Cold melting of invar alloys

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An anomalously strong volume magnetostriction in Invars may lead to a situation whereby 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 state 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 ferromagnets, due to anomalously strong volume magnetostriction. A possible candidate in which this effect can be observed is a FePt disordered Invar alloy in which the volume magnetostriction is especially large.

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Among various approaches to the theory of crystal melting (see review[1]) the dislocation model (see Refs. 2–8, and references therein) occupies a 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 unit length of the dislocation. Here W is the internal energy change, and ΔS is the corresponding entropy change. At elevated temperatures the free energy ΔF 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 ΔS 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

$$T_m^{(hot)} = \beta W_{el} a, \tag{1}$$

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

When considering ferromagnetic crystals, whose internal energy also incorporates 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 accounts, at most, for 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 Ref. 9, may result in an enormous enhancement of the dislocation exchange self-energy so that it becomes comparable with the elastic self-energy. 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 where 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 intention to address in detail the problem of what is the state of the crystal below the transition temperature and what is the order of the transition. We only mention that we do not currently see any reason why the analysis of, say, Edwards and Warner[5] should not be 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 glassylike 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]

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

Here b is the magnitude of the dislocation Burgers vector, μ is the shear modulus, and ν is the Poisson ratio. When calculating the energy (2), the integral of the dislocation induced strain field is truncated 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 ferromagnet 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 ferromagnet in the molecular-field approximation (see, e.g., Ref. 12)

$$\mathcal{W}_{ex} = -\frac{\omega M^2}{2}, \tag{3}$$

where M is the local magnetization, and

$$\omega = \frac{3k_B T_C}{n p_{eff}^2 \mu_B^2} \tag{4}$$

is the molecular-field constant. Here n is the atomic density, and p_{eff} is the effective number of Bohr magnetons μ_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 Eq. (3), hence it has been neglected.

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

$$M = \bar{M}(1+\alpha p), \tag{5}$$

where $\bar{M}$ is the spontaneous magnetization of the ferromagnet in the absence of the dislocation, and α is a proportionality coefficient known empirically that 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]

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

with ρ and θ being the cylindrical coordinates. Substituting Eqs. (5) and (6) into the energy (3) and integrating, using the same truncations as when calculating the elastic energy, one finds the exchange self-energy of a dislocation per unit length

$$W_{ex} = -\frac{\omega \bar{M}^2 \alpha^2 b^2 \mu^2}{18\pi}\left(\frac{1+\nu}{1-\nu}\right)^2 \ln\frac{R}{r_0}. \tag{7}$$

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

$$W = W_{el} + W_{ex} = f(T) W_{el}, \tag{8}$$

where

$$f(T) = 1 - \frac{\omega \bar{M}^2(T)\alpha^2(T)E(T)}{9}\frac{1+\nu(T)}{1-\nu(T)}. \tag{9}$$

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

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

The second term in Eq. (9) reflects the contribution of the dislocation exchange energy. It is usually very small, about 10^{-3}, in conventional ferromagnets and hence, may be neglected. In Invars, however, the situation changes dramatically. This is connected to the fact that the coefficient α of the volume magnetostriction may be several tens of times larger than, say, in Fe or Ni.[14] In the ferromagnetic phase this second term increases with decreasing temperature and may become comparable to one, so that $f(T)$ 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 we should now apply the same condition (1) but use in it the total self-energy (8) of the dislocation instead of the elastic energy. As for the entropy due the dislocation induced changes in the magnetic system, it can still be neglected. The melting temperature can be then found as a solution of

$$T_m = \beta f(T_m) W_{el} a. \tag{10}$$

This equation may have more than one solution. 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, $\bar{M}=0$; hence, $f(T)=1$. Equation (10) then coincides with Eq. (1) and leads to the standard description of the hot melting. As for the cold melting temperature, it is connected to the hot melting temperature by the condition

$$T_m^{(cold)} = T_m^{(hot)} f[T_m^{(cold)}]. \tag{11}$$

Equation (11) can be solved when using the low-temperature values of the material parameters and the Curie-Weiss equation

$$\bar{M}(T) = M_0\sqrt{1-\frac{T}{T_C}} \tag{12}$$

for the spontaneous magnetization. Here M_0 is the spontaneous magnetization at zero temperature. In this case we have

$$T_m^{(cold)} = T_C \frac{\gamma - 1}{\gamma - \frac{T_C}{T_m^{(hot)}}}, \tag{13}$$

where

$$\gamma = \frac{\omega M_0^2 \alpha^2 E}{9} \frac{1+\nu}{1-\nu}. \tag{14}$$

In the known ferromagnets $T_C < T_m^{(hot)}$; hence, the cold melting temperature may be positive only if $\gamma > 1$. Although rather rough approximations have been used (see the discussion of Invar properties in Ref. 9), when deriving Eq. (13), the condition $\gamma > 1$ is in fact more general and only reflects 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 is instructive to consider Fe-Pt Invar alloys with a content close to $Fe_{0.72}Pt_{0.28}$ that are characterized by high values of α. The volume magnetostriction becomes especially large in $Fe_{0.72}Pt_{0.28}$ alloys with a disordered distribution of Fe and Pt atoms over lattice sites. It may reach the value $\alpha = -2.4 \times 10^{-11} (\mathrm{dyn/cm^2})^{-1}$ at room temperature.[13] Unfortunately, detailed information on the temperature dependence of α in these alloys is not available. Nevertheless, we shall use this value in the estimates below.

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

Knowing the temperature of the hot melting $T_m^{(hot)} = 1812$ K for this alloy one could have found the temperature $T_m^{(cold)} = 168$ K for the cold melting from Eq. (13). However, we prefer doing the same calculation by using the experimental data on the temperature dependence of the magnetization $\overline{M}(T)/M_0$ (Ref. 15) and the elastic constants.[16] The resulting temperature is even higher $T_m^{(cold)} = 298$ K, and is rather close to room temperature. This also provides a justification for using the room-temperature value of the parameter α in this estimate.

Therefore, the prediction of our model is that at temperatures below $T_m^{(cold)} = 298$ K a spontaneous multiple generation of dislocations may become possible in Fe-Pt Invar alloys. It is interesting to note that an intense generation of dislocations has actually been observed in disordered Fe-Pt Invar alloys for temperatures between 300 and 77 K in several experiments (see, e.g., Ref. 17, and references therein). Our estimate for the temperature of the cold melting lies close to the upper limit of this range. However, the experimentally observed phenomenon is rather complicated. This generation goes hand in hand with the martensitic transitions from the fcc to bcc phases, also observed in the same temperature range, and the two effects can hardly be separated from each other.

There are reasons to believe that these effects are strongly connected. On one hand, dislocations may be generated as a result of accumulation and discharge of elastic strains in the vicinity of boundaries between the martensite and austenite (host) phases during the process of the martensite growth.[18] A multiple generation of dislocations is observed only in disordered alloys with larger values of the parameter α, which favors the connection with the mechanism of the cold melting discussed above. As for ordered alloys with a smaller value of α, a generation of dislocations is not observed.

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

A detailed experimental and theoretical study of the properties of Invar alloys at temperatures close to and below the cold melting temperature are of 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 $T < T_m^{(cold)}$ dislocations of the same sign start attracting rather than repelling each other, meaning that the theory of the deformation hardening should be completely revised.

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