ISSN 1516-392X

COMPARISON BETWEEN THE PHASES FORMED FROM DIFFERENT RATES OF PROCESSING Y_2O_3-Nb_2O_5 SYSTEM[1]

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Abstract

The understanding of phase diagram is a crucial issue in materials science, however, it requires hard study and long time to process and create them. There are, now a days, handbooks with these information available, although some of these system are dated from 19th century, which made doubtable the available data. The Y_2O_3-Nb_2O_5 system is one of them, and it is also poorly understood. This work has the aim to compare the phase stability with the work done by Yashima *et al* and Lee *et al* where they select some compositions in the yttria rich side of this system and by X-ray diffraction identified which were those. In this work the same compositions were studied, seven in the total, but instead of processing at 1500°C and 1700°C for four hour like both did, the heat treatment was done at 1200°C for 60 hours. This temperature was chosen because many of the furnaces available can not reach high temperatures like 1500° and 1700°C making unpractical the experiments. After analyzing the results it was concluded that five of the compositions match the present phases in the system, only the Y_2O_3 - 25%mol Nb_2O_5 and Y_2O_3 - 30%mol Nb_2O_5 presented intermediate peaks between the main peaks with low intensity. It is possible to conclude that phase stability does not require high temperature to be stabilized.

Keywords: Stability phase; Y_2O_3-Nb_2O_5 system; X-ray diffraction; Yttria; Niobium oxides.

COMPARAÇÃO ENTRE AS FASES FORMADAS POR DIFERENTES TAXAS DE PROCESSAMENTO NO SISTEMA Y_2O_3-Nb_2O_5

Resumo

A compreensão de um diagrama de fase é essencial na ciência dos materiais, no entanto, faz-se necessário um estudo árduo e longo para criação e desenvolvimento destes diagramas. Existem, atualmente, *handbooks* com algumas destas informações disponíveis, porém alguns destes sistemas datam do século 19, cujos valores são dúbeis. O sistema composto pelos óxidos Y_2O_3-Nb_2O_5 é um destes diagramas pouco estudado e averiguado. Este trabalho objetiva comparar a estabilidade das fases com o trabalho realizado por Yashima *et al* and Lee *et al* em que foram selecionadas composições no lado rico em ítria e com identificação das fases por raios-X. Neste trabalho as mesmas composições foram estudadas, sete no total, mas ao invés de processadas a 1.500°C e 1.700°C por quatro horas, o tratamento térmico realizado foi a 1.200°C por 60 horas. Esta temperatura foi escolhida porque os fornos disponíveis não atingiam as temperaturas superiores. Após análise, concluiu-se que cinco das composições confirmaram as fases verificadas no sistema, somente as composições de Y_2O_3 - 25%mol Nb_2O_5 and Y_2O_3 - 30%mol Nb_2O_5 apresentaram picos intermediários aos picos principais com baixa intensidade. Assim, a estabilidade das fases não requer elevadas temperaturas de tratamento para sua estabilização.

Palavras-chave: Estabilidade de fase; Sistema Y_2O_3-Nb_2O_5; Difração de raios-X; Ítria; Nióbia.

[1] *Technical contribution to 66th ABM Annual Congress, July, 18th to 22th, 2011, São Paulo, SP, Brazil.*

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ISSN 1516-392X

1 INTRODUCTION

1.1 Y_2O_3-Nb_2O_5 System

The phase diagram of Y_2O_3-Nb_2O_5 system has been poorly understood. The existing diagram is dated from 1989 (Figure 1),[1] and it was built after chemical and gravimetric analyses using X-ray diffraction and DTA.[1] The solubility limits of Nb_2O_5 in Y_2O_3 and of Y_2O_3 in $YNbO_4$ have not been determined properly, indicated by the dasehd lines on Figure 1.

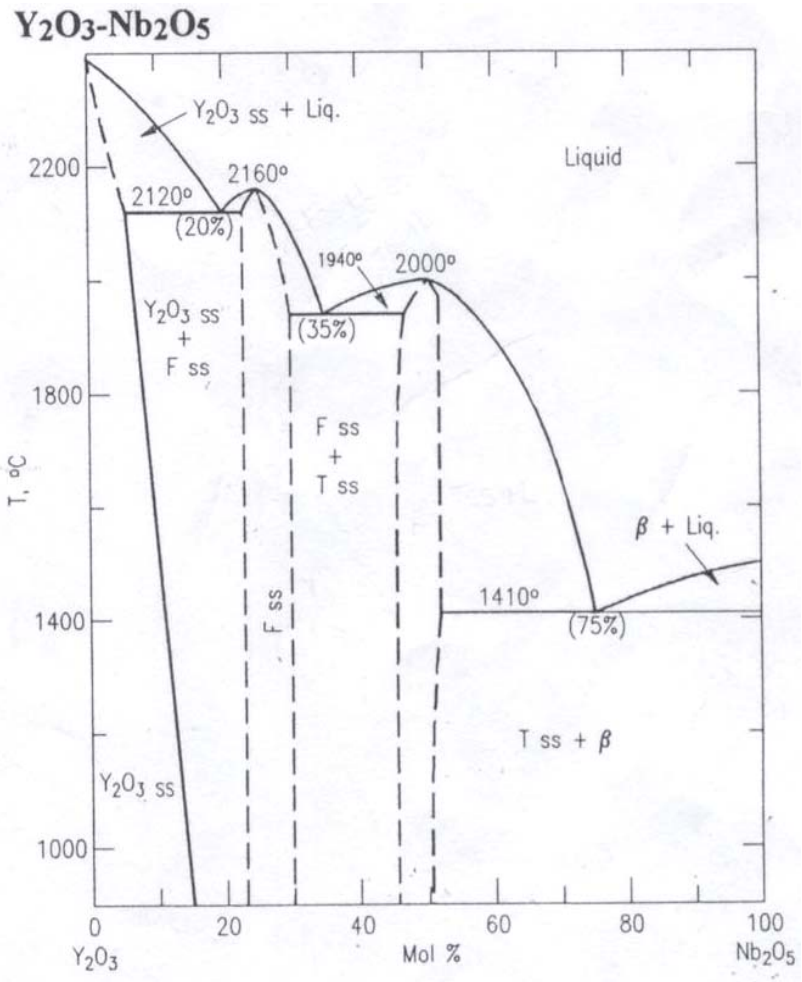

Figure 1. Phase diagram of Y_2O_3-Nb_2O_5 system accepted on literature. (Tss – tetragonal $YNbO_4$ solid solution, Y_2O_3ss – cubic solid solution, Fss – fluorite type $Y_6Nb_2O_{11}$ solid solution, β – monoclinic Nb_2O_5).[1]

This work has the aim to check the results published on 1998 by Yashima et al.[2] and Lee et al.,[3] where they studied this system after treatments at 1500° and 1700°C on the yttria rich side. This work aimed to apply a 1200°C temperature and check if the phase diagram accepted on literature has the desired confidence.

2 EXPERIMENTAL PROCEDURE

The powders of Y_2O_3 and Nb_2O_5 used had high level of purity, respectively 99,6% and 98,5% . The niobium oxide came from Companhia Brasileira de Mineração e

ISSN 1516-392X

Metalurgia – CBMM,[4] and the yttria was imported from Starck.[5] The chemical analyses provided by the powders manufacturers are presented on Tables 1 and 2.

Table 1. Chemical analysis of niobia powder[4]

Chemical Element	Amount	Chemical Element	Amount
Fire loss (organic traces)	0,50%	Na	500 ppm
Ta	2000 ppm	P	100 ppm
Fe	1000 ppm	C	100 ppm
Si	1000 ppm	S	100 ppm
Ti	1500 ppm	Pb	5 ppm
K	1000 ppm	Sn	5 ppm

Table 2. Chemical analyses of yttria powder[5]

Chemical Element	Amount (%w)
Al	0,02
Ca	0,02
C	0,1
Fe	0,05
Mo	0,01
Si	0,1
Zr	0,1

The compositions studied are listed on Table 3.

Table 3. Compositions used to prepare the samples

Compositions (mol %)	
Nb_2O_5	Y_2O_3
0	100
5	95
10	90
15	85
20	80
25	75
30	70
35	65
40	60
45	55
50	50

After weighing the powders in an analytical balance, it was used a chemical route to prepare the samples consisting on mixing the oxides in a ball mill with dense zirconia balls, homogenization on distilled water and sinter at high temperatures. It was used

ISSN 1516-392X

1200°C for sixty (60) hours on a muffle furnace for high temperatures model EF 1800 by Maitec INTI located at EEL-USP.
The bulks were milled and the powders obtained were taken to X-ray analysis in Shimadzu difratometer model XRD6000 radiation CuKα with graphite monocromator at EEL-USP; the angular interval was 10-80° with 0,05° as step; the counting time was 1 second. The diffraction pattern was analyzed using Powder Cell software version 2.4 from 2000 as well FullProf Suite Program (1.00), version of february 2007, that has its calculation based on Rietveld method;[6] and the phases identified by comparison. The phases identification was done using the patterns information obtained from PDFWin database[7] and also from handbook.[8]

3 RESULTS

The work published by Yashima et al.[2] and by Lee et al.[3] resulted on a phase assemblage, reproduced on Table 4, which is shown the phases for each of the composition studied depending on the temperature and the time used for sintering.

Table 4. Results obtained by Lee *et al* after X-ray identification[2,3]

Composition (mol %)		Resulting Phases	
Nb_2O_5	Y_2O_3	1700°C, 4 h	1500°C, 48 h
0	100	C	C
5	95	C+F	C+F
10	90	C+F	C+F
15	85	C+F	C+F
20	80	F	C+F
25	75	F	F
30	70	F+M	F+M
35	65	F+M	F+M
40	60	F+M	F+M
45	55	F+M	F+M
50	50	M	M

Where “C” represents the C-type Y_2O_3 cubic phase (space group Ia3, number 206, Pearson symbol cI80),[8,9] “F” represents a fluorite cubic phase (space group space group Fm3m, number 225, Pearson symbol cF12),[8,9] and “M” the monoclinic $YNbO_4$ phase, which is a tetragonal form at the temperatures analyzed (space group C12/c1, number 15, Pearson symbol mC28).[8,9]The results obtained are shown on Table 5.

Table 5. Results obtained experimentally

Composition (mol %)		Resulting Phases
Nb_2O_5	Y_2O_3	1200°C, 60 h
0	100	C
5	95	C + F
10	90	C + F
15	85	C + F
20	80	C + F
25	75	C + F
30	70	F + M
35	65	F + M
40	60	F + M
45	55	F + M
50	50	M

ISSN 1516-392X

The letters represent the same phases used on Table 4. There was no significant traces of tetragonal phase presence, which makes believe that it is a congruent phase that appears only with a specific amount, otherwise there will not be possible to identify itself. Except on 25% mol, the fluorite phase appears with cubic one, whichy was not verified on Table 4. The monoclinic phase identified corresponds to β phase at Figure 1.

4 DISCUSSION

According to Figure 1, the phases correspondents to the compositions studied are identified on Table 6.

Table 6. Phases identified from literature diagram on Figure 1

Composition (mol %)		Resulting Phases
Nb_2O_5	Y_2O_3	
0	100	Y_2O_3 ss
5	95	Y_2O_3 ss
10	90	Y_2O_3 ss
15	85	Y_2O_3 ss + Fss
20	80	Y_2O_3 ss + Fss
25	75	Fss
30	70	Fss
35	65	Fss + Tss
40	60	Fss + Tss
45	55	Fss + Tss
50	50	Tss

Where "Y_2O_3 ss" is the cubic solid solution of yttria, with cubic structure; "Fss" is the fluorite-type $Y_6Nb_2O_{11}$ solid solution; and "Tss" is the tetragonal $YNbO_4$ solid solution. Comparing the results on table 6 with those presented on Table 4, it's possible to verify differences after 70% mol of Y_2O_3. The works of *Yashima* et al.[2] and Lee et al.[3] identified the distinguished cubic types on compositions of 85, 90 and 95% mol of yttria, which is not obtained from the diagram.
Now, analyzing the results on Table 6 with the ones obtained experimentally, it is possible to see that at 50% there is presence of monoclinic phase, unverified on the literature. The tetragonal phase also starts to be identified at 70% mol of yttria, and its presence starts to be more significant at higher percentages of niobia, data absent on experimental study.
From Yashima et al.[2] and Lee et al.[3] work and this, there are only one composition that show phases differently, 25% mol of Y_2O_3. Looking at Figure 1, it's possible to see that this point correspond to a monophase field, fluorite one. A possible variance could have had change the results, and weighting the exactly amount of oxides are impossible, we can get a high precision value but not the exact one.
It's clear though that the diagram accepted for Y_2O_3-Nb_2O_5 system needs improvement and with these three works and further ones, it will be possible to build a better and more representative phase diagram for these oxides.

5 CONCLUSION

It was concluded that after analyzing the phase diagram accepted in the literature for Y_2O_3-Nb_2O_5 system, it got clear that some parts of it need to be redefined, specially

ISSN 1516-392X

those which separate phase boundaries. The advantage of new techniques like X-ray diffraction, and software for characterization made possible to explore and detect points unknown before.

Acknowledges

The authors would like to thank the support of FAPESP and the help from EEL-USP and AMR-DCTA laboratories crew.

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