Recent important advances in materials science


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This paper summarises some recent advances in four key areas in Materials Science: blue light emitters, high temperature alloys, high temperature superconductors and the phase problem in diffraction. A surprising observation with blue light emitting diodes and lasers made from GaN is that the material emits intense blue light even though it has a high density of defects. We have analysed a particular type of defect and have shown that it contains no dangling bonds, which explains why it does not act as a recombination centre. We then consider the problem of designing a new high temperature alloy, which has good room temperature ductility, using thermodynamic calculations. NiTi can be greatly strengthened up to 600°C by the addition of Al which forms Ni2TiAl precipitates in the NiTi matrix. To increase the strength above 600°C a quaternary element must be added to reduce the lattice misfit between precipitates and matrix. We are using the cluster variation method to predict which elements to add, and have shown that V reduces the misfit in theory and in practice. High temperature superconductors are widely believed to be periodic structures. We have shown that in YBa2Cu3O7–§, with §<0.1, there is a structural perturbation on the scale of the superconducting coherence length. Finally, recent work on the well-known “phase problem” in crystallography is reported. We have shown that phases may be directly and uniquely obtained from three beam convergent-beam electron diffraction patterns.

Key words: High temperature superconductors, high temperature alloys, blue light emitters, phase problem, gallium nitride, high resolution electron microscopy, intermetallic materials, NiTi, structure amplitudes.

Avances recientes importantes en ciencia de materiales

Este artículo resume algunos recientes avances en cuatro áreas clave de la Ciencia de Materiales: emisores de luz azul, aleaciones de alta temperatura, semiconductores de alta temperatura y el problema de la fase en difracción. Una sorprendente observación con los diodos y láseres que emiten luz azul hechos a partir de GaN es que estos materiales emiten intensa luz azul incluso aunque tengan una alta densidad de defectos. Hemos analizado un tipo particular de defecto y mostrado que no contiene enlaces insatisfechos, lo que explica porqué no actúa como centro de recombinación. Luego consideramos el problema de diseñar una nueva aleación de alta temperatura, que tuviera una buena ductilidad a temperatura ambiente, usando cálculos termodinámicos. El NiTi puede ser considerablemente reforzado hasta 600°C mediante la adición de Al que forma precipitados de Ni2TiAl en la matriz de NiTi. Para aumentar la resistencia por encima de 600°C debe añadirse un cuarto elemento para reducir el desajuste de la red entre los precipitados y la matriz. Usamos el método de variación de los agregados para predecir que elementos añadir, y hemos mostrado que el V reduce el desajuste tanto en la teoría como en la práctica. Hemos mostrado que en el YBa2Cu3O7–g, con g<0.1, hay una perturbación estructural a la escala de la longitud de coherencia superconductora. Finalmente, damos cuenta de un reciente trabajo sobre el bien conocido “problema de la fase” en cristalografía. Hemos mostrado que las fases pueden ser obtenidas directamente y de forma única a partir de los patrones de difracción de electrones de tres haces convergentes.

Palabra clave: Superconductores de alta temperatura, aleaciones de alta temperatura, emisores de luz azul, problema de la fase, nitrato de galio, microscopía electrónica de alta resolución, materiales intermetalicos, NiTi, amplitud de estructura.

1. INTRODUCTION

Substantial advances have been made recently in our understanding of materials and in designing materials for specific applications. This paper describes recent research into some key materials science problems: (i) blue light emitting diodes and lasers; (ii) designing new high temperature metallic alloys from first principles; (iii) the structure of high-temperature superconductors; (iv) a new direct method to solve the well-known phase problem.

2. BLUE LIGHT EMISSION FROM GaN

The successful development of blue and green light emitting diodes and lasers with long lifetimes is a key materials science problem worth many billions of dollars. The reason for the intense world-wide interest in blue/green light emitting materials is their potential application in colour displays, high density data storage systems, compact disc players, traffic lights, etc. Gallium nitride is a very promising blue light emitting material for such devices, and when alloyed with In and Al a
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A wide range of wavelengths from the visible into the ultraviolet can be obtained. Since red light emitting diodes and lasers already exist, the development of gallium nitride would enable diodes and lasers to be produced in all the main visible colours, thus facilitating their use in full colour displays, traffic lights, etc. Using colour mixing, an intense white light source could also be produced.

GaN blue LEDs and lasers have been fabricated already and there is considerable interest in understanding the defect microstructure of these wide band gap materials (see for example ref 1). A surprising result which is not understood is that existing GaN devices emit very intense blue light even though the GaN epilayers have a very high density of defects. A similarly high defect density in other solid state laser materials, for example GaAs or another blue light emitting material ZnSe, results in very low intensity light emission because the defects give rise to states in the band gap which act as recombination centres. We have studied in detail a common defect in GaN, a double positioning boundary, to try to understand why it does not act as a recombination centre. GaN grown on many substrates (e.g. GaP) grows by island growth and a double positioning boundary on [12 10] frequently forms as a consequence of coalescence of faulted with unfa ulted islands during growth. Fig 1(a) shows a plan-view of epitaxial wurtzite GaN grown on a [TT]B GaP substrate showing the GaN islands that have coalesced and the boundaries between the islands. The double positioning boundary on [12 10] studied here is marked DB-I. Fig 1(c) shows a cross-section of the same specimen. Faulted islands nucleated on stacking faults coalesce with unfa ulted islands to produce the boundaries as observed. The misorientation between the islands is very small so the epilayer is single crystal material. There is a high density of DB-I defects. Fig 1(b) shows an HREM image of a DB-I defect, imaged down [0001]. One might normally expect such a defect to act as a recombination centre.

Using HREM plus diffraction contrast we have shown that the boundary has a displacement \(1/2 <101>\). We have built an atomic model for this boundary which is consistent with this displacement (Fig 2). Image simulations using this atomic model give a calculated high resolution image (inset in fig 1(b)) which is very similar to the experimental image. We therefore have some confidence that our model is correct. It is clear from Fig 2 that the Ga and N atoms retain four-fold coordination across the boundary and the atoms have Ga-N bonding everywhere. Hence the boundary is of low energy with no dangling bonds and this suggest that it does not have states in the band gap of GaN, and hence that it does not act as a recombination centre, consistent with the intense blue light emitted from this material. Further details will be published elsewhere (2).

3. DESIGNING NEW INTERMETALLIC ALLOYS

Turbine disc alloys for aerospace engines operate at about 850°C and they are normally made from nickel-based superalloys which have a density of 8.3 g cm\(^{-3}\). There is an urgent industrial need for turbine disc materials that operate at 850°C but which have a significantly lower density. The standard approach to designing a new high temperature alloy is to take an intermetallic material such as TiAl (density 3.8 g cm\(^{-3}\)) or NiAl (density 5.3 g cm\(^{-3}\)), which has reasonable mechanical

strength at 850°C, and to try to improve its room temperature ductility. As is well known, a major problem with intermetallics such as TiAl or NiAl is their brittleness at room temperature.

We are trying a different approach, which is to take an intermetallic which has good room temperature ductility, and to design strength at high temperature into this alloy. The intermetallic NiTi (density 6.5 g cm\(^{-3}\)) has significantly lower density than Ni-based superalloys and it has good ductility at room temperature, hence if this alloy can be used in turbine discs at 850°C this would be of major benefit.

The specific yield stress, that is (yield stress)/density, of NiTi is significantly lower than that of Ni-based superalloys at all temperatures. However, doping with Al produces a dramatic improvement and results in a higher specific yield strength than Ni-based superalloys at temperatures up to 600°C (3), but above this temperature the specific yield stress drops rapidly. We have shown that for Al doping of greater than 4 at %, Ni\(_2\) TiAl\(^{2+}\)-phase precipitates form in the NiTi \(\beta\)-phase matrix. It is these precipitates which are responsible for greatly strengthening the alloy up to temperatures of 600°C, but above this temperature the yield stress drops rapidly (3) and the misfit strain between the \(\beta\) precipitates and the \(\beta\) matrix causes structural instability (4). In order to reduce the lattice misfit between the matrix and precipitate we propose to add a quaternary element which will partition into either the \(\beta\) or the \(\beta\)' phase, which will reduce the lattice mismatch and will hence stabilise the precipitates.

We are using the cluster variation method (CVM) to predict the partitioning of quaternary elemental additions between the \(\beta\) and \(\beta\)' phases, and to predict the effect of these additions upon the lattice misfit between the \(\beta\) precipitates and the \(\beta\) matrix. The predictions made by the CVM method are substantiated by X-ray diffraction misfit measurements on experimental alloys and the resultant microstructures are examined using transmission electron microscopy (TEM) techniques. The microstructure consists of array of cuboidal \(\beta\)' (Ni$_2$TiAl) precipitates aligned along \(<100>\) directions within a matrix of \(\beta\)(NiTi). CVM calculations predict preferential partitioning to the \(\beta\)' phase of Ag, Cu and V. Experimental XRD results verify that V does indeed partition to the \(\beta\)' phase and 2 at % V doping decreases the absolute misfit by about 0.05%, in good agreement with the theory.

The above work suggests a general method for designing strength into binary alloys at high temperatures. The addition of a ternary element can cause precipitation which increases the strength up to a certain temperature, but above this temperature the misfit strain energy causes microstructural instability and the strength decreases. In order to reduce the misfit strain energy a carefully selected quaternary element is added, which by partitioning in either the matrix or the precipitate reduces the lattice misfit, thus stabilising the microstructure. It is believed that strength at even higher temperatures may be achieved. The use of computer modelling greatly facilitates the choice of appropriate quaternary elements for doping.

4. THE STRUCTURE OF HIGH TEMPERATURE SUPERCONDUCTORS

It is widely believed that high-temperature superconductors have periodic crystal structures, and numerous theories of high-temperature superconductivity (none of which is yet successful) assume a periodic crystal structure and hence a periodic band structure. Recent work questions this assumption, at least for the well known high-T\(_c\) material YBa$_2$Cu$_3$O$_{7-\delta}$ (5). High quality YBa$_2$Cu$_3$O$_7$ exhibits reasonably sharp diffraction spots in X-ray or electron diffraction patterns, hence the belief that the material has a regular periodic crystal structure (apart from the effects of defects such as twins of course). However, electron diffraction patterns recorded from high quality YBa$_2$Cu$_3$O$_{7-\delta}$, with \(\delta <0.1\), exhibit very weak diffuse streaks between the diffraction spots. Such streaks can be due to thermal vibrations of atoms or static displacements of atoms. It has been shown in this case that the streaks are consistent with there being static displacements of some of the apical oxygen and planar copper atoms.

High resolution electron microscopy just reveals an irregular grid of dark lines superimposed upon the lattice image. A detailed analysis shows that these lines correspond to a mild perturbation of the structure along boundaries which partition the crystal into cells of dimensions 10-20Å in the ab plane and less than 5Å in the c direction. These dimensions are comparable with the zero-temperature superconducting coherence lengths in the ab plane and along c. The cell boundaries lie parallel to the oxygen-pyramidal planes containing the apical oxygen and planar oxygen atoms.

These observations from HREM images and selected area electron diffraction patterns indicate that YBa$_2$Cu$_3$O$_{7-\delta}$, with \(\delta <0.1\), is not strictly periodic. It is not yet clear whether the perturbation of the crystal potential at the cell boundaries is sufficiently strong to influence the superconducting properties of the materials.

5. SOLVING THE PHASE PROBLEM

The "phase problem" is very well-known in the determination of crystal structures using X-ray diffraction. For an incident beam of wave vector \(\mathbf{k}\), the amplitude scattered by a unit cell in the direction \((\mathbf{k} + \mathbf{g})\) is given by

\[
F_g = \sum_j \exp(2\pi i \mathbf{g} \cdot \mathbf{r}_j)
\]

where \(F_g\) is the structure factor, \(\mathbf{r}_j\) is the position of the \(j\)th atom in the unit cell having an atomic scattering factor, \(f_j\), and the summation is over the \(j\) atoms in the unit cell (\(F_g\) is called the structure factor for X-ray diffraction and the structure amplitude for electron diffraction).

The intensity scattered in the direction \((\mathbf{k} + \mathbf{g})\) is then given by

\[
I_g \propto |F_g|^2
\]

The above equation holds for both kinematical and two-beam dynamical diffraction theory. Thus phase information is lost: this is the well-known phase problem.

We have recently proposed an electron diffraction method of measuring the phase directly and uniquely from centrosymmetric crystals (6), (7). The method uses a three-beam convergent-beam electron diffraction pattern. From the geometry of the intensity distribution in the convergent beam discs, the phases as well as the amplitudes of the three structure ampli-
tudes can be measured uniquely and directly. The method does not involve matching computed and experimental convergent beam patterns and it is independent of crystal thickness.

Although phases are lost in diffracted intensities calculated using kinematical or two-beam dynamical diffraction theory, they are retained in three-beam dynamical diffraction theory. The problem lies in extracting the phases experimentally from a three-beam diffraction situation. We have shown that along certain directions in reciprocal space the three-beam equations can be decoupled so that they reduce to the very much simpler two-beam form. (In terms of Bloch waves, one of the three Bloch waves is not excited along these directions). Lines can be drawn on the convergent beam electron diffraction patterns along which the patterns have two-beam form. The position of the lines is independent of the crystal thickness. The phases and the magnitudes of the three structure amplitudes can then be determined from three distances measured with a ruler on the diffraction pattern. Preliminary results indicate that the phases are lost in diffracted intensities calculated using kinematical or two-beam dynamical diffraction theory, but in none of these is the phase determined very accurately.

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