Lattice-parameter change induced by accommodation of precipitate/matrix misfit; misfitting nitrides in ferrite

M. Akhlaghi [a], T. Steiner [a,b], S.R. Meka [a,*], A. Leineweber [a,1], E.J. Mittemeijer [a,c]

[a] Max Planck Institute for Intelligent Systems (formerly MPI for Metals Research), Heisenbergstrasse 3, 70569 Stuttgart, Germany
[b] Robert Bosch GmbH Heat Treatment Processes and Heat Treatment Technology (CR/APM4), Postbox 300240, 70442 Stuttgart, Germany
[c] Institute for Materials Science, University of Stuttgart, Heisenbergstrasse 3, 70569 Stuttgart, Germany

ABSTRACT

Upon nitriding of iron-based alloys, development of misfitting coherent nitride precipitates in a ferrite matrix induces an overall expansion of the ferrite lattice. This lattice expansion was quantitatively determined by X-ray diffraction from the change of the lattice parameter of ferrite of homogenously nitrided Fe—Cr and Fe—V alloys. Adopting the experimentally verified (by X-ray diffraction and transmission electron microscopy) notion that the misfitting precipitates *diffract coherently with the matrix*, the extent of this hydrostatic lattice-strain component could be calculated, in general, as function of the precipitate/matrix misfit, the volume fraction of precipitates and the elastic properties of the matrix and precipitates. The experimentally observed and the predicted dependencies of lattice dilatation agree very well for both nitrided Fe—Cr and Fe—V alloys. This is the first time that this type of lattice expansion was experimentally identified and quantitatively explained.

© 2015 Acta Materialia Inc. Published by Elsevier Ltd. All rights reserved.

1. Introduction

Solid-state phase transformations involving volume misfit between parent and product phases can induce unusual, non-equilibrium phenomena, such as, the establishment of metastable phases (e.g. cubic AlN in a ferrite matrix [1,2]), non-monotonous variation of transformation rate (e.g. during austenite–ferrite and austenite–martensite transformations [3–5]), unusual morphologies (as octapod shaped, amorphous silicon-nitride particles in a ferrite matrix [6]). These effects are often attributed to the complex interplay of the chemical Gibbs energy change driving the transformation and the deformation energy associated with volume misfit accommodation [7,8]. Precise understanding of the effects of misfit-strain energies on the thermodynamics and kinetics of phase transformations and on the resulting microstructure is essential to optimize the properties of engineering components [9].

The elastic strain fields surrounding individual (tiny) precipitates have been exposed by transmission electron microscope (TEM) diffraction-contrast images [10–12] which allow (local) determination of the sign and (approximate) magnitude of the occurring misfit. The lattice distortions associated with misfit-strain fields induce diffuse scattering in X-ray diffraction (XRD) experiments [13], which can be used to reveal characteristics of the strain fields around (very) small precipitates [14]. The presence of misfitting inclusions of larger dimensions induces (X-ray) diffraction-line broadening, characteristic for the presence of *micro*strains [13,15,16]. However, it is not generally recognized that the (average, overall) lattice-parameter values of misfitting systems are different from their (misfit) strain-free values, thereby exposing the presence of a (hydrostatic) *macro*strain. Thus, straightforward determination of the lattice parameter (e.g. from the peak position in (X-ray) diffractograms) provides important information not only on the course of a precipitation process by compositional change of the parent matrix, but also on the extent of the developing misfit-strain fields. The last feature plays a cardinal role in the present work.

The state of stress invoked by misfitting inclusions in a matrix has been dealt with largely theoretically in the literature [17–20]. Experimental verification of such theoretical predictions is relatively rare: adopting a theory for point imperfections in a solid matrix, the effect of misfitting precipitates on the lattice distortions of the matrix, and in one case also of the precipitates, was investigated for the case of *incoherent* precipitate/matrix interfaces [21–23]. Since this early work, no further development and application of this approach appears to have taken place.

---

* Corresponding author.
  E-mail address: s.meka@is.mpg.de (S.R. Meka).
[1] Present address: Institute of Materials Science, Technical University Bergakademie Freiberg, 09599 Freiberg, Germany.

Against the above background, the present work is devoted to prediction and experimental verification of lattice distortions introduced upon the development of misfitting second-phase particles in a solid matrix, with (largely) *coherent* precipitate/matrix interfaces, employing X-ray diffraction. To this end, systems composed of misfitting nitride particles in a ferrite matrix, as developing during internal nitridation of iron-based alloy substrates (Fe—Cr and Fe—V alloys), have been chosen as model systems. The tiny CrN and VN precipitates are (largely) coherent with the ferrite matrix [24–27] and yet exhibit pronounced volume misfit with the matrix. The coherency of the precipitate/matrix interface gives rise to peculiar diffraction effects involving coherent diffraction of the assembly precipitate plus matrix (so no precipitate reflections occur) and asymmetrically broadened diffraction-line profiles. It will be shown that the effect of misfit strain is sensitively expressed in lattice-parameter changes and that good agreement between theoretically predicted and experimentally measured data can be achieved.

2. Elastic strain field in a misfitting system: lattice-parameter changes

A continuum theory for the fully elastic accommodation of the misfit of a point imperfection in a matrix has been presented by Eshelby [28,29]. The theory was developed to (also) predict the slope of the dependence of the lattice parameter of a crystalline solid solution on solute content (cf. Vegard's law [30]). However, for this application the theory failed, as electronic interaction on the atomic scale can be dominant over elastic straining effects [18]. Therefore, the theory is more likely applicable to the case of precipitation of misfitting second-phase particles. On this basis, cases of particle-matrix misfit strain for elastically anisotropic matrices could be dealt with leading to the prediction of precipitate-particle shape [17,31–33].

In the following subsections, formulae are presented that describe the changes of the relative volume/lattice-parameters of the matrix (Section 2.1), the misfitting particles (inclusions; Section 2.2) and of the assembly, i.e. matrix plus misfitting particles (inclusions; Section 2.3).[2]

2.1. Change of the lattice parameter of the matrix

Insertion of the undeformed inclusions *B* in the holes of the matrix *A* leaves the whole assembly in a state of self-stress. Considering (i) a *finite* matrix *A* containing, in the strain-free condition, holes of radius r_A^0 and (ii) particles *B*, of strain-free radius r_B^0, the relative volume increase of the matrix *A* due to the insertion of the misfitting inclusions *B* into the holes of the matrix *A* can be written as [18]:

$$\frac{\Delta V_A}{V_A} = \frac{16}{3}\pi\frac{\mu_A}{K_A}C_6\varepsilon\left(r_A^\circ\right)^3 n \tag{1}$$

with

$$C_6 = \frac{3K_B}{3K_B + 4\mu_A} \tag{2}$$

where *n* is number of inclusions *B* per unit volume and *K* and *μ* represent the bulk modulus and the shear modulus, respectively.

The linear misfit parameter, *ε*, can be calculated from $\left(r_B^\circ - r_A^\circ\right)/r_A^\circ = \left(\sqrt[3]{v_B^0} - \sqrt[3]{v_A^0}\right)/\sqrt[3]{v_A^0}$, where v_B^0 and v_A^0 are the molar volumes of the strain-free precipitate particle and the matrix, respectively. The volume fraction of inclusion y_B can be taken as $y_B = 4\pi\left(r_B^\circ\right)^3 n/3$. For the case of a matrix of cubic crystal structure with a (strain-free) lattice parameter a_A, $\Delta V_A/V_A$ can be approximated by $3\Delta a_A/a_A$, and Eq. (1) can be rewritten as [21]:

$$\Delta a_A = \frac{4\mu_A C_6}{3K_A}\frac{\varepsilon}{(1+\varepsilon)^3}y_B a_A \tag{3}$$

It is important to note that the matrix is of finite dimensions. In an *infinite* matrix, the volume change of the matrix due to the introduction of misfitting inclusions is zero (the matrix only experiences shear strains); then, the volume change of the assembly is fully confined to the precipitates. The matrix dilatation that is predicted for a matrix of *finite* size is a consequence of the image forces required to achieve a stress-free surface of the finite assembly.

2.2. Change of the lattice parameter of the misfitting phase

A misfitting inclusion with a radius larger or smaller than that of the hole in the matrix will experience hydrostatic compression or tension, respectively. For the case of a *finite* assembly of matrix *A* plus misfitting inclusions *B*, the fractional volume change of the inclusions can be written as [23]:

$$\frac{\Delta V_B}{V_B} = -3\varepsilon(1 - C_6) + \frac{16}{3}\pi\frac{\mu_A}{K_B}C_6\varepsilon\left(r_A^\circ\right)^3 n \tag{4}$$

For the case of precipitates of cubic crystal structure with a (strain-free) lattice parameter a_B, $\Delta V_B/V_B$ can be approximated by $3\Delta a_B/a_B$, and it follows for the change of the lattice parameter, Δa_B, of the misfitting second phase:

$$\Delta a_B = \left[-\varepsilon(1 - C_6) + \frac{4\mu_A C_6}{3K_B}\frac{\varepsilon}{(1+\varepsilon)^3}y_B\right]a_B \tag{5}$$

The total relative volume change of the inclusions results from the *sum* of the fractional volume change of the inclusions in an *infinite* assembly (first term in Eqs. (4) and (5)) and the fractional volume change of the inclusions due to the image forces acting (also) on the inclusions in a *finite* assembly (second term in Eqs. (4) and (5)).

2.3. Change of the lattice parameter of the assembly (matrix plus misfitting phase)

The relative volume change of the whole, finite assembly comprising the finite matrix and the misfitting inclusions can be given as [18]:

$$\frac{\Delta V}{V} = 4\pi C_6\varepsilon\left(r_A^\circ\right)^3 n + \frac{16}{3}\pi\frac{\mu_A}{K_A}C_6\varepsilon\left(r_A^\circ\right)^3 n = 4\pi\frac{C_6}{C_6'}\varepsilon\left(r_A^\circ\right)^3 n \tag{6}$$

with

$$C_6' = \frac{3K_A}{3K_A + 4\mu_A} \tag{7}$$

For an aggregate of cubic crystal structure and a (strain-free) lattice parameter *a*, thus approximating $\Delta V/V$ by $3\Delta a/a$, the resulting change of the lattice parameter, Δa, of the aggregate for a volume fraction y_B precipitate particles *B* is given by:

$$\Delta a = \frac{C_6}{C_6'}\frac{\varepsilon}{(1+\varepsilon)^3}y_B a \tag{8}$$

---

[2] In the derivations of the following formulae, in order to calculate the image force term for a *finite* matrix and a *finite* assembly, it is assumed that the volume fraction of misfitting particles is small: only the matrix elastic constants are used to calculate the image force term for matrix and assembly. Further, the matrix and the misfitting particles are taken to be elastically isotropic.