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Thermal vacancies and the yield anomaly of FeAl

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We review here the George–Baker model for the yield strength anomaly of FeAl which is based on hardening by thermal vacancies at intermediate temperatures and dislocation creep at high temperatures. Results of up-quenching and down-quenching experiments, which corroborate the vacancy hardening mechanism, are discussed. Some implications of the model are compared with available experimental results. © 1998 Elsevier Science Limited. All rights reserved

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INTRODUCTION

It has become clear in recent years that FeAl exhibits a yield strength anomaly,[1–11] i.e. its strength instead of decreasing with temperature, shows an anomalous increase at intermediate temperatures ($0{\cdot}35 \approx 0{\cdot}45\,T_m$). Early work often failed to note this because specimens were not carefully annealed at low-enough temperatures to eliminate thermal vacancies. (FeAl alloys contain high concentrations of vacancies at elevated temperatures,[12–14] which remain after even relatively slow furnace cooling.[15] Rather long anneals—on the order of several days at low temperatures—are required to eliminate them.[12]) Quenched-in vacancies cause significant room-temperature hardening in FeAl,[14–16] which makes it difficult to discern the yield anomaly at elevated temperatures.[5,10] An example of this is shown in Fig. 1 where specimens annealed at 973 K for 2 h (top curve) exhibit the conventional decrease in strength with increasing temperature followed by a plateau region and a further decrease in strength with increasing temperature. In contrast, specimens given a long-term vacancy-minimizing anneal (5 days at 673 K, bottom curve), show a clear anomalous increase in strength at intermediate temperatures (between 450 and 850 K).

Because the strength anomaly in FeAl was discovered only recently, attempts to explain it are also quite recent. A first attempt was made by Yoshimi and Hanada[4] who proposed, based on transmission electron microscopy observations in Fe–39Al single crystals, that the ⟨111⟩ dislocations in FeAl decompose into ⟨001⟩ and ⟨110⟩ segments, which then act as pinning points against ⟨111⟩ slip. Subsequent work has clearly shown that this decomposition does occur, but apparently only at larger strains, and infrequently (if at all[17]) at the lower strains at which the yield strength is typically measured.[18,19] Glide decomposition is not important, therefore, in explaining the yield anomaly.

Morris[20] applied to FeAl alloys a mechanism originally proposed to explain dislocation locking in β brass.[21–25] The mechanism involves the diffusion of point defects between ⟨111⟩ partial dislocations gliding on the {110} planes such that one partial climbs up while the other climbs down, causing the APB between the partials to be rotated out of the glide plane. The climb-dissociated dislocation segments are thought to act as pinning points (with their density presumably increasing with temperature to account for the increase in yield strength with temperature). As discussed in an earlier paper,[26] some of the implications of this mechanism, e.g. the effects of strain rate and deviations from stoichiometry, are inconsistent with the available experimental data. For example, less climb locking should occur with increasing

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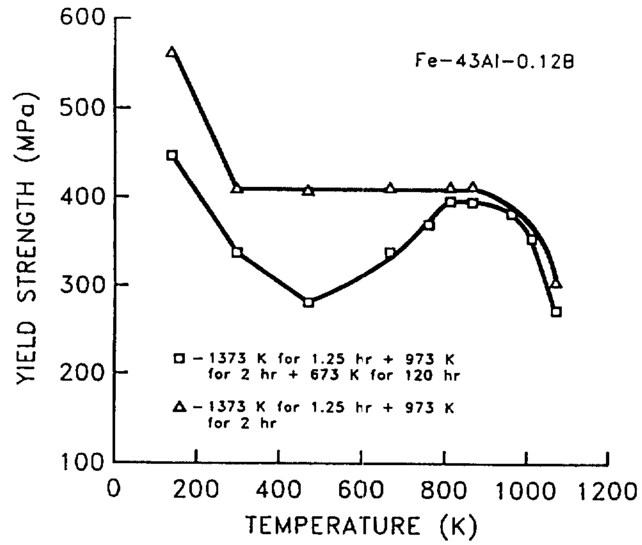

Fig. 1. Effect of long-term, vacancy-minimizing anneal on the temperature dependence of the yield strength of Fe–40Al–0·12B.[10]

strain rate (because less time is available for the stress-assisted diffusion of point defects), leading to a decrease in the yield stress with increasing strain rate. However, experiments show that the yield strength of FeAl alloys is virtually independent of strain rate in the anomalous temperature region, and increases with strain rate above the peak temperature.[6,26,27]

In addition to these mechanisms proposed specifically for FeAl, there are others that have been proposed for various B2 alloys which may, in principle, be applicable also to FeAl. For example, Umakoshi *et al.*[28] proposed that the ⟨111⟩ dislocations cross slip from the {110} to the {112} planes, where they become pinned in a manner analogous to that in Ni_3Al.[29] In FeAl, however, there appears to be no driving force for such cross slip: the APB energy is lower on the primary {110} plane than on the cross-slip {112} plane,[30] and the so-called torque term does not exist on the {110} slip plane.[31] In summary, none of these mechanisms seems satisfactory in explaining the yield anomaly in FeAl.

GEORGE–BAKER MODEL OF THE STRENGTH ANOMALY

Carleton *et al.*[10] were the first to suggest that the yield strength anomaly in FeAl may be vacancy-induced. They reasoned that if one starts with well-annealed FeAl in which the vacancy concentration is low (bottom curve in Fig. 1), new thermal vacancies are unavoidably generated when the specimens are heated to elevated temperatures and brought to thermal equilibrium prior to testing. The concentration of such thermally generated vacancies increases exponentially with temperature. If the vacancies in turn produce sufficient hardening, the yield strength would show an anomalous increase with temperature. With further increases in temperature, however, another possibility needs to be considered, namely that the thermal vacancies accelerate dislocation creep, thereby making plastic flow easier.[26] Together, these two competing mechanisms produce a peak in the yield stress versus temperature curve.[26] Of course, in material that has not been well-annealed (i.e. in which quenched-in vacancies from a previous heat treatment remain), the process of heating to intermediate temperatures will not produce additional vacancies, and a strength anomaly will not be observed (top curve in Fig. 1).

George *et al.*[32] corroborated the vacancy-hardening mechanism by performing experiments in a Gleeble thermo-mechanical simulator in which resistive heating of test specimens can provide extremely rapid heating rates ($\sim$300 K s^{-1}). Threaded, buttonhead tensile specimens (gage diameter, 3·2 mm; gage length, 37 mm) were given the standard vacancy-minimizing anneal (5 days at 673 K) and then rapidly heated (up-quenched, in 1·8 s) to the temperature of the yield strength peak (T_p), held there for varying lengths of time, and then tensile tested at a strain rate of $2{\cdot}4\times10^{-3}$ s^{-1}. The temperature, measured with a thermocouple spot-welded to the center of the gage section, was found to vary by not more than 10 K along the gage length.

The results of the up-quenching experiments are shown in Fig. 2. Since the generation of the

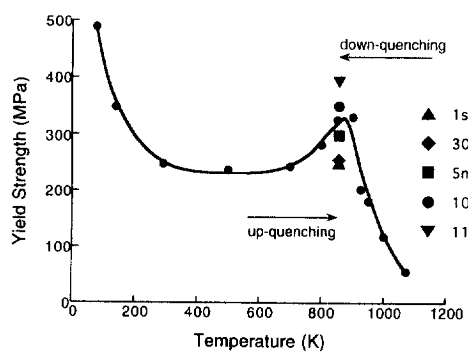

Fig. 2. Yield strengths after various up-quenching and down-quenching heat treatments compared to those measured in a standard tensile test (solid curve).[32] The heating and cooling rates during up-quenching and down-quenching (300 and 100 K s^{-1}, respectively) were considerably faster than those in the standard tensile test. The tensile strain rates, however, were the same for all tests.

equilibrium vacancy concentration at T_p is not instantaneous, the yield strength after very short hold times (1 s) was found to be comparable to that at room temperature. With increasing hold time at T_p the yield stress was found to increase progressively—presumably because the vacancy concentration increases with increasing hold time. At longer hold times ($\geq$ 0·5 h) the yield strength became independent of hold time—presumably because the vacancy concentration reached the equilibrium value in about half an hour and there was no change in vacancy concentration with further increases in hold time.

In another set of experiments, specimens were equilibrated at high temperatures (1073 or 1173 K), down-quenched to T_p (at 100 K s^{-1}), and immediately tensile tested. As shown in Fig. 2, the yield strengths of these specimens were found to be higher than those of specimens slowly heated to T_p from room temperature, an effect consistent with higher (than equilibrium) vacancy concentrations in the down-quenched specimens.

The quenching experiments were performed without any tensile loads being imposed on the specimens. Tensile loading occurred only after the quench was completed. The time required to reach 0·2% strain (at which the yield stresses were measured) was ~0·8 s in all cases (since a constant strain rate of $2{\cdot}4\times10^{-3}$ s^{-1} was used in all the tests). This time is short compared to the hold times at which a change in the yield strength was noted (30 s, 300 s, and 0·5 h). Clearly, the changes in yield strength at T_p are a result of changes during the stress-free holding period, rather than during the tensile test. The simplest explanation is that the vacancy concentration increases with increasing hold-time, resulting in an increase in the yield strength. Another important point to note in Fig. 2 is that the up-quenching and down-quenching experiments produce different yield strengths at T_p. If the yield anomaly was due to a 'dislocation' mechanism (cross-slip pinning, climb dissociation, or glide decomposition), the yield strengths at T_p would be independent of how the specimen arrived there. The vacancy mechanism, in contrast, depends sensitively on thermal history, consistent with the effects shown in Fig. 2.

MATHEMATICAL FORMULATION OF MODEL

Although the detailed mechanism by which vacancies pin (or drag) dislocations is unclear, that they do so is clear because vacancies can dramatically harden FeAl at room temperature.[14–16] The room-temperature hardness of FeAl varies approximately as the square root of the vacancy concentration C_v,[14] suggesting solid-solution-type hardening.[33] If one assumes that similar hardening also occurs at elevated temperatures, the increase in yield strength in the anomalous region (where strength increases with temperature) can be written:[26]

$$\Delta\sigma = \beta\mu(C_v)^{1/2} \tag{1}$$

where β defines the strength of the hardening and μ is the shear modulus. The temperature dependence of the vacancy concentration is given by:

$$C_v = C_o \exp(-E_f/kT) \tag{2}$$

where C_o is a pre-exponential factor and E_f is the formation enthalpy of a vacancy. Combining these two equations one obtains the following expression for the temperature-dependence of the yield stress increment responsible for the strength anomaly:

$$\Delta\sigma = \{C_o' \exp(-E_f/kT)\}^{1/2} \tag{3}$$

where the constants β and μ have been incorporated in the modified pre-exponential term C_o'. Although B and μ are expected to decrease with increasing temperature, both declines are presumably small in comparison with the exponential increase in vacancy concentration. Therefore, eqn (3) predicts an increase in strength with increasing temperature, but no strain rate dependence.

At high temperatures (around the peak temperature and higher), if there are sufficient numbers of mobile vacancies, deformation is by dislocation creep, and the yield stress may be written as:[26]

$$\sigma = \mu\{\dot{\gamma} \exp(E_d/kT)/D_o'\}^{1/m} \tag{4}$$

where $\dot{\gamma}$ is the shear strain rate, m is a material constant, E_d is the activation enthalpy for vacancy diffusion, and D_o' is a modified pre-exponential factor which is weakly temperature dependent.

Equations (3) and (4), along with simple expressions describing the yield stress behavior at lower temperatures, were fitted[26] to the experimental yield stress versus temperature data for Fe–40Al polycrystals.[3] The result (for T > 300 K) is shown in Fig. 3 where the circles represent experimental data, the solid lines represent best fits of our model to the experimental data, and the dotted lines show how the yield strength

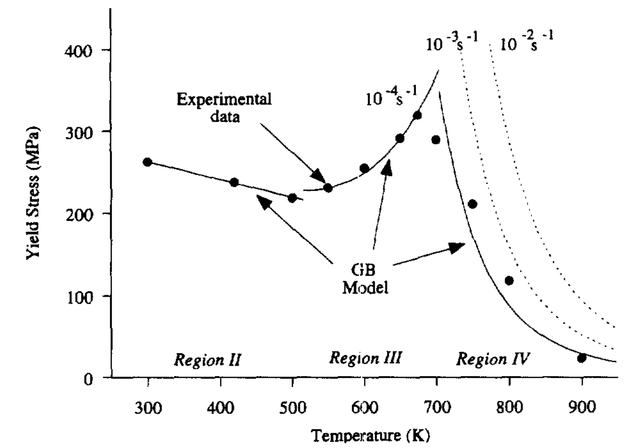

Fig. 3. Graph of yield stress versus temperature for large-grained, well-annealed Fe–40Al.[34] See text for details.

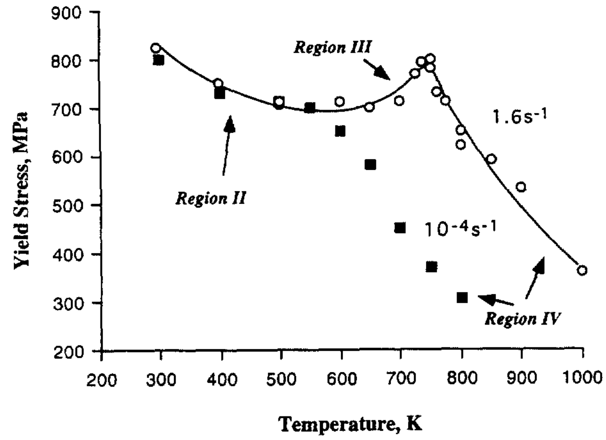

Fig. 4. Effect of strain rate on the yield anomaly of large-grained, well-annealed Fe–50Al.[38]

(beyond the peak temperature) changes with increasing strain rate (eqn (4)).

COMPARISON WITH EXPERIMENTS

Since eqns (3) and (4) are empirical, and arbitrarily good fits can be obtained by choosing the appropriate fitting parameters, the only way to judge whether our approach is reasonable is by determining values for the various constants in the equations and examining whether they are physically reasonable. This has been done in earlier papers[26,34] and the key findings are summarized here.

The best fit of eqn (3) with the experimental data yields a value for E_f of 92 kJ mole^{-1}. This is remarkably close to the experimental value for E_f of 95 kJ mole^{-1} obtained by Würschum *et al.*,[35] a result which strongly supports our model. Similarly, the best fit of eqn (4) with the experimental data yields a value for E_d/mk of $8{\cdot}2\times10^3$. Using the E_d of 259 kJ mole^{-1} measured by Würschum *et al.*,[35] we get a value for m of 3·8, which is reasonable for dislocation creep where values lie typically between 3 and 7.[36]

Another way to evaluate the model is to use eqn (1) to determine whether the thermal vacancies present in FeAl at the peak temperature[14] can, in fact, produce the observed magnitude of strengthening. This has also been done[26] and it was concluded that strength increases comparable to those observed in the anomalous region (~80 MPa) are explainable with the vacancy concentrations ($\sim10^{-4}$) present at T_p.

As discussed earlier, eqn (3) exhibits no strain rate dependence whereas eqn (4) is strain-rate-dependent. A consequence of this is that the point of intersection of these two regions shifts to higher (or lower) temperatures as the strain rate increases (or decreases) (Fig. 3). These implications have been confirmed experimentally in B-doped[26] and B-free[27] Fe–40Al: in both, the yield stress in the anomalous region is relatively insensitive to strain rate, but the peak temperature and the peak stress depend on strain rate (because of the strain-rate dependence of Region IV, Fig. 3). In fact, at low-enough strain rates, Region IV shifts so much to the left that the yield anomaly almost completely disappears.[27]

The effects of stoichiometry are also consistent with the vacancy-hardening mechanism.[26,34] In the Fe-rich alloys (say, 40–45% Al), there are few vacancies at low temperatures, and anti-site atom strengthening is relatively weak.[16] Therefore, their yield stresses at low temperatures tend to be similar (albeit increasing slightly with increasing Al concentration), and the onset of the strength anomaly occurs at around the same temperature. With increasing temperature, the vacancy concentration increases, but by about the same amount in all the alloys (at least at temperatures to 973 K[14]). Consequently, the yield stress peak also occurs at around the same temperature in all the Fe-rich alloys.

As one approaches the stoichiometric composition, however, the equilibrium vacancy concentration increases dramatically, both as a function of Al concentration and temperature[14]. One effect of these vacancies is to increase the yield strength at low temperatures (much as the non-equilibrium, quenched-in vacancies do in Fig. 1). Another effect is to make dislocation creep possible at lower temperatures so that Region IV (see Fig. 3) is shifted to the left. Together, these two have the effect of completely obscuring the yield strength anomaly in Fe–48Al and Fe–50Al.[37] If the strain rate is increased, however, our model predicts that Region IV will shift to the right. Consistent with this, as shown in Fig. 4, recent experiments have revealed a yield anomaly even in Fe–50Al when it was tested at a high strain rate of $1{\cdot}6\,s^{-1}$,[38] whereas previous experiments at a strain rate of 10^{-4} showed no such anomalous region.[37]

CONCLUDING REMARKS

The George–Baker model, which is based on hardening by thermal vacancies at intermediate temperatures and dislocation creep at high temperatures, explains many of the features associated with the yield strength anomaly of FeAl. A shortcoming of the model is that it lacks a detailed description of the way in which vacancies pin (or drag) dislocations. Another shortcoming is that neither the orientation dependence nor the tension-compression asymmetry of the yield anomaly in single crystals[6,7] have yet been incorporated in the model.

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REFERENCES

1. Chang, K. M., *Metallurgical Transactions*, 1990, **21A**, 3027.
2. Guo, J. T. , Jin, O., Yin, W. M. and Wang, T. M., *Scripta Metallurgica Materialia*, 1993, **29**, 783.
3. Xiao, H. and Baker, I., *Scripta Metallurgica et Materialia*, 1993, **28**, 1411.
4. Yoshimi, K. and Hanada, S., in *Structural Intermetallics*, ed. R. Darolia, J. J. Lewandowski, C. T. Liu, P. L. Martin, D. B. Miracle, and M. V. Nathal. TMS, Warrendale, PA, 1993, 475.
5. Yoshimi, K., Hanada, S. and Tokuno, H., *Metallurgical Transactions JIM*, 1994, **35**, 51.
6. Yoshimi, K, Hanada, S. and Yoo, M. H., *Acta Metallurgica et Materialia*, 1995, **43**, 4141.
7. Yoshimi, K., Hanada, S. and Yoo, M. H., *Intermetallics*, 1996, **4**, 159.
8. Klein, O. and Baker, I., *Scripta Metallurgica et Materialia*, 1994, **30**, 1413.
9. Baker, I., Xiao, H., Klein, O., Nelson, C. and Whittenberger, J. D., *Acta Metallurgica et Materialia*, 1995, **43**, 1723.
10. Carleton, R., George, E. P. and Zee, R. H., *Intermetallics*, 1995, **3**, 433.
11. Li., X. and Baker, I., *Scripta Metallurgica et Materialia*, 1997, **36**, 1387.
12. Rieu, J. and Goux, C., *Mem. Sci. Rev. Metall.*, 1969, **65**, 869.
13. Weber, J., Meurtin, M., Paris, D., Fourdeux, A. and Lesbats, P., *Journal de Physique*, 1977, **38**, 332.
14. Chang, Y. A., Pike, L. M., Liu, C. T., Bilbrey, A. R. and Stone, D. S., *Intermetallics*, 1993, **1**, 107.
15. Nagpal, P. and Baker, I., *Metallurgical Transactions*, 1990, **21A**, 2281.
16. Pike, L. M., Chang, Y. A. and Liu, C. T., in *Processing, Properties, and Applications of Iron Aluminides*, ed. J. H. Schneibel and M. A. Crimp. The Minerals, Metals, and Materials Society, Warrendale, PA, 1994, p. 217.
17. Munroe, P. R. and Baker, I., *Philosophical Magazine*, 1995, **72**, 1301.
18. Yoshimi, K., Hanada, S. and Yoo, M. H., MRS Symp. Proc., Vol. **460**, Mater. Res. Soc., Pittsburgh, PA, 1997, 313.
19. Kad, B. K. and Horton, J. A., *Mater Sci. Eng.*, 1997, **A239–240**, 118.
20. Morris, D. G., *Philosophical Magazine*, 1995, **71A**, 1281.
21. Saka, H. and Kawase, M., *Philosophical Magazine*, 1984, **49A**, 525.
22. Saka, H. and Zhu, Y. M., *Philosophical Magazine*, 1985, **51A**, 629.
23. Saka, H., Kawase, M., Nohara, A. and Imura, T., *Philosophical Magazine*, 1984, **50**, 65.
24. Saka, H., Zhu, Y. M., Kawase, M., Nohara, A. and Imura, T., *Philosophical Magazine*, 1985, **51A**, 365.
25. Zhu, Y. M. and Saka, H., *Philosophical Magazine*, 1989, **59A**, 661.
26. George, E. P. and Baker, I., *Philosophical Magazine*, 1998, **A77**, 737.
27. Li, X. and Baker, I. *Scripta Metall. Mater.*, 1996, **34**, 1219.
28. Umakoshi, Y., Yamaguchi, M., Namba, Y. and Murakami, M., *Acta Metallurgica*, 1976, **24**, 89.
29. Pope, D. P. and Ezz, S. S., *Int. Met. Rev.*, 1984, **29**, 136.
30. Fu, C. L. and Yoo, M. H., *Acta Metallurgica et Materialia*, 1992, **40**, 703.
31. Yoo, M. H., Horton, J. A. and Liu, C. T., *Acta Metall.*, 1988, **36**, 2935.
32. George, E. P., Carleton, R., Cohron, J. W. and Zee, R. H., unpublished research, 1995.
33. Fleischer, R. L., in *The Strengthening of Metals*, ed. D. Peckner. Reinhold, New York, 1964, p. 93.
34. Baker, I. and George, E. P., *MRS Symp. Proc.*, Vol. 460, 1997, p. 373.
35. Würschum, R., Grupp, C. and Schaefer, H.-E., *Physics Review Letters*, 1995, **75**, 97.
36. Ashby, M. F. and Frost, H. J., in *Constitutive Equations in Plasticity*, ed. A. S. Argon. MIT Press, Cambridge, MA, 1975, p. 117.
37. Baker, I., Xiao, H., Klein, O., Nelson, C. and Whittenberger, J. D., *Acta Metall. Mater.*, 1995, **43**, 1723.
38. Baker, I. and Yang, Y., *Mater. Sci. and Eng.*, 1997, **A239–240**, 109.