu_B$ per atom. In principle, one should also consider a term proportional to $(\nabla M)^2$ in the energy (3). Its contribution to the exchange energy is, however, two orders of magnitude smaller than the leading term in (3) and, hence, it has been neglected.

The hydrostatic pressure $p$ created by an edge dislocation causes a local change of the magnetization

$$M = \overline{M}(1 + \alpha p) \quad (5)$$

where $\overline{M}$ is the spontaneous magnetization of the ferromagnetic in the absence of the dislocation, $\alpha$ is a proportionality coefficient known empirically. It is usually rather small but may take anomalously high values in Invar alloys [13][14].

The hydrostatic pressure in the vicinity of an edge dislocation is [11]

$$p(\rho, \theta) = -\frac{\mu b}{3\pi} \frac{1 + \nu \sin \theta}{1 - \nu} \frac{\ln \rho}{\rho} \quad (6)$$

with $\rho$ and $\theta$ being the cylindrical coordinates. Substituting (4) and (5) into the energy (3) and integrating, using the same cuts as when calculating the elastic energy, one finds the exchange self energy of a dislocation per its unit length
\[ W_{ex} = -\frac{\omega M^2 \alpha^2 b^2 \mu^2}{18\pi} \left( \frac{1+\nu}{1-\nu} \right)^2 \ln \frac{R}{r_0}. \] (7)

Now adding the exchange energy (7) to the elastic one (2), the total dislocation self energy per its unit length takes the form

\[ W = W_{el} + W_{ex} = f(T)W_{el} \] (8)

where

\[ f(T) = 1 - \frac{\omega M^2(T)\alpha^2(T)E(T)(1+\nu(T))}{9} \left( \frac{1}{1-\nu(T)} \right). \] (9)

\[ E = 2\mu(1+\nu) \] is the Young modulus. It is emphasized in equation (9) that material parameters in Invars are temperature dependent.

A similar analysis can be carried out with respect to the interaction between the dislocations. It leads to the conclusion that equation (8) is, in fact, more general. A similar equation with the same factor (9) holds also for the total internal energy of the system of dislocations which includes both the internal self energies of the individual dislocation and the interactions between them.

The second term in equation (9) reflects the contribution of the dislocation exchange energy. It is usually very small, about \(10^{-3}\), in conventional ferromagnetics and, hence, may be neglected. In Invars, however, the situation changes dramatically. It is connected with the fact that the coefficient \(\alpha\), connected to the volume magnetostriction, may be several tens times larger than, say, in Fe or Ni \[14\]. In the ferromagnetic phase this second term grows with lowering temperature and may become comparable to one, so that the function \(f(T)\) may become very small or even change its sign.

Now we discuss how the exchange contribution to the dislocation energy influences the melting criterion (1) for the temperature at which the spontaneous generation of dislocations becomes possible. Direct analysis shows that now we should take the same condition (1) but substitute there the total self energy of the dislocation (8) instead of the elastic one. As for the entropy due the dislocation induced changes in the magnetic system, it can be still neglected. Then the melting temperature can be found as a solution of the equation

\[ T_m = \beta f(T_m)W_{el}. \] (10)

This equation may have more than one solutions. One solution can be found at high temperatures and corresponds to the conventional hot melting temperature \(T_{m(hot)}\). Usually the melting temperature exceeds the Curie temperature where the local magnetization disappears, \(M = 0\), hence, \(f(T) = 1\). Then equation (10) coincides with (1) and leads to the standard description of the hot melting. As for the cold melting temperature, it is connected with hot melting temperature by the condition

\[ T_{m(cold)} = T_{m(hot)} f(T_{m(cold)}) \] (11)

Equation (11) can be solved when using the low temperature values of the material parameters and Curie-Weiss equation
\[ M(T) = M_0 \sqrt{1 - \frac{T}{T_C}} \tag{12} \]

for the spontaneous magnetization. Here \( M_0 \) is the spontaneous magnetization at zero temperature. Then

\[ T_{m}^{(\text{cold})} = T_C \cdot \frac{\gamma - 1}{\gamma - \frac{T_{m}^{(\text{hot})}}{T_C}} \tag{13} \]

where

\[ \gamma = \frac{\omega M_0^2 \alpha^2 E (1 + \nu)}{9} \left( \frac{1 - \nu}{1 - \nu} \right) \tag{14} \]

In the known ferromagnetics \( T_C < T_{m}^{(\text{hot})} \), hence, the temperature of the cold melting may be positive only if \( \gamma > 1 \). Although rather rough approximations have been used (see discussion of Invar properties in [9]), when deriving equation (13), the condition \( \gamma > 1 \) is in fact more general and reflects just the fact that the energy necessary for creation of a dislocation becomes negative. This condition can be used as a good indicator when looking for Invar alloys in which cold melting may be observed.

It can be worth considering Fe-Pt Invar alloys, with a content close to Fe\(_{0.72}\)Pt\(_{0.28}\), which are characterized by high values of \( \alpha \). The volume magnetostriction becomes especially large in Fe\(_{0.72}\)Pt\(_{0.28}\) alloys with disordered distribution of Fe and Pt atoms over the lattice sites. It may reach the value \( \alpha = -2.4 \times 10^{-11} (\text{dyn/cm}^2)^{-1} \) at room temperatures [13]. As for a detailed information on the temperature dependence of \( \alpha \) in these alloys, unfortunately, it is not available. Nevertheless, we shall use this value in the estimates to be done below.

This alloy is characterized by the following parameters: \( T_C = 371\text{K} \), \( p_{\text{eff}} = 2.13 \) [15], and \( n = 7.6 \times 10^{22} \text{cm}^3 \). Then equation (4) leads to \( \omega = 5190 \). At \( M_0 = n p_{\text{eff}} \mu_B = 1.5\text{kG} \), \( \nu = 0.3 \), and \( E = 1.2 \times 10^{12} \text{ dyn/cm}^2 \) one gets \( \gamma = 1.66 \). Therefore, we see that the condition \( \gamma > 1 \) is holds very well.

Then knowing the temperature of the hot melting, \( T_{m}^{(\text{hot})} = 1812\text{K} \), for this alloy one could have found the temperature \( T_{m}^{(\text{cold})} = 168\text{K} \) for the cold melting which follows from equation (13). However, we prefer doing the same calculation by using the experimental data on the temperature dependence of the magnetization \( \tilde{M}(T)/M_0 \) [16], and elastic constants [16] temperature. The resulting temperature is even higher \( T_{m}^{(\text{cold})} = 298\text{K} \) and is rather close to the room temperature. This also provides a justification for using the room temperature value of the parameter \( \alpha \) in this estimate.

Therefore, the prediction of our model is that at temperatures below \( T_{m}^{(\text{cold})} = 298\text{K} \) a spontaneous multiple generation of dislocations Fe-Pt Invar alloys in may become possible. It is interesting to note that an intensive generation of dislocations is really observed in disordered Fe-Pt Invar alloys in the temperature range from 300 to 77K in several experiments (see, e.g., [17] and references therein). Our estimate for the temperature of the cold melting lies close to the upper limit of this range. However, the experimental observed phenomenon is rather complicated. This generation goes hand in hand with the martensite transitions from FCC to BCC phase, also observed in the same temperature range, and the two effects can be hardly separated one from another.
There are reasons to believe that they are really tightly connected. On one hand, dislocations may be generated as a result of accumulation and discharge of elastic strains in the vicinity of the boundaries between the martensite and austenite (host) phases in the process of the martensite growth \([18]\). A multiple generation of dislocations is observed only in disordered alloys with larger values of the parameter \(\alpha\) which favors its connection with the mechanism of the cold melting discussed above. As for ordered alloys with a smaller value of \(\alpha\) a dislocation generation is not observed in them.

On the other hand, we believe that the martensite transitions, which are much more intensive in disordered Fe-Pt alloys \([17]\), may be themselves induced by the dislocation generation in the process of the cold melting. It is known that appearance of strain-induced martensites is strongly facilitated by defects consisting of properly arranged dislocations which play the role of active centers in the formation of the martensite \([18]\). We assume that the dislocation generation leads to creation of such centers, and these centers induce martensite transitions.

A detailed experimental and theoretical study of the properties of Invar alloys at temperatures close and below the cold melting temperature present a special interest. One may expect highly unusual plastic properties of Invars in this region. As an example of what one may expect, we mention that at \(T < T_{m}^{(\text{cold})}\) dislocations of the same sign start attracting rather than repelling each other, meaning that the theory of the deformation hardening should be completely revisited.
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