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TRAPPING OF OXYGEN BY ZIRCONIUM IN DILUTE
NIOBIUM-ZIRCONIUM ALLOYS

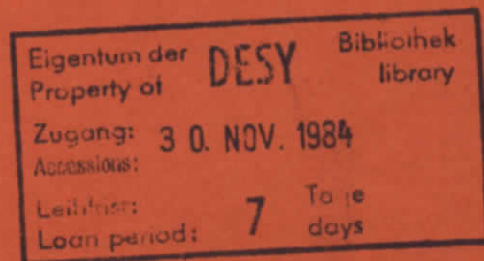
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TRAPPING OF OXYGEN BY ZIRCONIUM IN DILUTE
NIOBIUM-ZIRCONIUM ALLOYS

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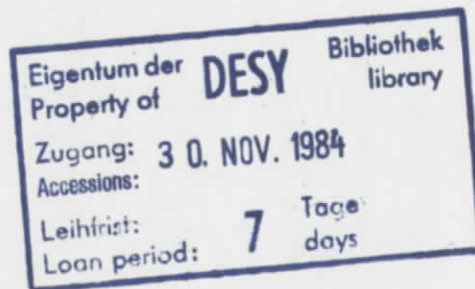
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ABSTRACT

We have shown by X-ray absorption spectroscopy that oxygen is trapped by Zr in dilute NbZr alloys. Oxygen occupies the nearest octahedral sites next to a Zr atom. There is one O atom trapped by each Zr atom. The angular information needed for the exact location of the O is obtained from a "lens" effect in the EXAFS which is observed when the O shadows a Nb back-scatterer. At 1075 °C and below there is no precipitation of zirconium oxides in Nb.

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The mechanical properties of refractory metals and alloys are severely influenced by the presence of dissolved oxygen and of oxides. The mobility and the concentration of the dissolved oxygen and the formation of oxides can be strongly affected by substitutional impurities (see, e.g. Hasson and Arsenault ¹). In this paper, we would like to present an example of how the interaction of impurities and oxygen can be investigated by X-ray absorption spectroscopy. The system under consideration is a dilute NbZr alloy with 2 at % Zr which was loaded with 2 at % of oxygen. The questions of interest are: does the Zr trap the oxygen atoms and, if so, where is the oxygen located; how many O atoms can one Zr atom trap; do Zr oxides precipitate in the niobium lattice?

It is well established that the extended X-ray absorption fine structure (EXAFS) can be used to determine interatomic distance and coordination numbers ^{2,3}. The near edge structure provides projected densities of electronic states and can be used as a fingerprint technique to monitor changes in the valence of an atomic species ⁴.

The standard EXAFS data evaluation uses the fact that the Fourier transform of the EXAFS is related in a simple way to the pair correlation function ^{2,3}. On the other hand, it is not possible, in general, to determine the exact lattice site of an atomic species just on the basis of an interatomic distance. To do so, higher correlations which contain angular information are needed. One of us has recently found a way to use a special type of higher correlation in EXAFS using three atoms in a row to obtain the missing angular information ⁵. When an atom L is located on the line

joining a backscatterer atom B and absorber atom A (shadowing of B by L), this atom L works as a "lens" for the photoelectron wave travelling between A and B and back again. The lens alters both the amplitude and the phase of the photoelectron wave and this can be detected. The effect is applicable even to hydrogen acting as a lens although hydrogen itself shows no backscattering on its own⁵. This is due to the fact that the forward scattering amplitude is substantially larger than the backward scattering amplitude. In this paper we would like to apply this effect to determine the lattice site of oxygen trapped by Zr in Nb.

High purity niobium and zirconium (99.999 % purity) was degassed in ultra high vacuum. A dilute Nb alloy with 2.0 at % Zr was prepared in a cold crucible under purified argon and rolled into foils of 22 μm thickness. One strip of this foil was loaded with oxygen at 1075 $^{\circ}\text{C}$ in a quartz tube. Following the loading the quartz tube was quenched into water at room temperature. In order to ensure a good thermal coupling of the alloy to the water the quartz tube was filled with one atmosphere of high purity helium gas prior to the quenching. The amount of oxygen dissolved in the niobium alloy was determined from the increase in weight and was found to be 2.0 at % O. Note that the limit of solubility of oxygen in the α -phase at 1075 $^{\circ}\text{C}$ is 2.3 at %⁶.

The X-ray absorption measurements were done at the beam line RÜMO of the Hamburger Synchrotronstrahlungslabor. A Si (220) double crystal monochromator was used to obtain a monochromatic beam. The harmonics were removed by detuning the monochromator. A zirconium foil between the second and a third ionisation chamber was used to achieve a continuous energy cali-

bration of the spectrometer. Further details of the set-up are described in references 4 and 5. The scattering amplitudes and phase shifts needed in order to analyze the X-ray absorption data were taken from appropriate model systems. These were metallic Nb and Zr, ZrO_2 and K_2HfO_4 . These systems were measured in addition to the NbZr and NbZrO alloys.

Figure 1 shows the near edge structure at the K edge of Zr in NbZr, NbZrO and ZrO_2 . The K edge of Zr in Nb is lower in energy by 8 eV compared to tetravalent Zr in ZrO_2 . The edge of Zr in NbZrO is located between these two. Since the X-ray absorption near-edge structure (XANES) is determined mainly by the Zr cell and the first neighboring cells, due to the short range of the electronic wavefunctions, this result is already a clear qualitative indication that the oxygen in a NbZr alloy is trapped near to the Zr atoms. The exact position of the oxygen can be found from the EXAFS.

Figure 2 shows the Fourier transforms of the EXAFS of Nb, NbZr and NbZrO. We first look at the lattice distortion produced by the Zr in Nb. The Zr atom, which is larger than the Nb atom, expands the lattice and the first and second neighbor contributions, separated in the pure Nb, merge into one shell in the case of NbZr. We have performed a detailed analysis of the first three shells in NbZr. Since the scattering phases and amplitudes vary only slowly with r , we have taken the scattering phases for a pair Zr-Nb from Zr metal⁷. The backscattering amplitude for Nb was transferred from metallic niobium. The results of the fit are given in table 1. The zero of kinetic energy E_0 was chosen at the first inflection point in the edge (figure 2) at 17988.0 eV for Zr, 17987.6 eV for NbZr

and NbZrO and 18976.3 eV for Nb. The free parameters of the fit were the distance r_j , the corresponding E_o and the Debye-Waller factor. The coordination numbers were held fixed at the known values for a bcc lattice.

The quality of the fit for the first and second shell is shown in figure 3. A Zr atom in Nb displaces the first shell of Nb atoms by +0.06 Å towards larger distances, whereas the second and third shells are within the accuracy of the data at their positions in pure Nb.

We now proceed with the analysis of the NbZrO . As is shown in figure 2, the first and second shells of NbZr are split in different shells and there appears an additional peak below the Nb shells which is due to the backscattering from oxygen. This peak was analyzed by means of K_2MoO_4 as a model compound. According to Gatehouse et al.⁸ the oxygen atoms form a regular tetrahedron around the Mo with an interatomic distance Mo-O of (1.76 ± 0.01) Å. The analysis of the oxygen peak in figure 2 gives an interatomic Zr-O distance of (2.04 ± 0.03) Å and a coordination number of (1.1 ± 0.2) . Figure 4 shows what we believe is the position of the trapped oxygen. It is between the Zr atom and its second nearest Nb neighbor. This is the octahedral site \bar{O}_1 closest to the Zr atom. Note that the irregular structure of the octahedrons in the bcc lattice allows for a second octahedral site \bar{O}_2 , between the Zr and its third nearest Nb neighbor which is further away from the Zr by a factor $\sqrt{2}$. The EXAFS shows unambiguously that the octahedral site \bar{O}_1 is occupied by the oxygen whereas \bar{O}_2 is not occupied. Indeed, the peak denoted by Zr-O-Nb in figure 2 evolves from one of the six second nearest Nb neighbors of Zr, shifted to larger distances by the oxygen. Although this contribution arises from only one Nb neighbor it is nevertheless clearly discernable. This is a consequence

of the "lens" effect mentioned above. The trapped oxygen is the lens which magnifies the photoelectron wave that emerges from the Zr atom and is scattered back by one of the 6 second nearest Nb neighbors. When the atom acting as a lens is oxygen this amplitude is magnified by a factor of almost two as observed in NiO⁵. A comparison of the second shell contribution in Nb with the Zr-O-Nb contribution in NbZrO (figure 2) is in good agreement with this number. An analysis of the Nb-O-Zr peak gives an interatomic distance of (3.64 ± 0.02) Å compared to 3.30 Å in pure Nb⁹. This means that the oxygen expands this distance by 0.34 Å. Note that the fit again results in a large change in E_o of 10 eV similar to the value found in NiO from reference 5. If the lattice site \bar{O}_2 were occupied (perhaps in addition) we would expect an enhancement of the third nearest neighbor contribution. This is not observed in the experiment as can be seen in figure 2. An occupation of the \bar{O}_2 site would probably also result in a larger Zr-O distance because the Zr- \bar{O}_2 distance is already 2.33 Å in the undistorted Nb lattice.

We have shown in this paper that X-ray absorption spectroscopy can be used to investigate the trapping of gases by impurity atoms in dilute alloys. In particular, we have found that oxygen is trapped by Zr in Nb when the sample is quenched from 1075 °C to room temperature. The near edge structure in the absorption coefficient can alone be used to decide whether trapping occurs or not. The details of the trapping are revealed by the EXAFS. In the present case it turns out that one of the nearest octahedral sites \bar{O}_1 next to a Zr atom is occupied by oxygen. The next nearest octahedral sites \bar{O}_2 are not occupied. The angular information needed to locate the oxygen is obtained by means of the lens effect. At

an oxygen to zirconium ratio of 1 to 1 in the alloy, and charging with oxygen at 1075 °C we have found one oxygen atom next to each zirconium atom. Under the present conditions of oxygen charging no precipitation of zirconium oxides in niobium occurs.

Acknowledgements

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9. The phase shift modification produces a change in the interatomic distance which is smaller than the quoted error when E_0 is a free parameter in the fit (see reference 5).

TABLE 1:

j =	1	2	3
r_j (Å) in <u>Nb</u> Zr	2.914 ± 0.01	3.30 ± 0.01	4.63 ± 0.03
δE_{Oj} (eV)	-3.8	+3.4	-5.1
N_j	8 !	6 !	12 !
$\delta \sigma_j^2$ (Å ²)	-0.0007	+0.0004	+0.0010
r_j (Å) in Nb	2.854 \AA	3.295 \AA	4.660 \AA

Table 1: Interatomic distances r_j , correction δE_{Oj} to the zero of kinetic energy and Debye-Waller factors for the first three neighbors in dilute NbZr and interatomic distances r_j in pure niobium metal at 77 K.

FIGURE CAPTIONS

Figure 1: Near edge structure at the K edge of Zr in NbZr (*), NbZrO (-) and ZrO₂ (+).

Figure 2: Fourier transforms of the EXAFS $\chi \cdot k^2$ of Nb (-), NbZr (+) and NbZrO (*) with 2.0 at % Zr and 2.0 at % O.

Figure 3: Fit of the EXAFS for the first and second Nb shells in NbZr (2 at % Zr) (+ experiment, - fit).

Figure 4: The two octahedral sites \bar{O}_1 and \bar{O}_2 around a substitutional Zr atom in Nb. The oxygen is trapped in the site \bar{O}_1 . The site \bar{O}_2 is not occupied.

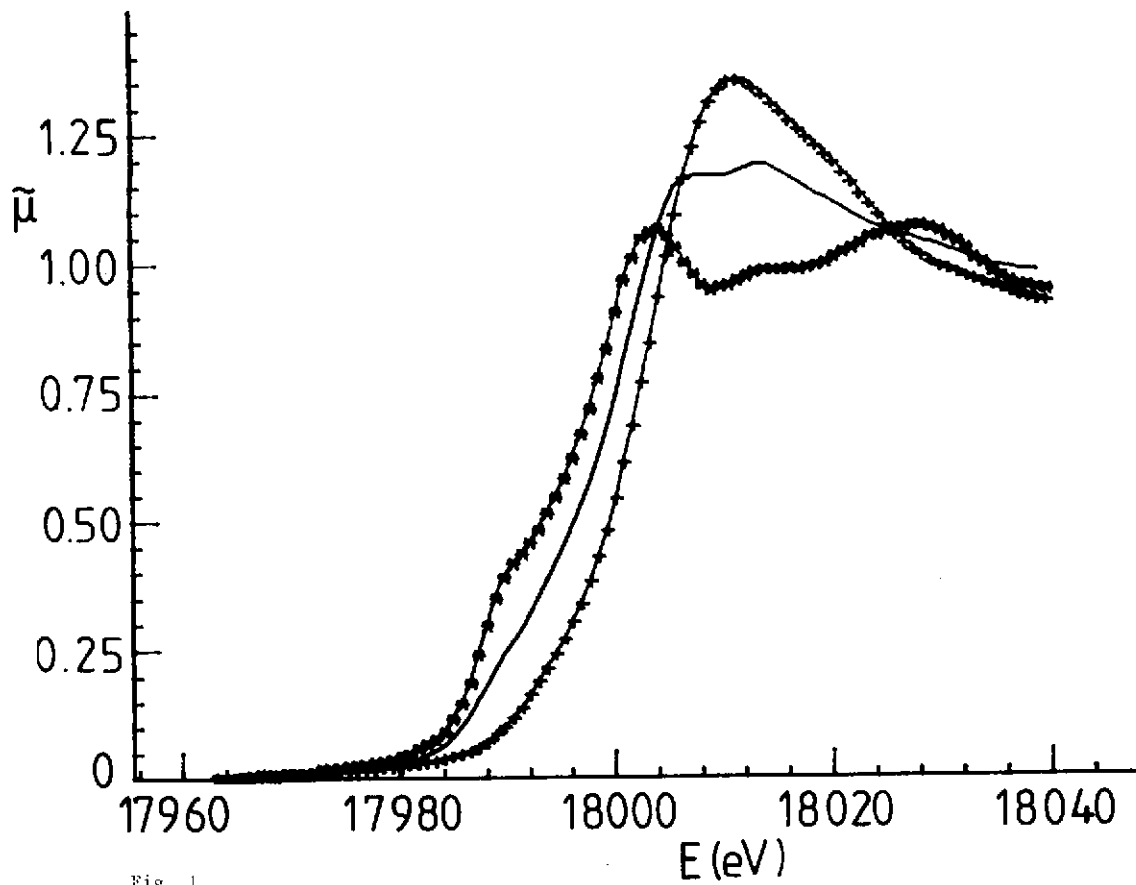


Fig. 1

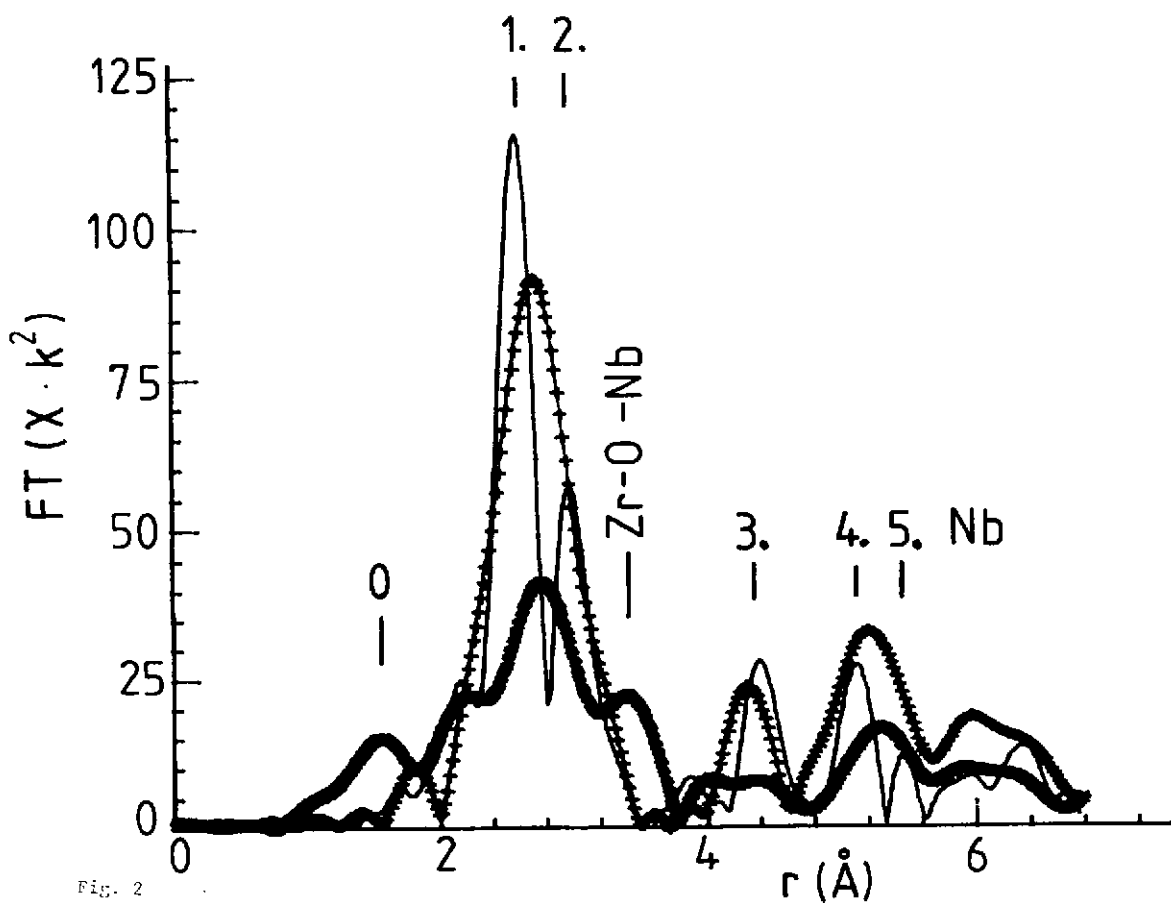


Fig. 2

