Anelasticity of Polycrystalline Yttrium at Low Concentrations of H and O

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Abstract. In order to clarify the nature of the numerous thermally activated processes occurring in yttrium, the anelastic relaxation spectrum of polycrystalline samples has been investigated between 1.1 and 600 K in the kHz range, by varying the concentration of interstitial hydrogen and oxygen and in presence of plastic deformation. Besides the main dissipation peak around 300 K due to the formation /dissolution of H pairs and the peak at liquid He temperature attributed to H tunnelling, four processes have been observed. The processes below 300 K can be interpreted by mechanisms involving hydrogen trapped by oxygen, and dislocations dragging interstitial H, whilst the large relaxation observed around 450 K has to be ascribed to oxygen motion in solid solution.

1. INTRODUCTION

Rare earths (Sc, Y, Lu...) have attracted great interest for their capability to retain large amounts of hydrogen in solid solution and in form of hydride with the exciting feature of observing a metal-insulator transition [1]. This transition is accompanied by spectacular changes in the optical properties: recently it has been observed that the yttrium hydride becomes transparent in the stoichiometric range between 1.8 and 2.9 atoms H per atom Y [2].

Although the anelasticity of Y has been extensively studied in last years, only the relaxation process observed around room temperature has been unambiguously interpreted [3]. High sensitivity internal friction measurements in yttrium have revealed an unexpectedly rich relaxation spectrum [4], even in samples which are generally considered pure in literature. The nature of these processes has not been clarified yet, but their appearance denotes that in "pure" yttrium several types of imperfections play a role which cannot be ignored if a full understanding of the physical properties of this element is required.

We report a study of the relaxation processes observed in pure polycrystalline yttrium in the temperature range 1.1-600 K. Evidence is given that the detected processes are correlated to the presence of interstitial hydrogen, oxygen, hydrogen-impurity complexes, and dislocations interacting with gaseous impurities.

2. EXPERIMENTAL

The samples were rectangular bars ($\sim 40 \times 4.4 \times 2$ mm³), cut from different plates of polycrystalline yttrium purchased from the Ames Laboratory, and here labelled as Y0, Y1, Y2. The possible variations of total amount of the interstitial gaseous impurities, which in the "as received" state was less than 2000 at ppm, were monitored during the experiments by the determination of the residual resistivity ratio RRR.

In the thermal treatments for H-outgassing and for reducing the dislocation density the samples were wrapped in zirconium foils and annealed at 1000 °C in vacuum in the 10^{-8} mbar range, and cooled to room temperature in less than 10 min.

The elastic energy loss (Q^{-1}) measurements were carried out on both cooling and heating at a rate lower than 1 K/min by electrostatically exciting the samples on different flexural vibration modes in the frequency range 1-33 kHz.

3. RESULTS AND DISCUSSION

3.1 The relaxation spectrum below room temperature

Figure 1 shows the anelastic relaxation spectra of sample Y0 in the "as received state" as cut from a plate (RRR=34), and sample Y1 after the 1st (RRR=27) and 3rd (RRR=26) annealing at 1000 °C. Five peaks can be resolved in the 1-300 K temperature range, here labelled as P2, P3, P4, P5 and P6 with increasing temperature. It is now accepted that P2 is due to H tunnelling [4, 5] and P6 to the formation/dissolution of H pairs [3]; instead, the nature of the other peaks has not been convincingly clarified yet.

A comparison between the two relaxation spectra indicates that: i) in sample Y0, where we expect the lowest O, N content (RRR=34) and an appreciable dislocation density due to cutting, the H tunneling peak P2, the H-pair peak P6 and peak P5 are predominant; ii) in sample Y1, the 1st annealing suppresses the processes P2 and P6, ascribed to hydrogen with certainty, reduces P5 and enhances P3 and P4. The RRR decreased from 52 in the "as received" state down to 27, indicating O contamination. After the 2nd and 3rd annealing, also P3 and P4 decrease due the progression of the H-outgassing.

Interstitial hydrogen and dislocations were certainly always present in samples Y0 and Y1. Indeed, due to the strong affinity of the rare earths to hydrogen, unwanted quantities of this element can remain in the material even after UHV annealings. Dislocations are produced not only by cutting (sample Y0) but also during the temperature variations, as in hcp polycrystals the anisotropic thermal expansion produces plasticity [6]. Thus, one would be inclined to interpret the intermediate temperature processes by a relaxation mechanism which involves dislocations and interstitial atoms [7]. However, the following considerations suggest that P5 is caused to a mechanism involving dislocations: i) the process is more developed in sample Y0 where the dislocation density is higher than in Y1 due to cold work; ii) a relaxation, with similar features, has been observed by Kappesser et al. [8] in plastically deformed polycrystalline Y; iii) the broadness of the relaxation curve, which is 100% broader than a single Debye peak, and the pre-exponential factor are not compatible with point defect relaxation.

The mechanism of peak P5 process should be similar to those reported in transition metals (Nb, Ta, V) and attributed to the relaxation of dislocations dragging interstitial H [7]. According to this picture, P5 can be attenuated but not completely eliminated because a few residual at ppm H persist after the annealings and the dislocation multiplication occurs during temperature variations [6].

Instead, stress-induced redistribution of point defects has to be invoked for P3 and P4 as suggested by us in a previous investigation [4]. The experimental curves of these two processes can be fitted by a nearly single Debye theoretical curve. In fact, the value of the activation energy E_w assumed for the theoretical curve, is nearly coincident with that E_s deduced by the peak shift with frequency and the attempt frequency τ_0^{-1} is typical of atomic vibrations (Table I).

Processes P3 and P4 could be due to a classical over-barrier hopping of H between tetrahedral and/or octahedral sites in the environment of a gaseous immobile impurity, more likely O(N). This hypothesis is supported by the fact that P3 and P4 are more pronounced in sample Y1 which has a larger oxygen content. A peculiarity (not shown in the figures) of the intermediate-temperature spectrum is that the heights of P4, P5 (and P3 to a less extent) are systematically lower on cooling than on heating; instead, thermal cyclings do not affect process P2 at all. This fact denotes that relaxations P3, P4 and P5 are measured in conditions of non-equilibrium; indeed, the two peaks P4 and P5 occur in the temperature range where resistivity measurements [1] indicated a transition (≈ 180 K) between mobile and immobile H in the time scale of the usual experiments.

TABLE I
Relaxation Parameters of the Processes

Process	τ_0 (s)	E_s (eV)	E_w (eV)	E_s/E_w
P3	3×10^{-13}	0.15	0.15	1
P4	5×10^{-12}	0.21	0.18	1.2
P5	10^{-19}	0.45	0.23	2
P6	1×10^{-13}	0.60	0.50	1.2
P7	$10^{-12}-10^{-14}$	0.75	0.70	1.1

Figure 1: Anelastic relaxation spectra on heating of sample Y0 at 1.8 kHz in the as-received state (curve 1, RRR=34) and of sample Y1 at 2 kHz after the 1st (curve 2, RRR=27) and 3rd annealing (curve 3, RRR=26) at 1000 °C.

Figure 2: Elastic energy dissipation measured on heating above 300 K of sample Y2 (6.5 kHz, RRR=27): after a rapid cooling from 1000°C (curve 1); after several heating-cooling cycles (curve 2); and after 0.4 % plastic deformation (curve 3). Curve 4 represents the energy dissipation on heating of sample Y0 at 1.8 kHz in the as received state.

3.2 The relaxation spectrum above room temperature

The extension of the Q^{-1} measurements up to 600 K (in samples Y0 and Y2) reveals the thermally activated process P7. The phenomenology of P7 is complex and can be described as follows. The process reaches the highest magnitude (Fig. 2, curve 1) only in the 1st heating run after the UHV annealing (1h, 1000 °C followed by cooling to room temperature in less than 10 min), decreases of about 50% in the subsequent runs until becomes nearly stable with proceeding the heating-cooling cycles up to 550 K (curve 2). The peak height of the 1st heating can be restored by repeating the annealing at 1000 °C followed by rapid cooling. Heating up to 600 K and cooling at 5 K/min restores only partially the peak height. Curve 4 of sample Y0 (having a lower O(N) content, RRR = 34) could be retraced during the heating and cooling measurements.

A surprisingly good theoretical fit of the nearly stable relaxation curves (curve 2) can be achieved in terms of a single-time Debye process with the value of the parameter E_w coincident with the activation energy evaluated by the peak shift E_s (Table I). This fact and the value of the attempt

frequency which is of the order of magnitude expected for point defects, suggest that process P7 is caused by stress-induced redistribution of interstitial oxygen. This type of impurity in Y has a solubility limit of about 3000 at ppm at 550 K [9]. This is just about the amount of the gaseous impurity content (where oxygen is dominant) of our samples, and thus the instability of P7 with thermal cyclings would find its explanation in the O precipitation. The attribution of P7 to point defect relaxation is corroborated by the observation that 0.4% plastic deformation in sample Y2 does not affect the magnitude of P7 but introduces a background which strongly increases with temperature. As regards the type of relaxation, the simple Snoek effect must be ruled out because in the hcp crystals octahedral and tetrahedral sites remain equivalent after application of any type of stress. Therefore, two possible mechanisms are proposed for P7: the redistribution of the O-atoms between the octahedral and tetrahedral sites which are non-equivalent, or the formation and dissolution of O-O pairs similarly to what proposed for H in P6. Further investigation is needed to clarify the mechanism.

The onset of dissipation above 450 K, more marked in sample Y0 which contains dislocations due to cutting, could be the tail of a peak, possibly a Snoek-Koester relaxation resulting from dislocations dragging interstitial oxygen.

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References

- [1] Vajda P., Hydrogen in Rare-Earth Metals, Including RH_{2+x} Phases, Handbook on the Physics and Chemistry of Rare Earths, Vol. 20, K.A. Gschneidner, Jr. and L. Eyring Eds. (Elsevier Science B.V., 1995).
- [2] Huiberts J.N., Griessen R., Rector J.H., Wijngaarden R.J., Dekker J.P., de Groot D.G. and Koeman N.J., *Nature* **380** (1996) 231-234.
- [3] Vajda P., Daou J.N., Moser P. and Remy P., *Sol. State Commun.* **79** (1991) 383-386.
- [4] Cannelli G., Cantelli R., Cordero F., Trequattrini F. Anderson I.S., and Rush J.J., *Phys. Rev. Lett.* **67** (1991) 2682-2685.
- [5] Leisure R.G., Schwarz R.B., Migliori A., Torgeson D.R., Svare I., and Anderson I.S., *Phys. Rev. B* **22** (1993) 887-892.
- [6] Youssef M.H. and Bordoni P.G., *Phil. Mag. A* **67** (1993) 883-895.
- [7] Nowick A.S. and Berry B.S., *Anelastic Relaxation in Crystalline Solids* (Academic Press, New York, 1972).
- [8] Kappesser B., Wipf H., Barnes R. G., and Beaudry B.J., *J. Alloys and Compounds* **211**, (1994) 249-252.
- [9] Fromm E. and Gebhardt E., *Gase und Kohlenstoff in Metallen* (Springer, Berlin, 1976) pp. 364-368.