Interstitial Solutes and Deformation in Nb and Nb Single Crystals

R. E. Ricker^{*}, D. J. Pitchure^{*}, and G. R. Myneni[‡]

^{}Materials Science and Engineering Laboratory
National Institute of Standards and Technology
100 Bureau Dr. MS 8553, Gaithersburg, MD 20899*

*[‡]Thomas Jefferson National Accelerator Facility
12000 Jefferson Ave., Newport News, VA 23606*

Abstract. Experiments were conducted on high purity single and polycrystalline niobium to determine the influence of low concentrations of interstitial impurities on mechanical properties and to evaluate the feasibility of using measurements of mechanical properties to detect, identify, and quantify the diffusible interstitial content.

Keywords: deformation, elasticity, forming, internal friction, interstitial embrittlement, plasticity, serrated yielding

PACS: 62.20.Fe Deformation and plasticity

INTRODUCTION

The influence of interstitial elements on deformation and fracture of metals and alloys has been studied extensively and reviewed in a number of publications.¹⁻³ Basically, interstitials interact with dislocations to impede plastic flow causing increases in the stresses required for yielding and plastic flow. These interactions can become complex and plastic flow anomalies are frequently observed as illustrated in Figure 1. In Figure 1(a), curve A illustrates the classic behavior expected of a polycrystalline metal or alloy while curve B includes the initial easy glide phase that should occur in single crystals or coarse grained materials. Figure 1(b) illustrates the different types of behavior that are frequently observed when interstitials are present. This figure shows single yield points (curve C), multiple yield points (curve D), serrations (curve E), and yield drops (curve F). These jerky or irregular flow effects are collectively known as Portevin-La Chatelier effects or PLCs.⁴ The classic interpretation for these effects is that, when interstitials are present, there are two flow stresses: one to move dislocations unimpeded by interstitials (the lower yield point) and another to break dislocations free from interstitials that are pinning them in place (the upper yield point).^{1,4,5} If a material is deformed at a temperature and rate such that interstitial diffusion allows the interstitials to move with the mobile dislocations, then complex interactions are possible and switching between flow at the two bounding stresses may occur resulting in yield points or serrations. Since interstitial diffusion is thermally activated, actual behavior will depend on time, temperature, strain rate, and strain as well as interstitial type and concentration.

FIGURE 1. Schematic illustrations of typical plastic flow curves for polycrystalline metals (A), single crystals (B) and interstitial solid solutions (C-F).

Interstitials also influence behavior during forming and the surface finish of the formed part. For a drop in the flow stress to occur, a volume of material traversing the cross-section of the sample must become locally softer than the surrounding material. This region will deform preferentially until it hardens enough to cause deformation elsewhere. If deformation reduces the cross-sectional area faster than the material can work harden, then fracture will occur and result in tears, splits, or cracks in the formed part. Even if fracture does not result, these brief periods of localized deformation will produce locally thinner areas and recesses in the surface. Increases in surface roughness could harm the performance of superconducting radio frequency (SRF) accelerator cavities by creating local hot spots that quench superconductivity.⁶ Therefore, reducing these effects could dramatically reduce or eliminate the need for post-forming polishing treatments and the associated costs of these treatments.

Interstitials also have a negative influence on the thermal and electrical properties of superconductor cavities.⁶ Interstitials cause scattering of unpaired electrons decreasing electrical and thermal conductivity. The residual resistivity ratio (RRR) is frequently used as an indicator of purity and poor RRR values (indicative of increased interstitial contents) have been linked to poor performance of SRF accelerator cavities.⁶ Since RRR measures the total impurity content and does not identify the specific elements of the impurities nor the state of these elements in the host lattice, correlations between measured RRR values and SRF cavity performance should be expected.

The current study is concerned with the mechanical properties of Nb. In particular, Figure 2 shows the range of tensile behavior that was observed for Nb samples with similar RRR values tested at two different strain rates.⁷ Since in the absence of impurities the force required to move a dislocation is nearly independent of speed for these strain rates,⁸ this change in strain rate should have little influence on the stresses of yielding and plastic flow if interstitial impurities were not present. However, there are significant differences shown in figure 2. The objective of this study is to examine the sensitivity of mechanical properties to interstitials and evaluate the feasibility of using mechanical property measurements, such as tensile tests and thermomechanical measurements, to detect, identify, and quantify interstitial content. Since only interstitials that are free to diffuse in the matrix can interact with dislocations, mechanical property measurements will only detect these “diffusible” interstitials. Interstitials bound in second phases, trapped at interfaces, or tied to substitutional

impurities will not be detected by mechanical measurements unless they also produce mechanical relaxations. Virtually all other techniques for determining the interstitial content of metals and alloys determine the total interstitial content and cannot distinguish between interstitials in harmful (diffusible) or benign (trapped) forms. The development of interstitial concentration measurement techniques based on mechanical properties would enable partitioning of the interstitial content over these forms. This would result in reducing the scatter typically observed in studies of the influence of interstitials on properties and enable better investigation of the influence of different processing treatments on interstitial concentrations and SRF cavity performance.

FIGURE 2. Range of plastic flow behavior in uniaxial tensile tests for RRR 375 niobium at two different strain rates ($5.6 \times 10^{-4} \text{ s}^{-1}$ and $1.0 \times 10^{-3} \text{ s}^{-1}$).¹⁶

Interstitial Impurities in Nb

The interstitials of concern in Nb SRF cavities are the elements C, O, N, and H. The reduction of oxide ores with C frequently results in C and O interstitials in metals such as Nb. Heat treatments in air can result in O and N absorption and C absorption may occur if organic solvents or lubricants are not properly cleaned off the surface before heating. The uptake of O and N during heat treatments has been a long-standing concern in the SRF community.

While H is an extremely mobile interstitial in Nb with a strong influence on the deformation and fracture, the SRF community has not been as concerned with the effects of H due to the low partial pressures of H_2 gas in the SRF cavity processing environments. However, Nb is an active metal that will spontaneously react with water or water vapor to produce H at high partial pressures. The passivating (continuous) surface oxide film seals the active Nb metal from exposure to water preventing this reaction, but conditions that break or remove this film in the presence of water will result in H uptake as the water is reduced on the surface of the metal according to reactions of the form,

where the values of the variables x and y depend on the stoichiometry of the oxide produced by the reaction. The free energy changes for these reactions are large (e.g. $\Delta G = -1765$ kJ/mol for Nb_2O_5) and assuming an activity of one for Nb and water in this reaction indicates that these reactions can produce hydrogen at fugacities as large as 2.13×10^{25} Pa (2.1×10^{20} atm) at room temperature.^{9,10} Therefore, processing steps such as grinding, welding, polishing, electro polishing, and etching that remove the protective oxide in the presence of water or water vapor will result in the spontaneous reduction of water molecules to form adsorbed H atoms on the surface of Nb metal.

The equilibrium fugacity or activity of the H_2 produced by these reactions exceeds the solubility limit for H in Nb. This could result in the formation of H_2 blisters or Nb-H phases.¹¹⁻¹³ It also exceeds that of the processing environments, and H_2 gas evolution should prevent the actual H activity on the surface from reaching these high theoretical equilibrium values. However, the adsorbed H atoms initially produced by this reaction must recombine to form H_2 molecules, and in solutions nucleate gas bubbles, before it can leave the surface. The relatively slow kinetics of recombination and bubble nucleation compared to reduction of adsorbed water molecules will result in significant H activities and absorption. Fortunately, these reactions also produce Nb oxides that can cover the surface sealing the underlying metal from water, but these oxides will also retard or block H out-gassing. The extent of H absorption will depend on the relative kinetics of these processes and the stability of the repassivating oxide in the processing environment.

Hydrogen produced by the reduction of water on the surface of Nb will rapidly diffuse into Nb even at room temperature. Figure 3(a) compares the diffusion coefficients in the literature for H, C, N, and O over a range of temperatures.¹⁴⁻¹⁶ This figure shows that, at room temperature, the H diffusion rate is several orders of magnitude greater than any of the other interstitials and that temperatures over 1700°C are required for C, N, and O to diffuse this rapidly. Figure 3(b) shows the time required for a 3.0 mm thick Nb sheet to reach 5 % and 95 % of saturation at different temperatures.¹⁶ This figure shows that significant absorption can occur in a matter of minutes at room temperature. Of course, desorption will occur just as quickly if the surface oxide film is not a barrier. Therefore, this interstitial impurity could be very important in understanding the effects of processing variables on the performance of SRF cavities.

FIGURE 3. Diffusivities for interstitial impurities as a function of temperature (a) and estimated times to reach 5% and 95% of the H saturation content for 3 mm thick Nb sheet (b).

EXPERIMENTAL

The objective of this study is to survey different mechanical property measurement and analysis techniques and evaluate the feasibility of using them to detect, identify, and quantify the diffusible interstitial content of Nb. Two different types of mechanical properties measurements were evaluated: (1) uniaxial tensile tests, (2) dynamic thermomechanical tests. The details of the equipment and methods used for these tests are described in other publications.^{7,18-20} The uniaxial tensile tests were conducted at room temperature using standard tensile testing apparatus.¹⁶ Data from different batches of pure Nb for SRF production were examined and tests were conducted on single crystal Nb samples cut from a coarse-grained ingot. Standard processing and testing methods used at the Jefferson Accelerator Facility, described previously,⁷ were used except as noted in the presentation of results. Two types of dynamic thermomechanical tests were used to measure elastic modulus and anelastic relaxations: (1) sinusoidal loading with continuous variation of temperature and (2) square wave strain relaxation/recovery experiments.¹⁸⁻²⁰ For the sinusoidal tests, the samples were loaded in 3-point bending over a fixed range of strain at a frequency of 1.0 Hz while the temperature was varied continuously at 1.0 °C per minute typically. The strain and temperature limits were varied staying below the yield strength of the material and within the temperature range of the equipment (-150 °C to 600 °C). The square wave tests were also conducted in 3-point bending, but they were conducted at 5 fixed temperatures: -100 °C, -50 °C, -25 °C, 0 °C, and 25 °C. For these experiments, the stress was cycled at 600 s intervals between 0 and 40 MPa with the strain monitored and measured. Samples of polycrystalline high purity Nb for SRF cavity production and single crystals were examined.

RESULTS

The results of uniaxial tensile tests on 3 Nb single crystal samples cut from the same ingot with the same crystallographic orientation are shown in Figure 4(a). While the compositions of these samples were initially identical, they were subsequently processed differently. The first one was processed in the manner normally used to fabricate SRF cavities. The second was processed in the same manner except that it was sliced from the ingot with electrical discharge machining (EDM). The third was process in the same manner at the first, but then given a post-processing heat treatment in vacuum at 1250 °C with Ti present to keep the partial pressure of the reactive interstitial elements low. Figure 4(a) shows that EDM slicing lowered the yield strength and the strain-to-failure compared to sample processed in the normal manner while the vacuum heat treatment lowered the yield strength and increased the strain-to-failure. Examination of the flow curves in Figure 4(a) indicates no obvious evidence of PLC effects beyond the initial yield drop at the onset of yielding. However, fitting a smooth curve to the plastic flow regions of the tensile curves and then plotting the residuals as shown in Figure 4(b) shows that the vacuum treatment that increased the strain-to-failure also significantly lowered the magnitude of the

oscillations in the plastic flow stress about the mean line of fit compared to the sample processed in the normal manner. This figure also shows that these oscillations appear to be composed of a relatively small number of simple harmonic oscillations with clearly defined periods and frequencies. While the stiffness and operational characteristics of the loading apparatus will influence these oscillations and may add oscillations of their own, these results show: (i) that the testing machine cannot be responsible for all of the oscillations (therefore, some of these oscillations must be due to variations in the flow stress), and (ii) that the vacuum bake-out must have removed some or all of the features responsible for the oscillations.

FIGURE 4. The results of tensile tests at a strain rate of $6.7 \times 10^{-5} \text{ s}^{-1}$ on 3 Nb single crystal samples cut from the same ingot at the same crystallographic orientation, but processed differently to illustrate the effects of processing on strength and ductility in (a) and on the oscillations in the flow stress during plastic flow in (b).

The magnitude distributions of these oscillations in the plastic flow stress were quantified by forming cumulative distribution functions and probability distribution functions of the oscillations about the mean line of fit to the flow curve as shown in Figure 5. Examination of this figure shows that the vacuum heat treatment resulted in significantly reducing the range and standard deviation of the stress oscillations about the mean line of fit in agreement with the data shown in Figure 4(b). However, these plots also show that while the oscillations for the vacuum heat-treated material appears to be from a single distribution of random events, the distribution for the standard processed material appears to be a combination of a similar distribution of random events and oscillations between flow stresses on either side of the mean line of fit.

FIGURE 5. The cumulative distribution functions (a) and probability density functions (b) of the residuals produced after fitting the plastic flow stress to a smooth line.

The periodic nature of these oscillations in the flow stress was examined by fast Fourier transforms (FFTs) and time series analyses using commercially available software. The results of this analysis are shown in periodograms of Figure 6 as the spectral power of the oscillations ($\text{MPa}^2/\text{unit strain}$) as a function of the period of the cycle in units of strain (m/m). Since there is a 10x change in scale between Figure 6(a) and 6(b), these figures show that power density of the noise in the flow stress for the standard SRF processed material is more than an order of magnitude greater than that for the same material given a vacuum heat-treatment. In addition, these figures show that this noise tends to occur at well-defined frequencies or over narrow frequency bands. The magnitude of this noise is related to the presence of interstitials; however, it is less clear how strain rate, diffusivity, and the properties of the tensile frame relate to the periodic nature and magnitude of these oscillations and how they might be used to evaluate the types and/or quantities of interstitials present.²¹

FIGURE 6. The periodograms or spectral power density as a function of period for the stress oscillation about the mean line of fit for single crystal Nb processed by the standard SRF procedures (a) and following a vacuum heat-treatment (b) (Note: 10x change in scale).

The results of the dynamic thermomechanical tests are shown in Figures 7 and 8. Figure 7 shows the results of temperature scans on the loss modulus (E'') of different Nb samples. Since this technique measures the phase angle between stress and strain while a sinusoidal load is applied, the elastic modulus is measured as a complex quantity ($E^* = E' + iE''$) with the imaginary component (E'') known as the loss modulus and the ratio (E''/E') is sometimes referred to as the internal friction.³ Anelastic

relaxation peaks will occur in the loss modulus at temperatures where the period of the loading frequency and the time constants for microstructural relaxations are equal.³ For dislocation-interstitial interactions of the Snoek type,³ the temperature of this peak is determined by the diffusion constant and the frequency of interstitials jumping between interstitial sites. The magnitude or strength of the peak will be related to the concentration of the interstitials and the orientation of the sample with respect to the crystallographic direction of the interstitial jumps (texture for polycrystalline samples). Figure 7(a) shows the results for the temperature range for Snoek type interactions with O, C, and N interstitials and the results for 2 different batches of polycrystalline Nb (labeled P and K) tested as received. In this figure, the calculated temperatures for these peaks using literature data on the diffusion coefficients of C, O, and N are indicated below the curves. This figure illustrates how this technique can be used to identify the diffusible interstitials present and estimate their concentrations. Calibration against samples with known concentrations and crystallographic or texture corrections may reduce uncertainties to acceptable levels. Figure 7(b) shows the results of similar measurement on single crystals samples over the region where H or O-H interactions may occur. Since this type of instrument relies on the boiling of liquid nitrogen to provide cooling, -150 °C (123 K) is the lower testing limit of this instrument. Calculations based on the hydrogen diffusion coefficients in the literature indicate that Snoek type peaks for H may be as low as -200 °C (73 K).¹⁴⁻¹⁶ However, the literature also indicates that H may form complexes with itself or O that slows diffusion and may produce loss modulus peaks in this temperature region. While there are some small indications of peaks in these scans, they were not clearly defined nor reproducible.

FIGURE 7. The imaginary component of the elastic modulus (loss modulus) measured during temperature scans over the regions of interaction peaks between interstitials and dislocations: (a) O, C, and N peaks after background subtraction for two batches of pure Nb (labeled P and K) tested as received, (b) scans on single crystals over the region for H and H-O interaction peaks.

FIGURE 8. Anelastic strain relaxations during square wave loading of Nb single crystal samples given different treatments (a) and at different temperatures (b). Note that the strain scale is greatly expanded to show the relaxations.

The results of the square wave anelastic strain relaxation tests are shown in Figure 8. Figure 8(a) shows the anelastic relaxations that occurred in strain during the hold time at the peak load for Nb single crystal sample given different treatments and Figure 8(b) shows the effect of temperature on the relaxation rate of a single crystal sample. These figures show that exponential relaxations are occurring at these stress levels and temperatures. That is, if all of the microstructural features (n) that can move in a thermally activated manner in response to the applied maximum stress (σ_c) are relaxing with time constants (τ_n) and magnitudes ($\varepsilon_n(\sigma_c)$), then the strain during the hold at the maximum stress level ($\varepsilon_c(t)$) can be expressed as,

$$\varepsilon_c(t) = \varepsilon_0 + \sum_n \varepsilon_n(\sigma_c) [1 - \exp(-t/\tau_n)] \quad (2)$$

where t is the time since the stress was increased to σ_c during the loading cycle. Unfortunately, the literature indicates that there may be over 20 independent relaxations in Nb.²² Therefore, detailed analysis of these transients is beyond the scope of the present work; but theoretically, the amplitude of each relaxation will be directly related to the concentration of the relaxing feature and the contribution of each individual feature with respect to the sample orientation. The amplitudes of the curves in Figure 8(a) varied with the processing conditions. Assuming that the heat treatments given these samples and the subsequent handling did not appreciably alter the dislocation density, this observation indicates that the interstitial content of the samples varied with these treatments. Also, since the temperature of internal friction peaks due to cold work (dislocations) vary little with loading frequencies,³ their activation energies must be small and their corresponding time constants (τ_n) should not vary appreciably with temperature. Therefore, it would appear that the primary relaxation contributing to the trend shown in Figure 8(b) is due to the presence of interstitials.

DISCUSSION

Different mechanical property measurement and analysis techniques were examined to evaluate their potential for detecting, identifying, and quantifying diffusible interstitials in Nb and the influence of SRF processing conditions on interstitial uptake and performance. A review of the literature indicated that the interstitials of concern are C, O, N, and H and the reasons for including H in this list were justified by reviewing H interactions with Nb. This included calculation of the equilibrium fugacity for H evolution on Nb by reaction with water at room temperature and calculation of H absorption (or desorption) times at representative temperatures. This review also found that the mechanical properties of Nb are sensitive to interstitial impurities and that pure Nb processed for SRF cavity production exhibits behavior in tensile tests that indicates the presence of interstitial impurities and that impurity content varies with processing conditions.

The experiments demonstrated the sensitivity of mechanical properties to diffusible interstitials in this material and the results were consistent with the hypothesis that SRF processing conditions influence the diffusible interstitial content. All three types of mechanical property measurements examined demonstrated sensitivity to the presence of interstitial impurities. Additional research and development will be required before any of the three could be used to quantify the diffusible interstitials present with reasonable uncertainties. The research and development required varies with each measurement approach, but all 3 require calibration and verification against standards with known interstitial contents.

Analysis of the tensile flow curves found that the oscillations in the load or stress occur over a relatively narrow range of frequencies or periods and indicated that the magnitude of these oscillations may be related to diffusible interstitial concentration. Since the period of the oscillations is related to the strain rate and the interstitial diffusion rate, it should be possible after subtraction of equipment noise and background peaks to relate the period and height of each peak to an interstitial and its concentration. However, our current scientific understanding of the origin of these effects does not contain enough detail to allow accounting for the effects of experimental variables such as sample size, sample shape, grain size, crystallographic orientations (texture), load frame dynamics, background noise, stress and strain rates on the periods and magnitudes of these peaks. Thorough research and quantification with a low-noise tensile frame over a range of temperatures and strain rates should enable the development of sufficient understanding to achieve this objective.

The dynamic thermomechanical measurements were also found to be sensitive to processing conditions and interstitial content. For continuous sinusoidal loading while increasing temperature, peaks were found in the imaginary component of the elastic modulus (loss modulus) or internal friction at the predicted temperatures for diffusible C, O, and N interaction with dislocations. The magnitude or strength of these peaks was found to vary with processing conditions indicating sensitivity to concentration. While the theoretical understanding of these peaks is well developed,¹ quantitative concentration estimates will require the development of calibration methods, calibration standards, and evaluation of sensitivity to experimental variables. Since this technique involves exposing samples to temperatures where diffusible interstitials

become mobile and 3-point bending is surface sensitive, this measurement technique could introduce or remove the interstitials it is attempting to measure. This could be avoided by using higher frequencies or special environmental chambers. Another potential solution would be to use a square wave loading cycle and measure the relaxation times directly from the resulting strain transients. The constant temperature strain relaxation/recovery experiments were conducted to evaluate this possibility. The theoretical basis for the relaxations in these measurements is the same as that for the loss modulus or internal friction peaks, but all of the relaxations are occurring simultaneously. Ideally, all of the relevant time constants would be predetermined and computer curve fitting would be used to estimate the magnitudes (concentrations) for each time constant (type of diffusible interstitial). The loading period and testing temperature can be optimized for a particular relaxation. Changing the loading period and analyzing the changes that occur over repetitive cycles can be used to subtract relaxations with long time constants. Changing the testing temperature can be used to identify activation energies or to create separation between relaxations with different activation energies. That is, while there are a large number of microstructural relaxations that may contribute to the relaxations measure in these experiments, there are analytical techniques that can be used to evaluate them.

CONCLUSIONS

Three different mechanical property measurement techniques were examined to evaluate their potential for detecting, identifying, and quantifying the diffusible interstitial content of Nb samples. All three approaches showed sensitivity to interstitials that varied with SRF processing conditions indicating sensitivity over the range of concentrations required in a study of the influence of processing conditions on interstitial content and SRF cavity performance. While all 3 demonstrated qualitative capabilities, quantitative measurements based on any of the techniques will require additional research and development to reduce uncertainties to acceptable levels. Time series or spectral (FFT) analysis of plastic flow during tensile tests would require the most research to enable the unambiguous identification of interstitial type and concentration. The development of quantitative concentration measurements based on either of the dynamic thermomechanical measurement techniques will require considerably less research, but considerable development, verification, and calibration against samples with known interstitial contents will be required for valid quantitative measurements with either technique.

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DISCLAIMER

While commercially available equipment and software were used for these studies, their use does not constitute an endorsement by NIST or the Jefferson National Accelerator Facility nor should it be taken to imply that these are the best available for this purpose.

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