

# Solidification sequences in the ternary Fe-V-Nb system

Samir Mansour<sup>1\*</sup>, Naima Boutarek<sup>1</sup>, Sif Eddine Amara<sup>2</sup>

<sup>1</sup>Laboratoire de Technologie des Matériaux, Faculté de Génie Mécanique et Génie des Procédés, Université des Sciences et Technologie Houari Boumediene BP 32 El Alia, 16311 Bab Ezzouar, Alger, Algérie

<sup>2</sup>Laboratoire de Métallurgie structurale, Faculté de Chimie, Université des Sciences et Technologie Houari Boumediene BP 32 El Alia, 16311 Bab Ezzouar, Alger, Algérie

\*Corresponding author. Tel: (+213) 795755004; Fax: (+213) 21207767; E-mail: mansourusthb@yahoo.fr

Received: 16 September 2013, Revised: 22 December 2013 and Accepted: 24 December 2013

## ABSTRACT

The present work is a continuation of research on alloys based on iron, with the aim to understanding the solidification behaviour of Fe-V-Nb alloys. Solidification sequences are proposed in relation to the observed microstructures for Fe-V-Nb synthesis alloys. Fe-V-Nb binary alloys with different concentrations are arc melted and characterized systematically by means of differential thermal analysis, optical and scanning electron microscopy coupled to an energy dispersive X-Ray microprobe analysis, quantitative XRF spectrometry and X-Ray diffraction. In the present work, the thermal and microstructural behavior of Fe-V-Nb alloys with different concentrations have been studied with the aim of answering some questions and especially paying attention to the microstructures and temperature transition. Two primary surfaces are identified:  $\alpha(\text{Fe})$  and  $\text{Fe}_2\text{Nb}$ . Moreover, one invariant line is also identified as a binary eutectic reaction ( $L \leftrightarrow \alpha + \text{Fe}_2\text{Nb}$ ), which is clearly shown according to the observed microstructure. In perspective, other shades of this ternary alloy will be studied for a path projection of liquidus surface. Copyright © 2014 VBRI press.

**Keywords:** Differential thermal analysis; Fe-V-Nb alloys; microstructure; phase transition; solidification sequences.



**Samir Mansour** is a researcher in laboratory of materials technology in the Department of materials science in the USTHB University of Algiers, Algeria. He will submit his PhD thesis in 2014. His research interest includes ternary alloys system, and has presented his work related to the experimental study of solidification in ternary Fe-V-Nb and Fe-Cr-Nb.

## Introduction

New systems of intermetallic compounds with more complex and higher melting points structures become emerging guidelines for the development of new material systems. [1, 2] For this purpose this study focuses on series of intermetallic alloys selected from the Fe-V-Nb system iron-rich side. Note that the Fe, V and Nb elements has attractive properties with views of the high-temperature stability, mechanical properties and resistance to the environment [3-6]. The objective of the present work is to study the thermal and microstructural behavior of Fe-V-Nb alloys with the aim of answering these questions and especially paying attention to the microstructures and temperature

transition. Usually the solidification in iron-rich alloys begins with the crystallization of the alpha primary phase which is made from to the alpha solid solution. It is the case for alloys 1 and 2. The novelty in this study is the crystallization of another primary phase less rich in iron (alloy 3) and assimilated to  $\text{Fe}_2\text{Nb}$  phase [7, 8].

## Experimental

### Materials

Pure elements, Iron, vanadium and niobium (99.99%) and hydrofluoric acid (HF, 48 wt%) were provided by Sigma-Aldrich, USA. The nitric acid 65% ( $\text{HNO}_3$ : 1M) was purchased from Carlo Erba reagents, France. The Ethanol absolute was provided by merck, Germany.

### Synthesis of alloys

Series of ternary iron-vanadium-niobium alloys were prepared with different compositions (60 to 75 wt.% Fe). The stoichiometric mixtures of those element were arc melted (Buhler MAM1 furnace type) several times (minimum 4 times), to ensure the homogeneity of our samples, in a pure argon gas atmosphere (5N) in a water-cooled copper crucible. Vanadium is

very prone to oxygen contamination and the presence of oxygen can seriously affect the thermodynamic phase diagram. In this case, the pure iron, vanadium and niobium were cleaned in nitric acid (HNO<sub>3</sub>; 1M), rinsed and dried, weighed in stoichiometric proportions and introduced directly to the elaboration furnace.

### Characterizations

Differential thermal analysis (DTA) specimens cut as small cylinders with  $\varnothing = 4$  mm x 10 mm in length (1 g maximum) were prepared from the alloys, and a Netzsch 404 S DTA apparatus was used for the thermal analysis. DTA measurements were taken in the cooling regime. The specimens were heated at 10 K·min<sup>-1</sup>, up to a maximum temperature of 1550°C, and cooled (at 10K·min<sup>-1</sup>) to room temperature. The heating and cooling rates were in an argon (5N) flow gas atmosphere (150 ml·min<sup>-1</sup>) to prevent all oxidation risks. The temperature measurements were carried out by (platinum) versus (platinum-10% rhodium) thermocouple and Al<sub>2</sub>O<sub>3</sub> powder was used as the reference. A standard temperature calibration was carried out by using the transformation temperatures of pure iron: Fe $\delta$ ↔Fe $\gamma$  at 1395°C, Fe $\gamma$ ↔Fe $\alpha$  at 910°C, and magnetic transformation of iron at 768°C. The reading of the transformation temperatures on our thermograms (with a traditional recording paper) is carried out by the measurement of the tension (20 mV in full scale) instead of the thermal accident observed. Then, this signal (in mV) is correlated to the corresponding temperature (°C) by means the calibration of our DTA apparatus [9, 10].

Samples were sectioned, polished and observed by optical and scanning electron microscopy (SEM). The microstructures of the alloys were studied using a Zeiss ICM 405 optical microscope and a Jeol JSM 63603LV scanning electron microscope equipped with EDX (Energy Dispersive X-ray) analysis used to determine accurately the composition (semi-quantitative) of the phases. The EDX analysis of different phases is performed under controlled conditions (counts·s<sup>-1</sup> and size of phases) in order to be able to compare the results from different specimens. Prior to microscopic observations, samples were treated with nitrofluorhydric solution (HNO<sub>3</sub>, HF and ethanol) for 30 s at room temperature.

The exact composition of each alloy studied was determined using the conventional wavelength-dispersive (Philips, X'Unique) X-Ray Fluorescence Spectrometry (XRF). The chemical compositions of all alloys studied have therefore been checked. Their compositions are summarized in **Table 1**.

For phase identification and crystallinity analysis, X-ray experiments were carried out using a Philips PW1730 diffractometer and a scanning rate of 0.004° s<sup>-1</sup> over the range  $2\theta = 20$ –140°, with unfiltered Cu-K $\alpha$  radiation ( $k = 1.54$  Å), and the system operating at 45 kV and 45 mA.

## Results and discussion

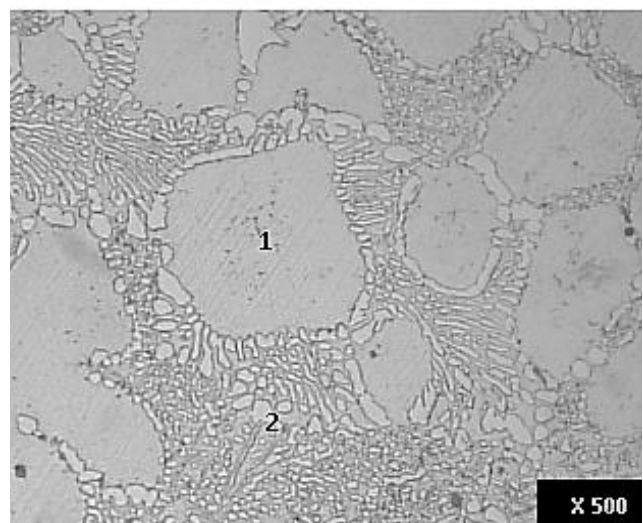
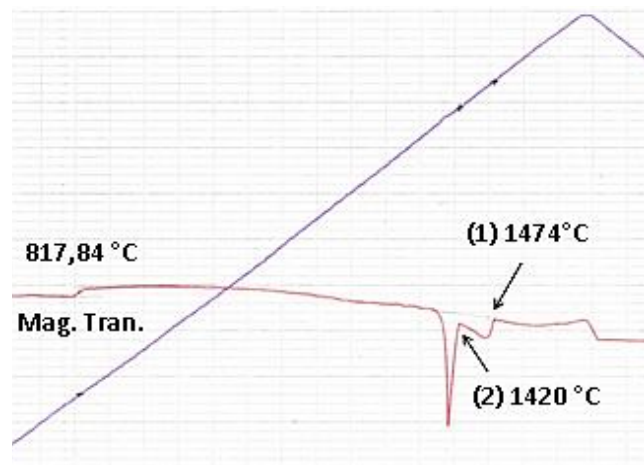
### Thermal analysis and microstructures

**Table 1** shows the alloy compositions, the transformation temperatures and the solidification sequences in relation to the observed microstructures. The  $\alpha$ -solid solution is identified as the primary crystallization phase in all studied compositions.

**Table 1.** Compositions, transformation temperatures and solidification sequences of the studied alloys.

Alloys	Compositions (at. %) (XRF analysis)			Transformation Temperatures (°C)	Solidification sequences
	Fe	V	Nb		
Fe <sub>75</sub> Nb <sub>10</sub> V <sub>15</sub> (1)	71.6	13.34	15.06	(1) 1474	L ↔ $\alpha$ Primary phase
				(2) 1420	L ↔ Eutectic structure
				(3) 817	Magnetic transformation
Fe <sub>65</sub> Nb <sub>14</sub> V <sub>21</sub> (2)	64.87	14.63	20.50	(1) 1447	L ↔ $\alpha$ Primary phase
				(2) 1416	L ↔ Eutectic structure
				(3) 767	Magnetic transformation
Fe <sub>60</sub> Nb <sub>16</sub> V <sub>24</sub> (3)	55.30	22.08	22.60	(1) 1455	L ↔ $\alpha$ Primary phase
				(2) 1409	L ↔ Eutectic structure
				(3) 971	Magnetic transformation

By comparing the results of the Differential thermal analyses DTA shown in **Fig. 1** and **2**, there is a clear improvement in the intensity of the second peak for the alloy 3, this is reflected by the increase of the eutectic structure density as shown in **Fig. 2**.



**Fig. 1.** DTA curve of the alloy1 on cooling with heating rate of 10K.min<sup>-1</sup> associated with the optical micrograph; (1) Gray area, (2) clear area.

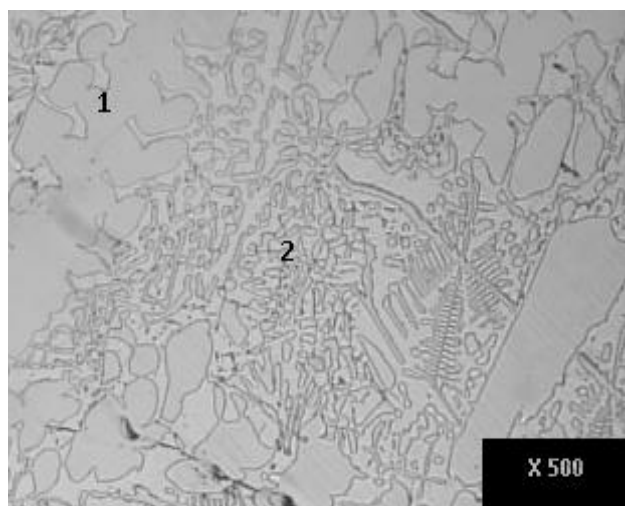
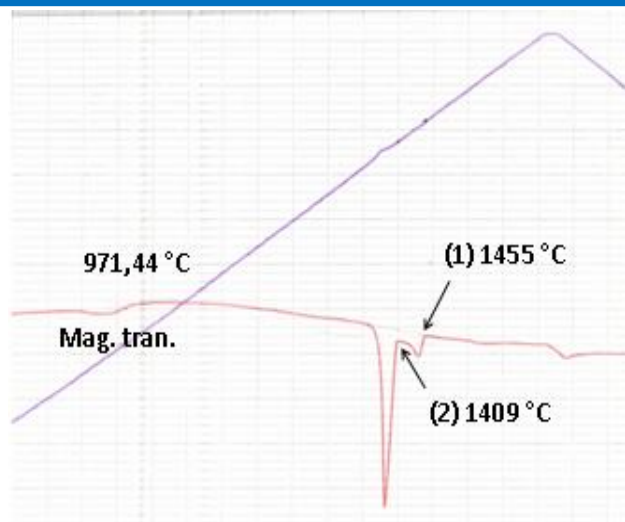


Fig. 2. DTA curve of the alloy3 on cooling with heating rate of  $10\text{K}\cdot\text{min}^{-1}$  associated with the optical micrograph; (1) Gray area, (2) clear area.

Fig. 3 shows the morphology of the alloy 1 obtained by scanning electron microscopy. According to the optical morphologies observed by the SEM, micrograph shows a homogeneous matrix of gray contrast and an eutectic structure. The specific analysis of the matrix (gray area) formed by EDX (1) revealed V-Fe binary phase rich in iron, which probably corresponds to the crystallization of  $\alpha$  ferritic solid solution. Analysis of the chemical composition of a white phase reveals a composition rich in niobium (2) which also contains iron, and to a lesser extent vanadium. This phase can be attributed to either a ternary phase Fe-Nb-V or a pseudo-binary phase Fe-(NbV) are based on iron and niobium-rich. The micrograph (Fig. 4.) of the alloy 3 shows the existence of two contrasts:

- A primary phase (white contrast) identical to that white frame identified in the eutectic structure of the samples 1 and 2 compositions. Given the large size of the explored areas, technical analysis is carried out under the best conditions and the results obtained are reliable.
- An array of gray contrast that the high magnification observation associated with the chemical composition analysis by EDAX revealed the crystallization of an eutectic structure identical to that previously observed but thinner and larger proportion.

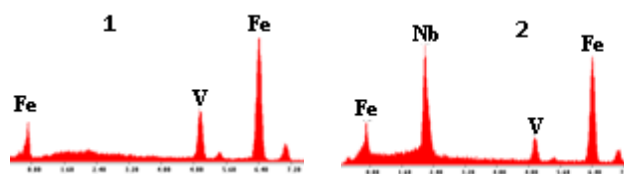
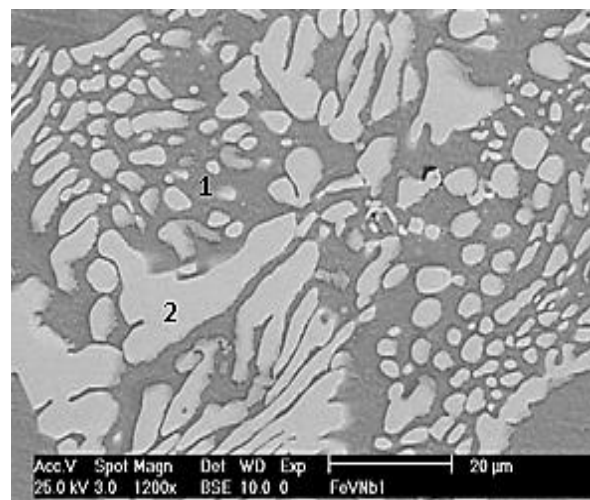


Fig. 3. Alloy 1 SEM microstructure, EDX spectrum analysis from: (1) Gray area, (2) clear area.

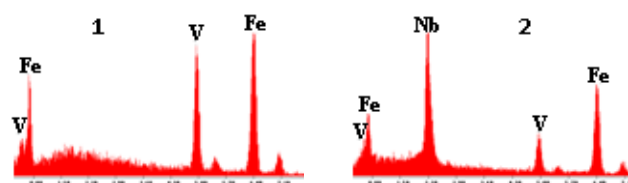
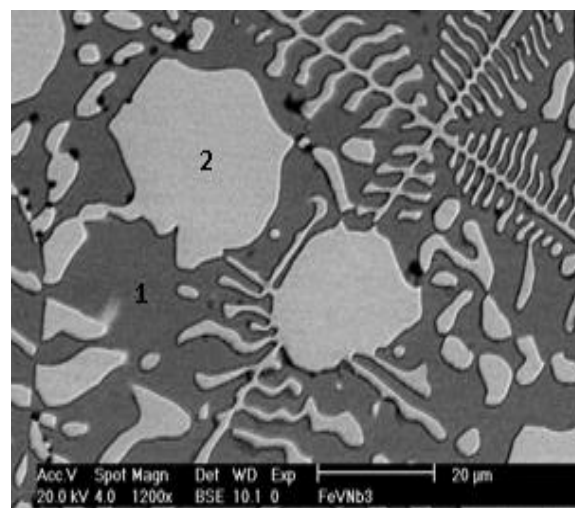


Fig. 4. Alloy 3 SEM microstructure, EDX spectrum analysis from: (1) Gray area, (2) clear area.

#### Phase identification by XRD

The superposition of X-ray diffraction spectrum of the three alloys is shown in Fig. 5. In addition to the lines (110), (200) and (211) of  $\alpha$  ferritic phase and compared to the spectra of samples 1 and 2, the spectrum of the sample 3 has two new peaks of high intensity at  $41.842^\circ$  ( $d = 2.158\text{\AA}$ ) and  $47.639^\circ$  ( $d = 1.907\text{\AA}$ ). The indexing of these



two lines permits the identification of  $\text{Fe}_2(\text{NbV})$  phase with a shift of the peaks compared to the ASTM card which can be explained by the substitution of part of the niobium atoms by those of vanadium.

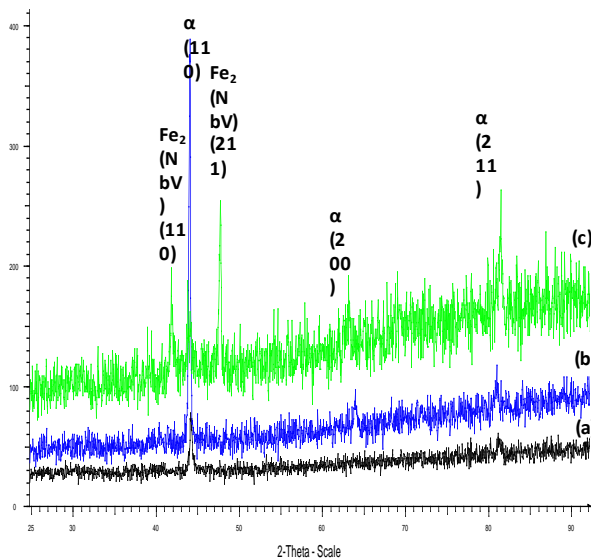


Fig. 5. Superposition of X-ray diffraction patterns of the three alloys. Alloy 1, (b) Alloy 2, (c) Alloy 3.

## Conclusion

The Phase diagram of Fe-V-Nb compounds in the rich region of Fe is investigated using DTA analysis, metallography and X-ray diffraction. Some changes were observed and based on the experimental results the following conclusions can be made:

- 1) The results obtained confirm that the  $\alpha$  ferritic solid solution, is the primary crystallization phase in alloy 1 and 2 and the second primary phase  $\text{Fe}_2\text{Nb}$  for the alloy 3.
- 2) Evidence for the invariant binary eutectic reaction ( $L \leftrightarrow \alpha + \text{Fe}_2\text{Nb}$ ) of the Fe-Nb system in the Fe-V-Nb ternary.
- 3) Proposal of drawing a draft projection of ternary iron-rich side on the crystallization of primary phases and eutectic monovariant line. At the end of this work we were able to partially define some fields belonging to the ternary diagram, knowing that in order to do the whole route studying several other points are required.

## Acknowledgements

This work has been realized with the contribution of the structural metallurgy team headed by the Professor R. Kesri in the LECMCM laboratory in the chemistry faculty, located in the USTHB University of Algiers.

## Reference

1. Boutarek, N.; Mansour, S. *Int. J. Mat. Res.* **2008**, *99*, 3.  
DOI: [10.3139/146.101638](https://doi.org/10.3139/146.101638)
2. Mohammadnezhad, M. Javaheri, V. *Mat. Des.* **2013**, *49*, 888.  
DOI: [10.1016/j.matdes.2013.02.043](https://doi.org/10.1016/j.matdes.2013.02.043)
3. Grujicic, M.; Tangrila, S.; Cavin, O.B. *Mat. Sci. Eng., A* **1993**, *160*, 37.  
DOI: [SC 29634-0921](https://doi.org/10.1016/0921-5093(93)90142-X)
4. Vilasi, M.; Francois, M. J. *All. Comp.* **1998**, *269*, 187.  
DOI: [S0925-8388\(98\)00142-X](https://doi.org/10.1016/S0925-8388(98)00142-X)
5. Cui, B.Z.; Sun, X.K. *J. Magn. Magnetic Mat.* **2002**, *250*, 212.  
DOI: [10.1016/S0304-8853\(02\)00379-7](https://doi.org/10.1016/S0304-8853(02)00379-7)

6. Fukumoto, K.; Kimura, A.; Matsui, H. *J. Nucl. Mat.* **1998**, *258-263*, 1431.  
DOI: [S 0022-3115\(98\)00324-9](https://doi.org/10.1016/j.jnucmat.2006.10.736)
7. Yamada, Y.; Moru, R.; Hirano, K. *J. Magn. Magnetic Mat.* **2007**, *310*, 1812.  
DOI: [10.1016/j.jmmm.2006.10.736](https://doi.org/10.1016/j.jmmm.2006.10.736)
8. Klementowicz, D. M.; Burrella, R.; Fortb, D.; Grosche, M. *Phys. B.* **2005**, *359-361*, 80.  
DOI: [10.1016/j.physb.2004.12.063](https://doi.org/10.1016/j.physb.2004.12.063)
9. De Mello, J.D.B.; Durand-Chare, M.; Hamart-Thibault, M. S. *Metall. Trans.A* **1983**, *14A*, 1793.  
DOI: [10.1007/BF02645549](https://doi.org/10.1007/BF02645549)
10. Fredriksson, H.; Brising, S. *Scand. J. Metall.* **5** (1976) 268.

## Advanced Materials Letters

Publish your article in this journal

ADVANCED MATERIALS Letters is an international journal published quarterly. The journal is intended to provide top-quality peer-reviewed research papers in the fascinating field of materials science particularly in the area of structure, synthesis and processing, characterization, advanced-state properties, and applications of materials. All articles are indexed on various databases including DOAJ and are available for download for free. The manuscript management system is completely electronic and has fast and fair peer-review process. The journal includes review articles, research articles, notes, letter to editor and short communications.

