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Quantitative Thin Film X-Ray Microanalysis of Nb Modified Ti_3Al

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Advanced titanium-aluminum intermetallic alloys (often simply called titanium aluminides) have certain properties which make them potentially attractive as advanced aerospace alloys.[1] In order to utilize these alloys in engineering applications, it is necessary to process the alloys in a variety of ways including casting, hot forming and welding. All of these processes modify the microstructure of the alloy, which in turn directly influences the properties. The key to optimizing the alloy's properties is to control the microstructure by careful control of the processing parameters. Control of the microstructure requires a thorough understanding of the evolution of the microstructure, including elemental partitioning between the various phases which form in the alloy. Analytical electron microscopy (AEM) is an ideal way to characterize the microstructures on a fine spatial scale. Such high spatial resolution microanalysis is required to understand the microstructural evolution in these alloys. In this case, the alloy is a Nb modified Ti_3Al, and the partitioning behavior of interest is between a variety of ternary phases which are produced as a function of alloy cooling rate from a single homogeneous high temperature β phase. The Nb is added to the alloy to enhance its performance, primarily through an improvement in ductility. In this work, the details of the procedure for quantitative analysis of these alloys are presented. The complete details of the phase transformations which occur in this alloy are discussed by Cieslak, et. al.[2]

Background:

To characterize elemental partitioning between phases quantitatively, the details of the microanalytical technique used to characterize the partitioning must be well understood. In the case of thin film x-ray microanalysis, this requires careful attention to the determination of the sensitivity factors used to calculate composition from x-ray intensities, careful examination of the potential for x-ray absorption which might influence the calculated results, and careful consideration of the impact of x-ray spatial resolution for the analysis. In this paper, all of these details will be addressed in some depth. The results presented here are then used in the work of Cieslak, et al.[2] in which the metallurgical details of the study are presented.

Elemental compositions can be determined from x-ray intensities via the Cliff-Lorimer standardless ratio technique[3], which is given here by,

$$
\begin{aligned}
C_{Nb}/C_{Ti} &= k_{NbTi}\,(I_{Nb}/I_{Ti}),\\
C_{Al}/C_{Ti} &= k_{AlTi}\,(I_{Al}/I_{Ti}),\\
C_{Ti} + C_{Al} + C_{Nb} &= 1,
\end{aligned}
\qquad (1)
$$

where C is composition (wt.%), I is background corrected x-ray intensity and k is the sensitivity factor. The values of k can be determined experimentally from standards or calculated from first principles. The value of the sensitivity factors will be examined experimentally and by calculation in this paper.

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The standardless ratio equations are valid only in the absence of x-ray absorption or fluorescence. To determine if absorption effects are significant, Goldstein, et. al.[4] has established the criterion,

$$\{0.5\, |\mu/\rho)^i - \mu/\rho)^j|\, d_l\} < 0.05, \qquad (2a)$$

where $\mu/\rho)^i$ and $\mu/\rho)^j$ are the mass absorption coefficients of the elements in the specimen (all permutations and combinations of Ti, Al and Nb must be considered here) and d_l is the x-ray path length through the specimen enroute to the detector. The x-ray path length is defined by the specimen/electron beam/detector geometry and is given by,

$$d_l = [\sin\beta / \cos(\theta_e - \beta)]\, \rho\, t\,, \qquad (2b)$$

where β is the angle between the beam and the foil surface (a complex function of detector azimuthal angle and two specimen tilt axes), θ_e is the detector elevation angle, ρ is the specimen density and t is the specimen (foil) thickness at the point of analysis. As written, the absorption criterion indicates the thickness at which absorption will alter the quantitation results by 5% (relative).

X-ray spatial resolution can be examined by several different techniques. The easiest procedure is to use the single scattering model approximation[4],

$$b = 625\, (Z/E_0)\, (\rho/A)^{1/2}\, t^{3/2}\ \text{(cm)}, \qquad (3)$$

where b is the exit beam diameter (cm), Z is atomic number, A is atomic weight, E_0 is the beam energy (keV), ρ is density (g/cm^3) and t is thickness (cm). To calculate the diameter of the x-ray generation volume the beam diameter is added in quadrature to b. To include 90% of the electrons, as is considered in Eq. 3, the beam diameter is 1.82 d_p, where d_p is the full width at half maximum (FWHM) beam diameter.[5] The most accurate procedure is to use Monte Carlo techniques[6]. Both approaches are used in the present work and the results compared.

Experimental:

The alloy used in this study contained 63.90 Ti - 14.80 Al - 21.30 Nb (wt.%), with a few ppm trace levels of Fe (600 ppm), N (60 ppm) and O (600 ppm). The material used in this study was in the form of a hot rolled sheet and contained a duplex microstructure of the α_2 phase (ordered hexagonal, $D0_{19}$) and β (bcc). As shown in Figure 1, a bright field TEM micrograph of the alloy, the matrix is predominantly α_2 with β at the grain triple points. The α_2 phase is large enough to determine the composition with the electron probe microanalyzer (EPMA). The composition of the α_2 is 65.4 Ti - 14.6 Al - 20.0 Nb (wt.%), and the phase is compositionally homogeneous. The α_2 was used as a thin film standard to determine the Cliff-Lorimer sensitivity factors and to examine absorption effects in the alloy.

Thin foils of the alloy were produced by using standard techniques for preparing self-supporting 3 mm disk specimens. The foils were thinned to electron transparency by jet polishing 100 µm thick disks in a 5% sulfuric acid in methanol solution at 16 volts. The AEM was performed in a JEOL 2000FX (at 200 kV) equipped with a Tracor-Northern 5402 EDS analyzer. The high take-off angle (72°) 7.5 µm Be window detector was used. The detector had an active area of 30 mm^2 and was 3 mm thick.

The k-factor determination and absorption experiments were performed in thin areas of the α_2 phase. A series of point analyses was made with a 50 nm beam in regions of the foil of various thickness. X-ray intensities were background corrected and integration was done over the full peak. The thickness of the foil was determined by a variety of techniques including the contamination spot technique, the differential x-ray absorption technique and the integrated x-ray count rate technique.[7] A comparison of the thickness determination results will be given later in this paper.

Results and Discussion:

Determination of k-factors: Figure 2 shows the results of the k-factor versus thickness. The results are plotted as log k vs. t, as suggested by Horita, et al.[8]. The Horita analysis is intended to produce the k-factor for an infinitely thin foil, in which any absorption effects are eliminated. The true zero thickness k-factor is given by a least squares extrapolation to zero thickness. The value of k_{NbTi} is 2.91 +/- 0.18 (2 σ counting error). In this case, the slope of the k versus t curve is zero, indicative of no absorption effect for thicknesses up to 280 nm. The value of k_{AlTi} at zero thickness is 1.07 +/- 0.04 (2 σ counting error). The change in k_{AlTi} with thickness is slight, increasing about 7.5% over 200 nm. The increase in k_{AlTi} with thickness is just detectable above the noise due to counting statistics.

The k-factors for these elements have also been calculated, by using the algorithm of Carr and Romig.[9] The k-factors are calculated by,

$$k_{ATi} = [(Q\omega a)_{Ti}\, A_A] \,/\, [(Q\omega a)_A\, A_{Ti}] \times [\varepsilon_A/\varepsilon_{Ti}], \tag{4}$$

where, Q is the ionization cross-section, ω is the fluorescence yield, a is the fraction of the K line which is K_α , A is the atomic weight, and ε is the detector efficiency. Here, all k's are referenced to Ti, so Eq. 4 must be written for k_{AlTi} and k_{NbTi} (the subscript A is for Al or Nb).

The cross-section model used is that given by Powell,[10] as modified by Brown.[11] The expression is,

$$Q = [6.51\text{X}10^{-21}/E_cU]\ n\ b\ \ln(cU), \tag{5}$$

where E_c is the critical ionization energy, U is the overvoltage (E_c/E_o, where E_c is the critical excitation energy and E_o is still the beam energy), n is 2 for K-shell excitations and b and c are given by 0.52 + 0.0029Z and 1.0, respectively (Z is atomic number).

The fluorescence yield is from Burhop,[12] and given by,

$$[\omega/(1-\omega)]^{1/4} = A + BZ + CZ^3, \tag{6}$$

where A, B and C are 0.015, 0.0327 and $-0.624\text{X}10^{-6}$ as given by Bambynek.[13]

The values of a are calculated by using the fitted equations of Schreiber and Wims[14] and are 0.882, 0.978 and 0.838 for Ti, Al and Nb, respectively.

The detector efficiencies are determined by calculating the absorption of each type of x-ray as it passes through the Be window, Au contact film and Si deadlayer. The efficiency calculation also considers transmission of x-rays through the detector. For these calculations, the mass absorption coefficients of Thinh and Leroux[15] are used. The Be window is 7.5 µm thick and the Au film and Si deadlayer are assumed to be 20 nm and 100 nm thick, respectively, as suggested by Zaluzec.[16] As indicated earlier, the detector here is 3 mm thick. The calculated detector efficiencies are 0.951, 0.714 and 0.988 for Ti, Al and Nb, respectively. For a complete description of the detector efficiency calculation, the reader is referred to the paper of Carr and Romig.[9]

With the above formulations and input data, the calculated k-factors are:

$$k_{AlTi} = 1.05 \qquad \text{and} \qquad k_{NbTi} = 3.07.$$

These values compare quite favorably to the measured values given above. The calculations match the measured values within the 2 standard deviation counting error.

X-Ray Absorption: As shown in Figure 2, x-ray absorption effects are small. No measurable effect was observed for Nb-Ti and only a small effect for Al-Ti in the ternary alloy. Approximately a 7.5% increase in k_{AlTi} was observed at a thickness of 200 nm. The thicknesses given in Figure 2 were measured by a variety of techniques as described by Romig and Carr.[7] The thicknesses were determined with the contamination spot technique and by differential x-ray absorption of the Nb K and Nb L lines. (The full details are given in the original references. [7,17]) The thicknesses determined by each technique agreed within 10 to 15% relative, with the contamination spot techniques typically giving slightly larger values. Further, all of the thicknesses were self consistent with the change in x-ray count rate with thickness. (In thin regions of the foil, where single scattering is appropriate one would expect the count rate to increase linearly with thickness.) Hence, it is reasonable to assume that the reported thicknesses are accurate to at least 10% relative.

The thin film criterion at 5% (Eq. 2a) was applied to the data collected from the α_2 phase. Using the absorption coefficients of Thinh and Leroux[15], and the specimen/detector geometry for the 2000FX, the 5% criterion is violated for thickness greater than 160 nm. This calculation is again consistent with the experimental observations.

Other elements, such as Cr and V, have also been considered as alloy additions to Ti_3Al. At the concentration levels used in these alloys (10 to 15 wt.%), absorption effects are similar to those observed in the Nb-modified material. The Cr and V modified alloys violate the thin film criterion (Eq. 2a) at foil thicknesses of approximately 160 nm.

X-Ray Spatial Resolution: X-ray spatial resolution has been examined in this alloy by using both the simple single scattering model, as given in Eq. 3 and by Monte Carlo modeling.[6] For foil thicknesses of up to approximately 350 nm, the results of the single scattering model and the Monte Carlo model are in excellent accord. A tabulation of values is given in Table 1. At larger foil thicknesses, the single scattering model begins to overestimate the beam spreading. However, at these large thicknesses the absorption correction becomes uncertain and reliable quantitative analysis is not possible.

Conclusions:

1. Reliable quantitative thin film x-ray microanalysis is possible on Nb-modified titanium aluminides.

2. At 200 kV, the sensitivity factors for standardless quantification are:

   Experimental: $k_{AlTi} = 1.07$ (+/- 0.04) $k_{NbTi} = 2.91$ (+/- 0.18)

   Calculated: $k_{AlTi} = 1.05$ $k_{NbTi} = 3.07$

3. X-ray absorption is not significant at the 5% level until the foil thickness (with the α_2 composition) exceeds approximately 160 nm. This calculation is consistent with experimental observation, in which the k_{AlTi} was observed to increase by approximately 5% at a thickness of 200 nm.

4. For reasonable foil thicknesses (less than 350 nm), beam spreading can be accurately calculated by the single scattering model. Spatial resolution can be calculated by adding the beam diameter (1.82 FWHM for 90% of electrons) and the spreading factor in quadrature.

TABLE 1

Beam Spreading as Calculated by Equation 3:

	....................90% Spot Size*.................						
Thickness	1 nm	2 nm	5 nm	10 nm	20 nm	50 nm	100 nm
10 nm	1.0	2.0	5.0	10	20	500	100
20 nm	1.2	2.1	5.0	10	20	50	100
50 nm	2.6	3.1	5.5	10	20	50	100
100 nm	6.7	6.9	8.3	12	21	50	100
200 nm	19	19	19	21	28	53	102
500 nm	74	74	74	75	77	89	124

*The diameter encompassing 90% of all the electrons in a Gaussian probe is 1.82 x FWHM. Most instrument manufacturers report FWHM as spot size.

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Figure Captions:

FIG. 1 - TEM Bright Field Micrograph of Ti-14.8Al-21.3Nb (wt.%).
Diffraction pattern inserts show the $[11\bar{2}0]$ α_2 zone (left) and the [110] β zone (right).

FIG. 2 - Relationships between k_{AlTi} and k_{NbTi} and foil thickness. Extrapolated value to infinitely thin foil is shown at t=0, where $k_{AlTi} = 1.07$ +/- 0.04 and $k_{NbTi} = 2.91$ +/- 0.18 (error from 2σ counting statistics). The error in thickness is approximately 10% relative. Measured k factors are consistent with calculations: $k_{AlTi} = 1.05$ and $k_{NbTi} = 3.07$ Data shows absence of absorption for Ti and Nb in the alloy and slight (5% at 200 nm) absorption of Al.

Figure 1

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Diffraction pattern inserts show the [11$\bar{2}$0] α_2 zone (left) and the [110] β zone (right).

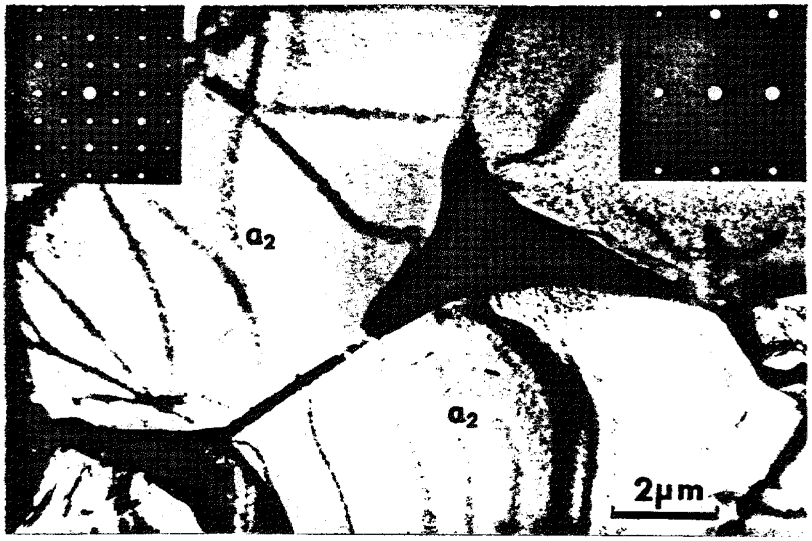

Figure 2

Relationships between k_{AlTi} and k_{NbTi} and foil thickness. Extrapolated value to infinitely thin foil is shown at t=0, where $k_{AlTi} = 1.07 \pm 0.04$ and $k_{NbTi} = 2.91 \pm 0.18$ (error from 2σ counting statistics). The error in thickness is approximately 10% relative. Measured k factors are consistent with calculations: $k_{AlTi} = 1.05$ and $k_{NbTi} = 3.07$ .Data shows absence of absorption for Ti and Nb in the alloy and slight (5% at 200 nm) absorption of Al.