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EXAFS Study of the Local Atomic Order in Ti_2AlX ($\text{X}=\text{Nb}$, Mo) B2 Intermetallic Compounds

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Abstract. Extended X-ray absorption fine-structure (EXAFS) has been used to study the local atomic order in Ti_2AlMo and Ti_2AlNb in the B2 phase. It is found that the Mo and Nb atoms have different behaviors. Whereas the Ti_2AlMo alloy is ordered as a pseudo-B2 structure in which the Mo and Al atoms are localized on one site and Ti atoms on the other, the Ti_2AlNb alloy exhibits a more disordered behavior since the Nb and the Ti atoms are distributed on both sites. EXAFS experiments allowed us to quantify the fraction of Nb on each site in Ti_2AlNb as well as the bond lengths in both alloys.

1. INTRODUCTION

Intermetallic alloys and particularly titanium aluminides are attractive materials for aerospace applications because of their low density and high temperature strength and their good oxidation resistance. However, they generally suffer of brittleness at room temperature. It has been shown that the addition of a 4d transition element like Nb or Mo could improve the low temperature ductility. Indeed, the systems based around the composition Ti_2AlNb may exhibit a large ductility when the so-called O-phase (orthorhombic) is present in the alloy [1]. However, the main phase present in the ternary phase diagram is ordered on a bcc lattice [2]. Conventional diffraction shows that the structure is of the B2 type (CsCl) where two sites (corner and center of the cubic unit cell, see Fig.1) are occupied by different atomic species. Since three elements have to fill two sites, the composition of each site is not defined and several possibilities may be assumed. Furthermore, the composition domain of stability of the B2 phase is very large; a fact that complicates the analysis since the exact stoichiometry is not known. The Ti-Al-Mo system is similar to Ti-Al-Nb since a large B2 domain exists around Ti_2AlMo , although no orthorhombic phase is reported.

The determination of the site occupancies and more generally of the ordering behavior in intermetallic alloys is of great importance since it may influence a number of macroscopic properties. Several techniques are available to work out the site occupancies, one of them, the Atom Location Channelling Enhanced Microanalysis [3](ALCHEMI) is commonly used for this purpose. The Extended X-ray Absorption Fine Structure (EXAFS) which is a tool for studying the local atomic environment can provide this information but it is also possible to extract much more relevant parameters like interatomic distances and Debye-Waller (DW) factors. In this paper we report on the use of the EXAFS technique on Mo-K and Nb-K edges in order to study the local order.

Fig. 1 : B2 structure.
○ : A site; ● : B site.

2. EXAFS PRINCIPLE

The principle of EXAFS relies on the behavior of the electron ejected with a kinetic energy from a central atom after an X-ray photon has been absorbed. The outgoing wave function of the ejected electron is then backscattered by the surrounding atoms giving rise to a system of constructing or destroying interferences depending on the wavelength of the electron and the distances to the neighbouring atoms. The EXAFS effect is detected as an oscillatory structure in the X-ray-absorption coefficient and contains quantitative information about the local environment of the absorbing atom. This information appears as structural parameters in the plane-wave EXAFS equation together with other quantities which depend on the electronic structure of the material,

$$k \cdot \chi(k) = -S_0^2 \sum_i \left(\frac{N_i}{r_i^2} \cdot |f_i(\pi, k)| \cdot e^{-2r_i/\lambda(k)} \cdot e^{-2\sigma_i^2} \cdot \sin(2kr_i + \phi_i(\pi, k)) \right) \quad (1)$$

where k is the magnitude of the photoelectron wave number, $|f_i(k)|$ is the backscattering amplitude for each of the N_i neighbouring atoms of the i^{th} type at a distance r_i from the excited one, σ_i is the Debye-Waller factor, $\phi_i(\pi, k)$ is the total backscattering phase shift experienced by the photoelectron and $e^{-2r_i/\lambda(k)}$ is a term taking into account the inelastic losses with $\lambda(k) = \Gamma/k$ being the electron mean free path. S_0^2 is a reduction factor that takes into account inelastic losses inside the central absorbing atom.

3. EXPERIMENTAL AND ANALYSIS PROCEDURES

3.1 Experimental

The samples have been processed by an arc melting technique under argon atmosphere using high purity starting metals. No heat treatment was applied to the Ti_2AlMo alloy while the Ti_2AlNb sample was annealed at 1140°C during 1 hour and water-quenched to retain only the B2 phase. For EXAFS experiments in transmission mode, small square samples of 10 mm x 10 mm were mechanically polished up to a 50 μm uniform thickness in order to obtain a Mo-K or Nb-K edge jump value around the unit. The surface damage was subsequently removed.

Our EXAFS spectra for both Ti_2AlMo and Ti_2AlNb samples have been recorded at LURE on the DCI storage ring (beam line XAS1 equipped with a Si (331) channel-cut monochromator) at liquid nitrogen temperature to reduce thermal disorder effects. The experimental data were collected in the transmission mode over 1000 eV beyond the Mo-K edge and over 700 eV beyond the Nb-K edge. The quality of the spectra is quite good as it can be shown on figure 2.a.

3.2 Analysis procedure

The raw data were background subtracted using a linear function and the oscillatory part $\chi(E)$ was extracted by fitting the atomic background absorption with a fifth-order polynomial. The $\chi(E)$ was then normalized to the threshold step with the Lengeler-Eisenberger method and converted to k -space through the usual relation : $k = (2m(E-E_0)^{1/2})/\hbar$ where E_0 is the threshold energy.

The $\chi(k)$ spectrum was then Fourier transformed to obtain a radial distribution function (RDF) (cf. fig.2b) and the signal from the two first shells was extracted by filtering the RDF with a suitable window and then Fourier back-transformed. It must be recalled here, that,

because the first nearest neighbouring (1nn) and the second nearest neighbouring (2nn) shells are very close together in the bcc crystal, it is not possible to separate these two contributions in the RDF. Simulations are then performed using the software package developed by Michalowicz [4]. This software uses McKale [5] theoretical phase and backscattering amplitudes.

Fig. 2.a : Mo-K and Nb-K XAS spectra from Ti_2AlMo and Ti_2AlNb alloys

Fig. 2.b : Radial distribution functions after Fourier transform of data in figure 2.a.

4. EXPERIMENTAL RESULTS AND DISCUSSION

4.1 Ti_2AlMo alloy

Knowing that the diffraction data exhibit a B2 structure, it was assumed that all the Ti atoms are located on one site (A) and the Al and Mo atoms fill the other one (B). This is also consistent with ALCHEMI experiments [6]. Furthermore, it is postulated that the Mo and Al atoms are randomly distributed on site B. Consequently, the local environment of the Mo atoms consists in a three shells model involving 8 Ti atoms as 1nn and 3 Al and 3 Mo as 2nn. Since the number of independent parameters N_{ind} is limited by the finite experimental data k range, these coordination numbers were maintained constant during the fit as well as the S_0^2 ($= 1$) and Γ ($= 0.8$) structural parameters quoted in eq.1. Then, the fitting procedure requires two floating parameters per shell : r_i , σ_i . Results of the best fit are shown in Fig.3 and summarized in table A.

We first note that the Mo-Al and Mo-Mo distances of the 2nn are not identical and are different from the lattice parameter value obtained for this alloy from X-ray diffraction ($a = 3.17 \text{ \AA}$). However, the mean distance found here is equal to $3.18 \text{ \AA}$, a value close to the lattice parameter if one considers the experimental uncertainty ($\approx 0.02 \text{ \AA}$). Secondly, the 1nn are peaked at the distance expected from the crystallographic data ($a\sqrt{3}/2 = 2.75 \text{ \AA}$) but with a larger Debye-Waller factor than the 2nn. The discrepancy in distances between the EXAFS and the X-ray diffraction data can be easily understood since the latter gives an average lattice parameter value while the former is a local measurement around the central atom. Consequently, it explains why the Debye-Waller factor is found to be rather high for Mo-Ti pairs. From these experimental results we conclude that a large static disorder exists in this compound. It could be speculated for example that Ti atoms form a perfect cubic sublattice while Mo and Al atoms

are randomly displaced from the expected perfect positions localized at the centers of the cube. However, other assumptions could be made and would be consistent with the experimental results. It is not yet possible to conclude about the exact configuration because it would require to study not only pair correlations, but also higher order correlations (triplet or more). Conceptually this information exists in the EXAFS signal because multiple scattering effects are included in, but one needs a more sophisticated theory to extract such informations. Nevertheless, such static disorder means that the atomic planes are highly corrugated and this is likely to impede the dislocations motion. High Peierls stress and high yield are therefore expected to occur in this compound.

Fig. 3 : Fit of the $k\chi(k)$ of the 1nn and 2nn in Ti_2AlMo

Table A : Results of the fit of the 1nn and 2nn neighbors from Mo-K in Ti_2AlMo

Shell	Atoms	N	$r (\text{\AA})$	$\sigma (\text{\AA})$
1	Ti	8	2.75 ± 0.02	0.080 ± 0.005
2	Mo	3	3.27 ± 0.02	0.070 ± 0.005
3	Al	3	3.10 ± 0.02	0.050 ± 0.005

4.2 Ti_2AlNb alloy

When studying the Ti_2AlNb at the Nb-K edge, it has not been possible to fit the experimental data by using a sublattice occupancy identical to that existing in the Ti_2AlMo alloy, i. e. Ti on site A and Nb and Al on site B. Consequently, it requires to consider a more complex configuration for the atoms that are then mixed on each sublattice. Indeed, it has been found from ALCHEMI experiments performed on a slightly different alloy composition [7] that Nb atoms can fill partially the sites A together with titanium. Hence, if we make the assumption that a site A is occupied by Ti and Nb atoms with a fraction labelled x, then we obtain the following compositions for each sublattice :

$$\begin{aligned} \text{sites A : } & \text{Ti}_{2-x}\text{Nb}_x \\ \text{sites B : } & \text{Ti}_x\text{AlNb}_{1-x} \end{aligned}$$

where x is unknown and has to be determined. It is obvious that two Nb atoms situated on a site A or a site B have different local environment. The EXAFS signal is then an incoherent superposition of the contributions of Nb atoms occupying each kind of sites. Thus, we must take into account the first and second neighbors for each Nb site. These Nb atoms occupying sites A and B see the following environments :

x Nb on sites A :

$$\begin{array}{ll} 1\text{nn} : & \text{Ti}_x\text{AlNb}_{1-x} \\ 2\text{nn} : & \text{Ti}_{2-x}\text{Nb}_x \end{array}$$

$(1-x)$ Nb on sites B :

$$\begin{array}{ll} 1\text{nn} : & \text{Ti}_{2-x}\text{Nb}_x \\ 2\text{nn} : & \text{Ti}_x\text{AlNb}_{1-x} \end{array}$$

However, this scheme yields to a 10 shells model! If we make the supplementary assumption that the $\text{Nb}^{\text{A}}\text{-Ti}^{\text{B}}$ and $\text{Nb}^{\text{B}}\text{-Ti}^{\text{A}}$ pairs are not discernible, and taking into account the fact that in the B2 structure there are 8 1nn and 6 2nn, we can work out the coordination numbers as :

for the first neighbors :

$$\begin{array}{ll} 4(2x^2-3x+2) & \text{Ti atoms} \\ 8(x-x^2) & \text{Nb atoms} \\ 4x & \text{Al atoms} \end{array}$$

for the second neighbors :

$$\begin{array}{ll} 9x-6x^2 & \text{Ti atoms} \\ 6x^2-6x+3 & \text{Nb atoms} \\ 3-3x & \text{Al atoms} \end{array}$$

In this way we have to consider a six shells model, but only one parameter (x) is needed to determine all coordination numbers. The fitting procedure has been performed using typically 13 free parameters ($N_{\text{ind}} = 14$) : x , 6 distances (r_i) and 6 DW factors (σ_i). The best fit was obtained for $x = 0.5 \pm 0.1$ (table B) : it means that niobium atoms are equally distributed on sites A and B. Therefore, the composition of the alloy can be written as :

The experimental spectrum and the best fit obtained are plotted on fig. 4. As in the case of the Ti_2MoAl alloy, the distances do not coincide with the lattice parameter ($a = 3.252 \text{ \AA}$), this result indicates that an important structural disorder also exists in this alloy.

Fig. 4 : Fit of the Nb-K $\chi(k)$ of the 1nn and 2nn in Ti_2AlNb

Table B : Results of the best fit at the Nb-K edge for the 1nn (shells 1,2 & 3)
and 2nn (shells 4, 5 & 6) in Ti_2AlNb

Shell	Atoms	N	r (Å)	σ (Å)
1	Ti	4	2.81 ± 0.02	0.080 ± 0.005
2	Al	2	2.92 ± 0.02	0.040 ± 0.005
3	Nb	2	2.85 ± 0.02	0.060 ± 0.005
4	Ti	3	3.24 ± 0.02	0.150 ± 0.005
5	Al	1.5	3.27 ± 0.02	0.060 ± 0.005
6	Nb	1.5	3.33 ± 0.02	0.090 ± 0.005

Here again we can determine a mean distance value deduced from the obtained 1nn and 2nn distances. In that case, each distance r_i has to be weighted by the coordination number N_i and the results agree well with the expected crystallographic values (Table C) within experimental uncertainties.

Table C : Comparison of the mean interatomic distances determined
from EXAFS experiments with X-ray diffraction measurements

Neighbors	EXAFS $\langle N_i \cdot r_i \rangle$ (Å)	X-ray diffraction
1nn	2.85	2.82
2nn	3.27	3.252

5. SUMMARY AND CONCLUSIONS

The EXAFS analysis of the data recorded at the Mo-K and Nb-K edges in B2 intermetallic alloys shows that a site occupancy can be determined within reasonable uncertainty. Results show that the site composition should be written as $(\text{Ti}_2)^A(\text{MoAl})^B$ and $(\text{Ti}_{1.5}\text{Nb}_{0.5})^A(\text{Ti}_{0.5}\text{Nb}_{0.5}\text{Al})^B$ for the two alloys studied here, respectively. Furthermore, it is shown that the local interatomic distances can, at an atomic scale, differ largely from the averaged values obtained with other techniques. It is worth noting that the existence of such differences in bond lengths should be taken into account in any kind of theoretical calculation or atomistic simulations.

The information contained in a EXAFS spectrum is not limited to the radial distances of the first shells. In principle, by analysing the multiple scattering effects, one should be able to obtain informations about shells lying at higher distances as well as about three atoms correlations [8]. It is also important to cross-check the present experimental results using the Al-K and Ti-K edges. Further works are in progress on these aspects.

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