

Elasticity mapping of precipitates in polycrystalline materials using atomic force acoustic microscopy

Anish Kumar,^{a)} Ute Rabe, Sigrun Hirsekorn, and Walter Arnold

Fraunhofer Institute for Non-Destructive Testing (IZFP), Campus E3.1, D-66123 Saarbrücken, Germany

(Received 9 March 2008; accepted 14 April 2008; published online 7 May 2008)

We determined the isotropic indentation modulus of precipitates in cubic materials by using the indentation modulus of the matrix as a reference. This eliminates major practical difficulty of repeatedly switching between a sample and a reference for measurement of indentation modulus using atomic force acoustic microscopy. The methodology has been demonstrated for mapping the elastic stiffness of ~ 500 nm sized $M_{23}C_6$ precipitates in alloy 625 and ferritic steel with a spatial resolution of ~ 50 nm. © 2008 American Institute of Physics. [DOI: 10.1063/1.2919730]

Various techniques based on contact-resonance spectroscopy, such as atomic force acoustic microscopy (AFAM),¹ ultrasonic atomic force microscopy (UAFM),² and resonance ultrasound microscopy (RUM),³ have emerged as tools for the measurement of elastic properties of the surface of a specimen with micrometer (RUM) or nanometer resolution (AFAM and UAFM). These techniques measure the resonance of the cantilever (AFAM and UAFM) or oscillator (RUM) with a tip contacting the specimen surface and derive its local indentation modulus by using a suitable mechanical model relating the resonance frequencies of the system to the tip-sample contact stiffness. AFAM has been extensively used for the measurement of elastic properties of thin films,⁴ piezoelectric ceramic materials,⁴ clay,¹ and glass-fiber/polymer matrix composites.⁵ However, no study is reported so far for the measurement of elastic stiffness of precipitates or secondary phases in dual-or multiphase polycrystalline materials using AFAM. One of the major inhibitions of using AFAM for such applications is the variation in the indentation modulus of the precipitate and the matrix in different crystal orientations. Polycrystalline materials such as metals or ceramics may be elastically isotropic on a macroscopic scale. However, techniques providing a lateral resolution in the micrometer or nanometer range probe the elasticity of the anisotropic individual grains in the polycrystalline aggregate.

The indentation modulus is an elastic constant which accounts for the compression and the shear deformation in the contact zone between mechanically anisotropic materials. Although originally used for nanoindentation,⁶ it has been shown that the indentation modulus is in the same manner as the elastic constant measured by elastic contact-resonance techniques such as AFAM.⁷

In this paper, we have analyzed the correlation between the isotropic indentation modulus M_{iso} being an average property of a polycrystalline material and the anisotropic indentation modulus M_{aniso} , depending on the crystal orientation, for materials with cubic symmetry. Its implication for measurement of the indentation modulus of precipitates in a matrix with cubic single-crystal symmetry using AFAM is also demonstrated.

In AFAM, at least two resonance frequencies of the atomic force microscopy (AFM) cantilever beam in contact

with the sample surface are measured by sweeping the frequency of the ultrasonic wave injected from the back surface of the specimen.¹ The resonance frequencies of the spring-coupled system shift to higher values called contact resonances due to the elastic restoring forces of the sample surface acting to the tip. The ratio k^*/K_c of the contact stiffness k^* to the spring constant of the cantilever K_c is calculated using a suitable mechanical model that describes the contact vibrations of the AFM cantilever beam.¹ The principle of the AFAM technique is discussed in detail elsewhere.^{1,4,7}

In the case of mechanical isotropy, the contact stiffness k^* is related to the elastic constants of the specimen and the tip apex using the Hertzian contact model for a spherical indenter,

$$k^* = \sqrt[3]{6PR_1E^{*2}}, \quad (1)$$

where $P=K_c d$ is the load applied by the cantilever on the specimen, d is the static cantilever deflection, R_1 is the contact radius, and E^* is the reduced modulus, which is given by⁷

$$1/E^* = 1/M_s + 1/M_{tip}, \quad (2)$$

where M_s and M_{tip} are the indentation moduli of the sample and the tip, respectively. For isotropic materials, the indentation modulus M_{iso} is calculated from Young's modulus E and Poisson's ratio ν ,

$$M_{s,tip} = E_{S,tip}/(1 - \nu_{S,tip}^2). \quad (3)$$

For anisotropic materials, the shape of the contact area and the surface displacements in the contact area depend on the orientation of the crystal lattices and on the single-crystal elastic constants of the contacting bodies. Theoretical examinations showed⁶ that the contact area is circular if there exists a three- or fourfold rotational symmetry axis perpendicular to the contacting surfaces, which holds, e.g., for (001) and (111) surfaces of cubic crystals. In this case, Eqs. (1) and (2) still hold, supposing the two isotropic indentation moduli according to Eq. (3) are replaced by new constants M_s and M_{tip} , which depend on the elastic single-crystal constants and on the orientation of the materials in the contact area.⁶

For indentation modulus measurements using AFAM, a reference material with known elastic constants, usually an amorphous material or a single-crystal material with known orientation, is used to derive the indentation modulus of the test sample using a relation which follows Eq. (1),

^{a)}Electronic mail: anish@igcar.gov.in. On leave from Metallurgy and Materials Group, Indira Gandhi Centre for Atomic Research, Kalpakkam 603102, Tamil Nadu, India.

$$k_S^*/k_R^* = (E_S^*/E_R^*)^{2/3}, \quad (4)$$

where k_S^* , E_S^* , k_R^* , and E_R^* are the contact stiffness and the reduced modulus of the sample and of the reference specimen, respectively. This approach requires contact-resonance frequency measurements on different samples and frequent sample change, which might cause changes in the tip condition or deviation in the stability of the system. In the case of measurement of the indentation modulus of a precipitate in a polycrystalline material, it would, therefore, be an advantage if the matrix itself could be used as a reference. If the orientation of the grain and the single-crystal elastic constants of the matrix are known, the anisotropic indentation modulus of the matrix can be calculated and used as a reference. However, it is often difficult to measure the single-crystal elastic constants of the matrix and the orientation of the individual grain in which the measurement is carried out. It is much easier to experimentally obtain the averaged polycrystalline Young's modulus E and Poisson's ratio ν by ultrasonic velocity and by density measurements. From these data, the isotropic indentation modulus M_{iso} can be directly calculated using Eq. (3). Hence, if there exists a correlation between M_{aniso} and M_{iso} of the material, it could be possible to use M_{iso} of the matrix as a reference to determine M_{iso} of the precipitate. In this direction, the variation in M_{iso} with M_{aniso} for various cubic materials is analyzed and shown in Fig. 1(a). The indentation moduli were calculated using the single-crystal elastic constants for various cubic elements,⁸ nickel based superalloy CMSX-4,⁹ Ni₃Al,¹⁰ and 2.25Cr-1Mo ferritic steel.¹¹ M_{aniso} for these cubic materials were determined as described in detail elsewhere.^{6,7} We have selected the planes with the extreme values of M_{aniso} [i.e., (100), (110), and (111)] for the present study. The ratios of the M_{aniso} in the (111) and (100) planes for various cubic materials, as derived in the present paper, match quite well with the simulated values for cubic materials with similar elastic anisotropy factor [$A = 2C_{44}/(C_{11} - C_{12})$] and Poisson's ratio combinations.⁶ M_{iso} was calculated by determining E and ν from the single-crystal elastic constants by using the Voigt-Reuss-Hill method.¹² It can be seen in Fig. 1 that M_{aniso} is lowest when measured in the (100) plane and highest in the (111) plane for most of the cubic materials except for a few bcc materials such as Nb, Mo, V, and Cr, which exhibit elastic anisotropy value less than 1. M_{aniso} in the (110) plane is almost similar (within 4 GPa for all the cubic materials) to M_{iso} . Furthermore, M_{iso} falls almost exactly in between the extreme values for M_{aniso} . The maximum variation in M_{aniso} in different planes for materials with high elastic anisotropies (~ 3) is about 7% of M_{iso} (Fig. 1).

Based on this analysis, it is expected that if a precipitate with fcc crystal structure precipitates in a fcc matrix with cube-to-cube relationship such as $M_{23}C_6$ carbide in austenitic stainless steels¹³ and nickel base alloys,¹⁴ and γ' precipitate in nickel base superalloys,¹⁵ the ratio of M_{aniso} for the matrix and the precipitate for any orientation of the matrix would be almost similar to the corresponding ratio of M_{iso} . Hence, in the case of AFAM measurements in a grain with unknown orientation, the M_{iso} of the fcc matrix can be used as a reference for determining the M_{iso} of the fcc precipitate, with an error of less than 10%. This worst scenario arises when the measurement is done in a plane of extreme indentation modulus close to (100) or (111), and the matrix and the precipitate have extremely different elastic anisotropies, i.e.,

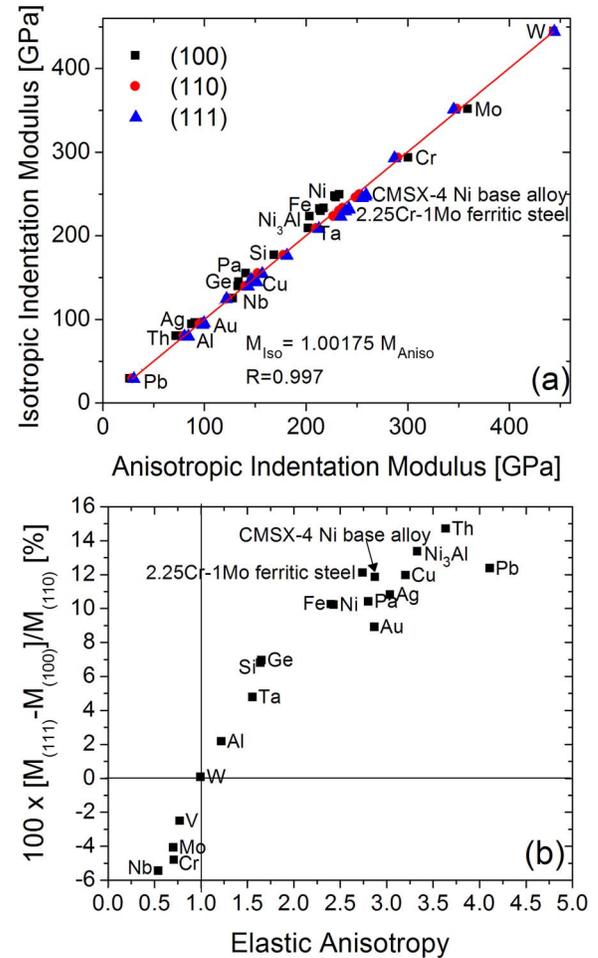


FIG. 1. (Color online) (a) Correlation between isotropic and anisotropic indentation modulus and (b) percentage variation in the difference in the extreme values of the anisotropic indentation moduli with the elastic anisotropy for various materials of cubic symmetry.

$A_{\text{matrix}} \sim 0.5$ and $A_{\text{precipitate}} \sim 3$ or vice versa. For most systems, the error is smaller than 2%. If the measurement is done in a plane close to (110), i.e., a plane with intermediate M_{aniso} , irrespective of the difference in the elastic anisotropy, this approach will not lead to an error of more than $\sim 2\%$. Similarly, if the elastic anisotropy of the matrix and of the precipitate is of similar order, this approach will not lead to an error of more than $\sim 2\%$, even if the measurement is done in the planes with extreme values of M_{aniso} . Furthermore, when a second phase precipitates from the matrix, there is always an orientation relationship between the two. It has been demonstrated by Zhang and Kelly^{13,16} that in case of cubic-cubic¹³ and hcp-bcc (Ref. 16) precipitate-matrix relation, the edge-to-edge matching of close packed planes of the precipitate and of the matrix occurs in all the alloy systems. This indicates that in any plane of measurement, the relative indentation modulus of the precipitate and of the matrix would be similar, i.e., if the measurement is carried out in a plane parallel to the close packed planes, both matrix and precipitate would show the highest modulus. In other directions both will respectively show lower modulus. If this is also considered, the maximum error involved can be estimated to be much less than that predicted above in the worst scenario for any cubic-cubic or bcc-hcp matrix-precipitate system.

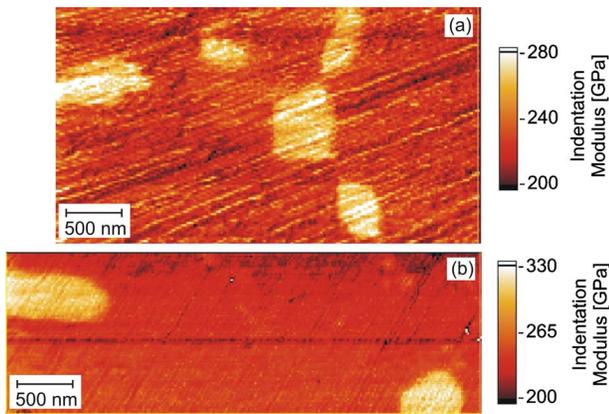


FIG. 2. (Color online) Distribution of the isotropic indentation modulus in (a) alloy 625 and (b) modified 9Cr-1Mo ferritic steel specimens containing $M_{23}C_6$ type carbides.

The applicability of the above approach has been demonstrated by the measurement of M_{iso} of $M_{23}C_6$ (Cr rich, M -Cr, Fe, Mo) carbide precipitates (fcc) in nickel base superalloy alloy 625 (fcc) and in modified 9Cr-1Mo ferritic steel (bcc). An alloy 625 specimen was obtained from an ammonia cracker tube exposed to service at ~ 873 K for $\sim 60\,000$ h in a heavy water plant.¹⁷ The specimen was post-service heat treated at 1123 K to dissolve the intermetallic precipitates, without dissolving the grain boundary carbides precipitated during service exposure.¹⁷ The ferritic steel specimen was studied in normalized (1313 K for 1 h) and tempered (1033 K for 3 h) condition. The chemical composition and detailed transmission electron microscopy studies showing precipitation of $M_{23}C_6$ carbides in the alloy 625¹⁷ and the ferritic steel¹⁸ specimens of the same heats and in similar heat treatment conditions are reported elsewhere. The specimens were polished with SiC papers up to 1200 grit, followed by polishing with $\frac{1}{4}$ μm diamond paste.

The first and the second contact-resonance spectra were obtained at every point of the area under investigation using a Solver P47H (m/s, NT-MDT Co., Russia) scanning probe microscope. As AFM sensors noncontact long (NCL) type cantilever with a monolithic silicon tip (m/s, Nanoworld AG, Switzerland) was chosen. The distribution of k^*/K_c values were derived using the contact-resonance spectra and the mechanical model described elsewhere.¹

As discussed above, M_{iso} of the matrix was used to determine M_{iso} of the $M_{23}C_6$ precipitates in the two alloys. The E and ν of the solution-annealed specimens of the same heat of alloy 625¹⁹ and of ferritic steel²⁰ specimen as used in the present study are 201 GPa and 0.308 and 213 GPa and 0.283, respectively. Using these values and Eq. (3), M_{iso} for alloy 625 and the ferritic steel matrix are calculated as 222 GPa and 231.5 GPa, respectively. Using these M_{iso} values and the average of the k^*/K_c values of the matrix, M_{iso} was determined for all the measurement points in the two systems using Eqs. (4) and (2). Figures 2(a) and 2(b) show the distribution of M_{iso} in alloy 625 and in the ferritic steel specimens, respectively. It can be seen that the indentation modulus of the carbide precipitate is higher in ferritic steel (~ 310 GPa) as compared to that in alloy 625 (~ 275 GPa). This is attributed to the higher amount of “Fe” in the $M_{23}C_6$ precipitate in case of ferritic steel as compared to nickel base superalloy. From simulation studies,²¹ it is observed that the

M_{iso} of $Cr_{23}C_6$ is 253 GPa and it increases to ~ 320 – 330 GPa by replacement of two to three atoms of Cr by Fe/Mo atoms. The consistency in the derived M_{iso} of $M_{23}C_6$ precipitates in alloy 625 (fcc) and in ferritic steel (bcc) and the agreement with the reported simulated values established the applicability of the developed methodology of using the M_{iso} of the matrix as reference for determining the M_{iso} of the precipitates in a polycrystalline material.

The approach described above has the advantage over the presently used method of indentation modulus determination using separate reference specimens that the tip is always in contact with the specimen. Any change in the tip condition or deviation in stability of the system can be visualized in the image clearly, and hence, no appreciable change in the contact resonance frequency of the matrix during a scan ensures the validity of the experiment. A further advantage is that this approach does not require the orientation of the grain and of the precipitates to be known and it provides M_{iso} of the material, which has higher engineering importance than M_{aniso} . This can be a useful tool for the determination of the modulus of submicron sized precipitates in polycrystalline materials for which experimental modulus values have not been reported so far, as in the case of the $M_{23}C_6$ carbides investigated in the present study.

One of us (A.K.) thanks the Alexander von Humboldt Foundation, Germany, for providing financial support with a postdoctoral fellowship. He is also thankful to Dr. Baldev Raj, Director, Indira Gandhi Centre for Atomic Research (IGCAR), Kalpakkam, for continuous encouragement and support. We are thankful to Mrs. Vani Shankar of IGCAR for providing the specimens and useful discussions.

¹U. Rabe, in *Applied Scanning Probe Methods II*, edited by B. Bhushan and H. Fuchs (Springer, Berlin, 2006), pp. 37–90.

²K. Yamanaka, T. Tsuji, A. Noguchi, T. Koike, and T. Mihara, *Rev. Sci. Instrum.* **71**, 2403 (2000).

³H. Ogi, H. Niho, and M. Hirao, *Acta Mater.* **54**, 4143 (2006).

⁴U. Rabe, S. Amelio, E. Kester, V. Scherer, S. Hirsekorn, and W. Arnold, *Ultrasonics* **38**, 430 (2000).

⁵A. B. Kos and D. C. Hurley, *Meas. Sci. Technol.* **19**, 015504 (2008).

⁶J. T. Vlassak and W. D. Nix, *Philos. Mag. A* **67**, 1045 (1993).

⁷U. Rabe, M. Kopycinska, S. Hirsekorn, J. M. Saldana, G. A. Schneider, and W. Arnold, *J. Phys. D: Appl. Phys.* **35**, 2621 (2002).

⁸G. Simmons, and H. Wang, *Single Crystal Elastic Constants and Calculated Aggregate Properties: A Handbook*, 2nd ed. (MIT Press, Cambridge, MA, 1971).

⁹D. Sieborger, H. Knake, and U. Glatzel, *Mater. Sci. Eng., A* **298**, 26 (2001).

¹⁰F. X. Kayser and C. Strassis, *Phys. Status Solidi A* **64**, 335 (1981).

¹¹T. G. Herold, P. C. Brand, and H. J. Prask, *J. Appl. Crystallogr.* **31**, 929 (1998).

¹²O. L. Anderson, *J. Phys. Chem. Solids* **63**, 909 (1963).

¹³M. X. Zhang and P. M. Kelly, *Acta Mater.* **46**, 4617 (1998).

¹⁴M. Sundararaman, P. Mukhopadhyay, and S. Banerjee, in *Superalloys 718, 625, 706 and Various Derivatives*, edited by E. A. Loria (The Minerals, Metals & Materials Society, Pittsburgh, PA, 1997), p. 367.

¹⁵A. K. Jena and M. C. Chaturvedi, *J. Mater. Sci.* **19**, 3121 (1984).

¹⁶M. X. Zhang and P. M. Kelly, *Acta Mater.* **53**, 1073 (2005).

¹⁷V. Shankar, K. B. S. Rao, and S. L. Mannan, *J. Nucl. Mater.* **288**, 222 (2001).

¹⁸V. Shankar, M. Valsan, K. B. S. Rao, R. Kannan, S. L. Mannan, and S. D. Pathak, *Mater. Sci. Eng., A* **437**, 413 (2006).

¹⁹A. Kumar, V. Shankar, T. Jayakumar, K. B. S. Rao, and B. Raj, *Philos. Mag. A* **82**, 2529 (2002).

²⁰A. Kumar, T. Jayakumar, B. Raj, and K. K. Ray, *Acta Mater.* **51**, 2417 (2003).

²¹J. Y. Xie, N. X. Chen, L. D. Teng, and S. Seetharaman, *Acta Mater.* **53**, 5305 (2005).