APPENDICES

APPENDIX A

Basic Backscattering Spectrometry for Thin Film

Film thickness can be determined from the spectra. The analysis begins by consideration the proportion of energy of backscattered particle by i^{th} element at any depth x below the surface $\left(E_1^i\right)$ and that of incident particle $\left(E_0\right)$,

$$K_i = \frac{E_1^i}{E_0}, \qquad [39]$$

where K_i is kinematic factor for i^{th} element which given by

$$K_i = \left[\frac{\left(M_2^2 - M_1^2 \sin^2\theta\right)^{1/2} + M_1\cos\theta}{M_1 + M_2}\right]^2, \qquad [39]$$

where θ, M_1, M_2 are scattering angle, masses of the incident particle and target atom, respectively, as shown in Figure A.1.

Since M_1, E_0 and θ are known, M_2 and the target element are determined. Number of atoms per unit area for i^{th} element $(Nt)_i$ can be calculated using equation

$$(Nt)_i = \frac{A_i\cos\theta_1}{Q\Omega\sigma_i}, \qquad [39]$$

where A_i, θ_1, Q, Ω and σ_i are integrated counts in the peak due to scattering from the i^{th} element in a thin film, incident angle, integrated charge deposited on the sample during the operation, solid angle subtended by the detector and the probability that a material will cause a collision, respectively.

σ_i can be calculated from equation

$$\sigma_i = \left(\frac{Z_1 Z_2 e^2}{4E}\right)^2 \left(\frac{4\left[\left(M_2^2 - M_1^2 \sin^2\theta\right)^{1/2} + M_2\cos\theta\right]^2}{M_2 \sin^4\theta \left(M_2^2 - M_1^2 \sin^2\theta\right)^{1/2}}\right), \qquad [39]$$

where Z_1, Z_2, e and E are atomic number of incident particle, atomic number of backscattered particle, electronic charge and energy before scattering, respectively. Then, average stoichiometric ratio for compound film (A_mB_n) can be calculated from equation

$$\frac{\mathrm{n}}{\mathrm{m}} = \frac{N_\mathrm{B}}{N_\mathrm{A}} = \frac{A_\mathrm{B}}{A_\mathrm{A}} \cdot \frac{\sigma_\mathrm{A}}{\sigma_\mathrm{B}}. \qquad [39]$$

The calculation of number of atom per unit volume for i^{th} element (N_i), requires knowledge of film density (ρ_{AB}). For this case, i = A, B, the calculations are given by

$$N_\mathrm{A}^\mathrm{AB} = \frac{\mathrm{m}\rho_\mathrm{AB}\mathrm{N}_0}{M_\mathrm{AB}};\ N_\mathrm{B}^\mathrm{AB} = \frac{\mathrm{n}\rho_\mathrm{AB}\mathrm{N}_0}{M_\mathrm{AB}} \qquad [39]$$

where N_0 is Avogadro's number and M_{AB} is molecular weight of compound A_mB_n. Finally, the film thickness (t) can be calculated from proportion of $(Nt)_i$ to N_i by the equation

$$t = \frac{(Nt)_\mathrm{A}}{N_\mathrm{A}^\mathrm{AB}} = \frac{(Nt)_\mathrm{B}}{N_\mathrm{B}^\mathrm{AB}}. \qquad [39]$$

In this study, coating film was simulated as multilayer. The values of m and n were varied in each layer. The total thickness was then calculated by combining of all layers. Computer simulation is appropriate to use in the analysis. Overlapping of the peaks is contributed by the elements containing in the alloy. The computer simulation was used to separate the integrated peak counts of each element contributing and overlapping the total counts.

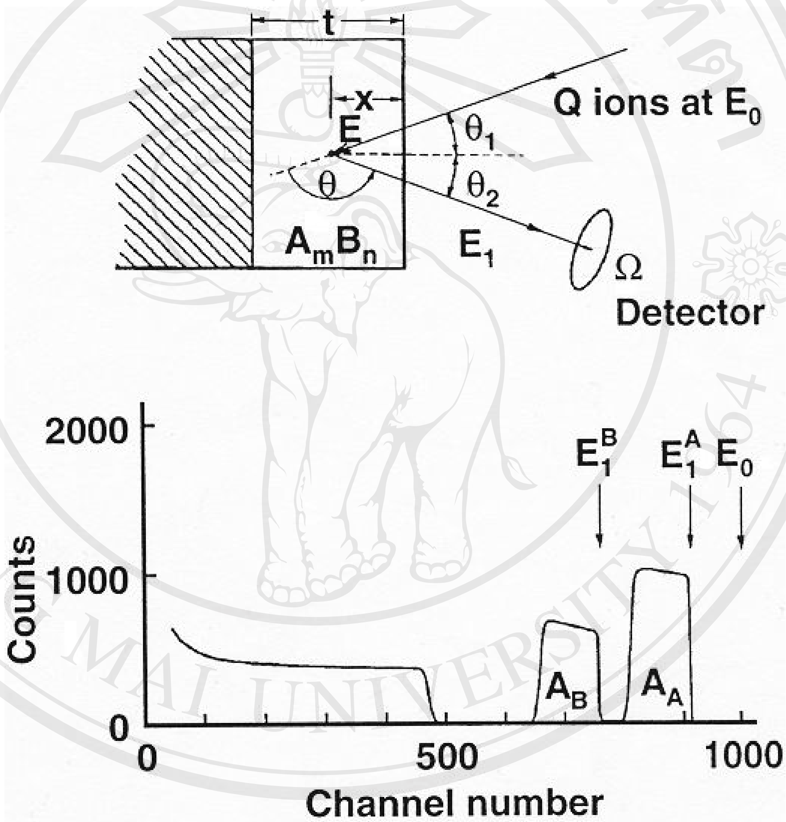

Figure A.1 Basic backscattering spectrometry for thin film [39].

APPENDIX B

XRD Reference Pattern

Table A.1 XRD reference pattern of the phases in these studies.

Compounds	JCPDS Code	2θ (degree)	Intensity (%)
TiAl	05-0678	38.958 45.546 65.495 79.631	100.0 60.0 60.0 60.0
TiB_2	35-0741	44.438 34.133 61.106	100.0 55.0 27.0
Ti_3Al	09-0098	40.894 38.784 53.888 71.716	100.0 70.0 60.0 60.0
	14-0451	41.167 72.032 77.926	100.0 30.0 30.0
Ti_2AlN	18-0070	40.022 13.009 76.372	100.0 80.0 80.0
Ti_2N	23-1455	36.884 43.716 61.435	100.0 65.0 40.0
Ti_3N_{2-x}	40-0958	40.740 38.697 37.426	100.0 92.0 55.0
$TiN_{0.3}$	41-1352	39.710 37.507 52.101	100.0 22.0 19.0
$TiN_{0.76}$	87-0626	42.665 36.727 61.923	100.0 96.5 45.7
$TiN_{0.9}$	31-1403	42.633 36.697 61.890	100.0 4.0 4.0
TiN	06-0642	42.612 36.806 61.982	100.0 75.0 55.0

Table A.1 (Continued)

Compounds	JCPDS Code	2θ (degree)	Intensity (%)
$Ti_4Al_2C_2$	29-0095	39.546	100.0
		13.009	39.0
		34.022	19.0
$Ti_{5.73}C_{3.72}$	77-1089	41.789	100.0
		35.937	98.8
		36.116	40.5
$Ti_6C_{3.75}$	79-0971	41.789	100.0
		35.937	99.0
		36.116	41.0
Ti_8C_5	72-2496	41.822	100.0
		35.967	99.8
		36.141	42.2
TiC	01-1222	41.989	100.0
		36.041	75.0
		60.899	50.0
	06-0614	41.404	100.0
		35.744	80.0
		60.241	50.0
	74-1219	39.134	100
		33.721	90.1
		56.541	49.1
$TiC_{0.2}N_{0.8}$	76-2484	42.580	100.0
		36.655	75.6
		61.793	44.8
$TiC_{0.3}N_{0.7}$	42-1488	42.352	100.0
		36.461	46.0
		61.444	40.0
$TiC_{0.7}N_{0.3}$	42-1489	42.024	100.0
		36.181	59.0
		60.930	46.0
TiO	08-0117	43.363	100.0
		62.965	50.0
		37.329	45.0
	02-1196	42.612	100.0
		36.650	80.0
		61.799	80.0
$(TiO_{1.2})_{3.12}$	75-0315	43.406	100.0
		63.063	43.8
		37.356	40.2

Table A.1 (Continued)

Compounds	JCPDS Code	2θ (degree)	Intensity (%)
TiO_2	02-0387	25.354	100.0
		48.104	90.0
		53.888	70.0
		55.296	70.0
		64.179	70.0
		75.374	70.0
		83.219	70.0
	03-0380	25.652	100.0
		30.808	85.0
		48.376	75.0
	34-0180	27.438	100.0
		39.188	27.0
		36.086	15.0
	75-1537	25.685	100.0
		48.791	21.4
		38.396	13.8
$Ti_{0.992}O_2$	86-0148	27.445	100.0
		54.342	47.9
		36.095	43.1
$Ti_{0.936}O_2$	89-0554	27.459	100.0
		54.363	44.4
		36.104	39.9
$Ti_{0.928}O_2$	89-0552	27.392	100.0
		54.275	45.0
		36.087	41.5
$Ti_{0.924}O_2$	89-0555	27.455	100.0
		54.352	44.8
		36.094	40.0
$Ti_{0.912}O_2$	89-0553	27.443	100.0
		54.348	45.4
		36.107	40.6
Al	03-0932	38.784	100.0
		44.600	80.0
		65.186	80.0
		78.306	80.0
	04-0787	38.473	100
		44.740	47
		78.229	24
Al_2O_3	10-0173	43.363	100.0
		35.136	90.0
		57.519	80.0
	71-1684	34.438	100.0
		42.520	87.9
		56.283	68.4

Table A.1 (Continued)

Compounds	JCPDS Code	2θ (degree)	Intensity (%)
C	26-1075	42.803	100.0
		44.600	96.0
		43.939	77.0
	26-1076	26.603	100.0
		44.670	7.0
		43.451	6.0
		54.794	6.0
		83.838	6.0
	26-1083	43.442	100.0
		43.932	65.0
		45.052	56.0
C_{60}	49-1717	41.266	100.0
		14.219	10.0
		12.390	4.0
		20.224	4.0

Table A.2 JCPDS number of the phases formed and possibly formed on MJ12 and MJ47 during nitridation and carburization.

Alloys	Temperature (K)	TiAl	TiB_2	Ti_3Al		Ti_2AlN	Ti_2N	Ti_3N_{2-x}	$TiN_{0.3}$	$TiN_{0.76}$	$TiN_{0.9}$	TiN
		05-0678	35-0741	09-0098	14-0451	18-0070	23-1455	40-0958	41-1352	87-0626	31-1403	06-0642
MJ12	As-received	✓	-	-	-	-	-	-	-	-	-	-
	1000	✓	-	✓	✓	-	-	-	-	-	-	-
	1100	✓	-	✓	✓	✓	✓	✓	-	✓	✓	✓
	1200	✓	-	✓	✓	✓	✓	✓	✓	✓	✓	✓
	1300	✓	-	✓	✓	✓	✓	✓	✓	✓	✓	✓
MJ47	As-received	✓	✓	-	-	-	-	-	-	-	-	-
	1000	✓	✓	✓	✓	-	-	-	-	-	-	-
	1100	✓	✓	✓	✓	✓	✓	✓	-	✓	✓	✓
	1200	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
	1300	✓	✓	✓	-	✓	-	✓	✓	✓	✓	✓

Table A.2 (Continued)

Alloys	Temperature (K)	$Ti_4Al_2C_2$	$Ti_{5.73}C_{3.72}$	$Ti_6C_{3.75}$	Ti_8C_5	TiC			$TiC_{0.2}N_{0.8}$	$TiC_{0.3}N_{0.7}$	$TiC_{0.7}N_{0.3}$
		29-0095	77-1089	79-0971	72-2496	01-1222	06-0614	74-1219	76-2484	42-1488	42-1489
MJ12	As-received	-	-	-	-	-	-	-	-	-	-
	1000	-	-	-	-	-	-	-	-	-	-
	1100	✓	-	-	-	-	✓	✓	✓	✓	-
	1200	✓	-	-	-	-	✓	✓	✓	✓	-
	1300	✓	✓	✓	✓	✓	-	-	✓	-	✓
MJ47	As-received	-	-	-	-	-	-	-	-	-	-
	1000	-	-	-	-	-	-	-	-	-	-
	1100	✓	-	-	-	-	✓	✓	✓	✓	-
	1200	✓	-	-	-	-	✓	-	✓	✓	-
	1300	✓	-	-	-	✓	-	✓	✓	✓	✓

Table A.2 (Continued)

Alloys	Temperature (K)	$(TiO_{1.2})_{3.12}$	TiO		TiO_2				$Ti_{0.992}O_2$	$Ti_{0.936}O_2$	$Ti_{0.928}O_2$
		75-0315	08-0117	02-1196	02-0387	03-0380	34-0180	75-1537	86-0148	89-0554	89-0552
MJ12	As-received	-	-	-	-	-	-	-	-	-	-
	1000	✓	✓	-	-	-	✓	-	✓	✓	✓
	1100	✓	✓	✓	✓	-	-	-	-	-	-
	1200	✓	✓	✓	✓	-	-	✓	-	-	-
	1300	-	✓	✓	✓	✓	-	-	-	-	-
MJ47	As-received	-	-	-	-	-	-	-	-	-	-
	1000	✓	✓	-	-	-	✓	-	✓	✓	✓
	1100	✓	✓	✓	✓	-	-	-	-	-	-
	1200	✓	✓	✓	✓	✓	-	-	-	-	-
	1300	-	✓	✓	✓	✓	-	-	-	-	-

Table A.2 (Continued)

Alloys	Temperature (K)	$Ti_{0.924}O_2$	$Ti_{0.912}O_2$	Al		Al_2O_3		C			C_{60}
		89-0555	89-0553	03-0932	04-0787	10-0173	71-1684	26-1075	26-1076	26-1083	49-1717
MJ12	As-received	-	-	-	-	-	-	-	-	-	-
	1000	✓	✓	✓	✓	✓	-	-	-	✓	-
	1100	-	-	✓	✓	✓	-	✓	-	-	✓
	1200	-	-	✓		✓	✓	✓	-	✓	✓
	1300	-	-	✓		✓	-	-	-	✓	-
MJ47	As-received	-	-	-	-	-	-	-	-	-	-
	1000	✓	✓	✓	✓	✓	-	-	-	✓	✓
	1100	-	-	✓	✓	✓	✓	✓	-	-	✓
	1200	-	-	✓	✓	✓	✓	-	✓	-	✓
	1300	-	-	✓		✓	✓	✓	-	-	-

Table A.3 JCPDS number of the phases formed and possibly formed on MJ12 and MJ47 during nitridation.

Alloys	Temperature (K)	TiAl	TiB_2	Ti_3Al		Ti_2AlN	Ti_2N	Ti_3N_{2-x}	$TiN_{0.76}$	$TiN_{0.9}$	TiN
		05-0678	35-0741	09-0098	14-0451	18-0070	23-1455	40-0958	87-0626	31-1403	06-0642
MJ12	As-received	✓	-	-	-	-	-	-	-	-	-
	1000	✓	-	✓	✓	-	-	-	-	-	-
	1100	✓	-	✓	✓	✓	-	-	✓	✓	✓
	1200	✓	-	✓	✓	✓	✓	✓	✓	✓	✓
	1300	✓	-	✓	-	✓	✓	✓	✓	✓	✓
MJ47	As-received	✓	✓	-	-	-	-	-	-	-	-
	1000	✓	✓	✓	✓	-	-	-	-	-	-
	1100	✓	✓	✓	✓	✓	-	-	✓	✓	✓
	1200	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
	1300	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓

Table A.3 (Continued)

Alloys	Temperature (K)	TiO		TiO_2				$Ti_{0.992}O_2$	$Ti_{0.936}O_2$	$Ti_{0.928}O_2$	$Ti_{0.924}O_2$
		02-1196	08-0117	02-0387	03-0380	34-0180	75-1537	86-0148	89-0554	89-0552	89-0555
MJ12	As-received	-	-	-	-	-	-	-	-	-	-
	1000	-	✓	-	-	✓	-	✓	✓	✓	✓
	1100	✓	✓	-	-	✓	-	✓	✓	✓	✓
	1200	✓	✓	-	✓	-	-	-	-	-	-
	1300	✓	✓	-	✓	-	-	-	-	-	-
MJ47	As-received	-	-	-	-	-	-	-	-	-	-
	1000	-	✓	-	-	✓	-	✓	✓	✓	✓
	1100	✓	✓	-	-	✓	-	✓	✓	✓	✓
	1200	✓	✓	✓	-	✓	-	-	-	-	-
	1300	✓	✓	-	✓	-	✓	-	-	-	-

Table A.3 (Continued)

Alloys	Temperature (K)	$Ti_{0.912}O_2$	$(TiO_{1.2})_{3.12}$	Al		Al_2O_3
		89-0553	75-0315	03-0932	04-0787	10-0173
MJ12	As-received	-	-	-	-	-
	1000	✓	✓	✓	✓	✓
	1100	✓	✓	✓	-	✓
	1200	-	✓	✓	-	✓
	1300	-	-	✓	-	✓
MJ47	As-received	-	-	-	-	-
	1000	✓	✓	✓	✓	✓
	1100	✓	✓	✓	-	✓
	1200	-	✓	✓	-	✓
	1300	-	-	✓	-	✓

Table A.4 JCPDS number of the phases formed and possibly formed on MJ12 and MJ47 during carburization.

Alloys	Condition	TiAl	TiB_2	Ti_3Al		TiC		TiO	TiO_2	$Ti_{0.992}O_2$	$Ti_{0.936}O_2$	$Ti_{0.928}O_2$
		05-0678	35-0741	09-0098	14-0451	06-0614	74-1219	08-0117	34-0180	86-0148	89-0554	89-0552
MJ12	As-received	✓	-	-	-	-	-	-	-	-	-	-
	Carburized	✓	-	✓	✓	✓	✓	✓	✓	✓	✓	✓
MJ47	As-received	✓	✓	-	-	-	-	-	-	-	-	-
	Carburized	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓

Table A.4 (Continued)

Alloys	Condition	$Ti_{0.924}O_2$	$Ti_{0.912}O_2$	$(TiO_{1.2})_{3.12}$	Al	Al_2O_3	C		C_{60}
		89-0555	89-0553	75-0315	03-0932	10-0173	26-1075	26-1083	49-1717
MJ12	As-received	-	-	-	-	-	-	-	-
	Carburized	✓	✓	✓	✓	✓	✓	✓	✓
MJ47	As-received	-	-	-	-	-	-	-	-
	Carburized	✓	✓	✓	✓	✓	✓	✓	✓