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# PHASE FORMATION OF LAVES (Fe<sub>2</sub>Nb) UNDER LOW TEMPERATURE HEAT TREATMENTS AFTER MECHANICAL ALLOYING 26<sup>th</sup> COBEM

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### **Abstract.**

Among the several chemical elements that are used on the formation of intermetallic precipitates, there is Niobium, which is responsible for increasing the mechanical strength of metallic alloys, through the precipitation of a second phase, as well as harden them with solid solution. Thus, materials with that element in its composition are of great interest on energy industries (steam turbines), chemical and oil industries, where materials with low density and high mechanical and corrosion resistance are relevant. For the Fe-Nb binary system, this work developed the composition Fe<sub>15</sub>Nb (at. %), through powder metallurgy using the Mechanical Alloying (MA) process. Currently, the phase diagram of the Fe-Nb system is not complete due to the inability of phase formation, by other techniques, with heat treatments at low temperature (below 1000 °C), and the knowledge of its phase equilibrium is of great relevance for the microstructural understanding, helping on projections and providing data for thermodynamic modeling. In this work, methanol was used as Process Control Agent (PCA), to investigate its effect on the MA process, comparing with the results of the milling without adding PCA. The alloy was analyzed after 20, 40 and 60 hours of milling in high-energy planetary ball mill, in an inert atmosphere of argon gas, at 350 rpm. The morphologic analysis results indicate reduction in particle size when methanol is used. Subsequently, heat treatments at 600 °C, 800 °C and 1000 °C for 48 hours, to phase formation and/or stabilization. Through the X-ray diffraction technique, it was observed the formation of Laves phase (Fe<sub>2</sub>Nb) after heat treatment.

**Keywords:** Mechanical Alloying, Fe-Nb System, Laves, Process Control Agents.

## 1. INTRODUCTION

In phase balance of Fe-Nb system are the intermetallic phases Fe<sub>2</sub>Nb and Fe<sub>7</sub>Nb<sub>6</sub>. Laves phase, Fe<sub>2</sub>Nb, is one of the most relevant of system due to its high fusion temperature (1914 K). In the phase diagram, Laves is located in rich portion of Fe, with solubility range approximately between 25 (1373 °C) and 33 (1523 °C) %at. Nb (Silva et al., 2021).

Metallic alloys of Fe-Nb system are widely used in industrial scenery because excellent mechanical properties that Niobium addition provide to alloys. These materials stand out by presenting low densities and high corrosion resistance, arousing interest of chemical, oil and energy industries (Suryanarayana, 2001).

These alloys are commonly obtained by arch fusion, conventional process, but that demands high temperatures and long process periods. An alternative to this is the Mechanical Alloying (MA), which these alloys could be obtained by High-Energy Milling (HEM). The efficiency in production of metallic powders was best reached in high-energy ball technique, for all milling processes. By aiming to create metallic alloys derived from powders, the mechanical alloying (MA) technique presented itself as a viable method. The impact of spheres, together the high rotation speed causes the

comminution of material (Barbedo et al., 2021) with subsequent thermal treatments in order to reach the balance of phases, making possible to reduce energy, raw material consumption and, consequently, costs. The simplicity, the benefit-cost ratio and the process temperature have motivated Roy (2006) to investigate experimentally the amorphization in solid phase as an alternative in solidification process, by Mechanical Alloying. It was possible to identify paramagnetic characteristics for Laves (Fe<sub>2</sub>Nb) phase. The addition of process control agents (PCA), such as methanol, reduced the occurrence of cold welding, characteristic phenomena of HEM, in a way to obtain balance between cold welding and fracture, increasing process efficiency (Suryanarayana, 2001; Nouri & Wen, 2014).

Even with the possibility of phase formation yet in milling stage, without temperature addition, thermal treatments could be desirable, mainly in cases that intermetallic formation is needed. Although, because system entropy increasing occurred by action of milling balls over powders, the accumulated energy makes possible the treatment in lower temperatures when compared to conventional processes, without necessity of material fusion (Suryanarayana, 1998).

## 2. EXPERIMENTAL PROCEDURE

### 2.1 Materials

Niobium (Nb) powder with 99.9% wt. purity and particle size between 2 and 10 µm, produced at the Engineering College of Lorena (USP) obtained by HDH (hydrogenation-dehydrogenation-hydrogenation) process. The iron (Fe) powder with 99.5% wt. purity and particle size between 10 and 50 µm, was produced by atomization, donated by Höganäs Company.

### 2.2 Methods

Fe and Nb powders were displaced in Fe<sub>15</sub>Nb proportion, totalizing a 60 g mass for powders mixture. Samples with Methanol addition and without PCA were milled, in a ratio of 3% of total mass.

Milling process was developed in a high-energy planetary mill, under Argon inert atmosphere, with milling speed of 350 rpm and a mass-ball ratio of 1:15, during 20, 40 and 60 hours.

Thermal treatments were developed in a furnace with Argon inert atmosphere, with heating process divided in two stages. In the first one, up to 400°C, it was used a 5 °C/min rate, and later, the ramp was altered to 20 °C/min up to temperatures of 600 °C, 800 °C and 1000 °C, respectively. After reaching the treatment temperatures, they were kept for 48 hours, with slow cooling until it reached room temperature into furnace.

## 3. RESULTS AND DISCUSSION

### 3.1 Characterization of powder

#### 3.1.1 Particle shapes and granulometric distribution

Powders resulted from 60 hours of milling were put in a Scanning Electron Microscopy (SEM) aiming to verify if morphology and granulometric distribution that comprises representation of the equivalent average size of particulate material and the frequency in which it occurs in a certain size range, that is, of its populations, which represent the fine, average and coarser particles (Barbedo et. al., 2021) of samples after MA process.

In Figure 1-a, after 60 hours of milling, it is possible to notice that sample without PCA, Figure 1-a, presents particles with irregular shape and with high incidence of agglomerates. It is due to the absence of control agent, which restricts the cold welding effect.

It is also possible to notice that this sample presents the largest particle average sizes, Figure 1-b, with trimodal distribution and with fine particle population up to approximately (10.77±0.40) µm, representing 31.50% of total volume of particles. A curve of particles with average size up to (62.35±0.40) µm, what corresponds to 43.35% of particle volume and a third population with average size up to (161.70±0.40) µm, with more rough powders, representing 25.20% of total volume. Morphologic analysis indicates the presence of irregular and angle shaped particles. For this milling time, methanol presented the fewest agglomeration formation either for size, either for amount, Figure 2-a.

In Figure 2-b, the sample milled with methanol presented the smallest particle average sizes. In trimodal distribution observed, it was possible to identify a population of fine particles from (4.00±0.40) µm to (11.36±0.40) µm, representing 43.60 % of total number of particles. Medium particles from (11.36±0.40) µm to (65.71±0.40) µm, representing 41.10% of total number of particles, and another population of particles also considered as medium size, because they are smaller than 100 µm up to 65.71, representing 15.30 % of total number of particles.

Each Gauss peak refers to a population of particles with different sizes, that represent the total distribution of powders. The more the number of populations and more distributed they are, the more efficient will be the packing of particles for subsequent processes such as compression and sintering, what causes better mechanical properties (Funk & Dinger, 1994).

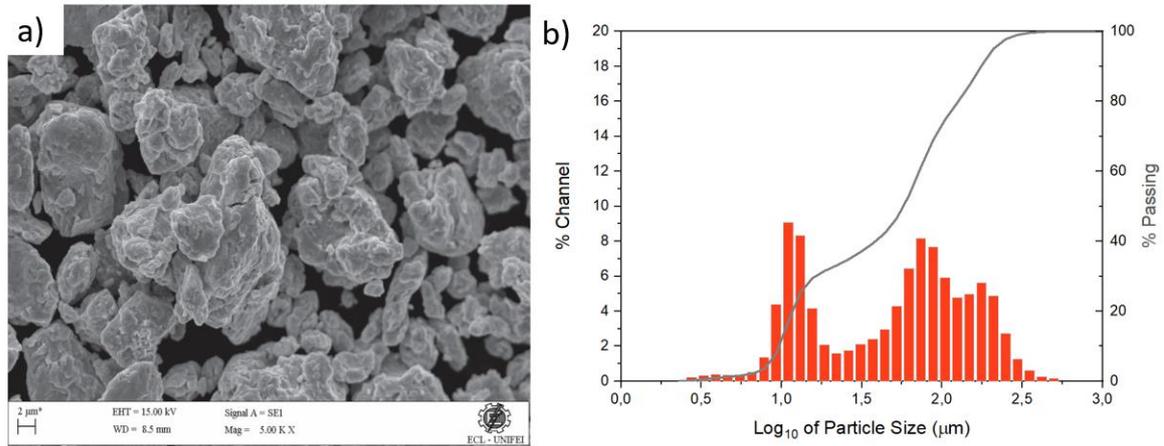


Figure 1. SEM/SE micrographs for 60 hours of MA for both alloys with 5000X resolution.: (a) Fe-15at.%Nb samples without PCA (reference), (b) Particle size distribution.

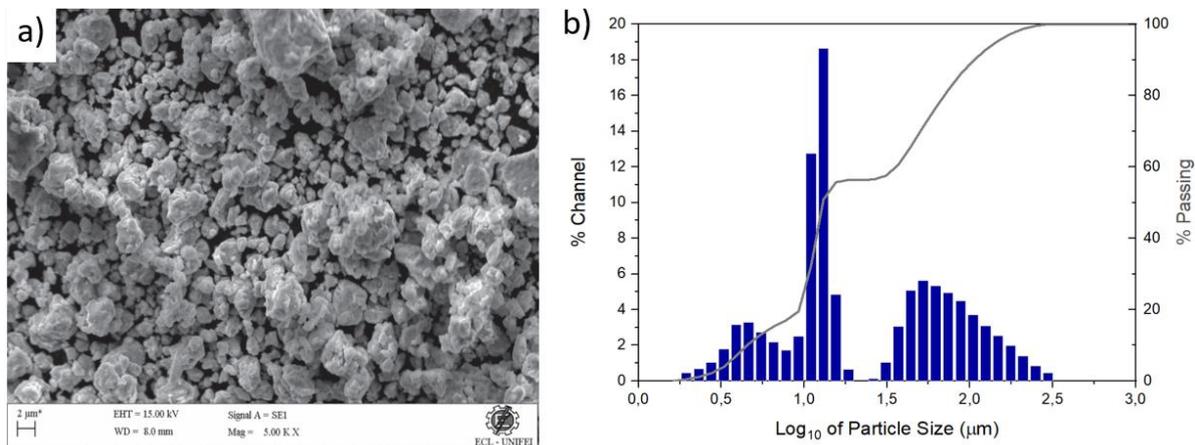


Figure 2. SEM/SE micrographs for 60 hours of MA for both alloys with 5000X resolution.: (a) Fe-15at.%Nb samples with methanol PCA, (b) Particle size distribution.

### 3.2 X-ray diffractometry

In general, for all conditions of PCA and temperature of thermal treatment, it was possible to identify Laves ( $\text{Fe}_2\text{Nb}$ ) phase formation, besides remaining Fe-alfa phase and the presence of oxidations on Fe and Nb.

#### 3.2.1 Samples with heat treatment at 600 °C

In Figure 1, it is possible to identify the formation of Laves phase after heat treatment at 600 °C for millings with times of 20, 40 and 60 hours, without PCA addition (Figure 1a) and with addition of Methanol PCA for the same three milling times (Figure 1b).

In the diffractograms, it is possible to observe the formation and stabilization of Laves phase since millings of 20 up to 60 hours. Furthermore, it is also possible to identify the oxidation formation  $\text{NbO}_2$  and  $\text{FeO}$  for both of the samples.

It is possible to notice that the material milled with methanol presented  $\text{Fe}_2\text{Nb}$  phase with less intensity when compared to sample without PCA. At Figure 1a, it is possible to verify that Laves phase presents significant intensity increase according to time increase in MA.

Besides this intensity increment, phase  $\text{NbO}_2$  is not identified for times above 40 hours, what indicates that for this condition of PCA and milling time the parameters adopted were enough for the use of whole Niobium fraction in the material for formation of solid phase and interest phase, i.e.  $\text{Fe}_2\text{Nb}$ .

The fewer intensity in Laves phase in sample milled with methanol could be justified by permanency of  $\text{NbO}_2$  phase during whole milling process, restricting Nb fraction available for growth of desired phase, Figure 1b.

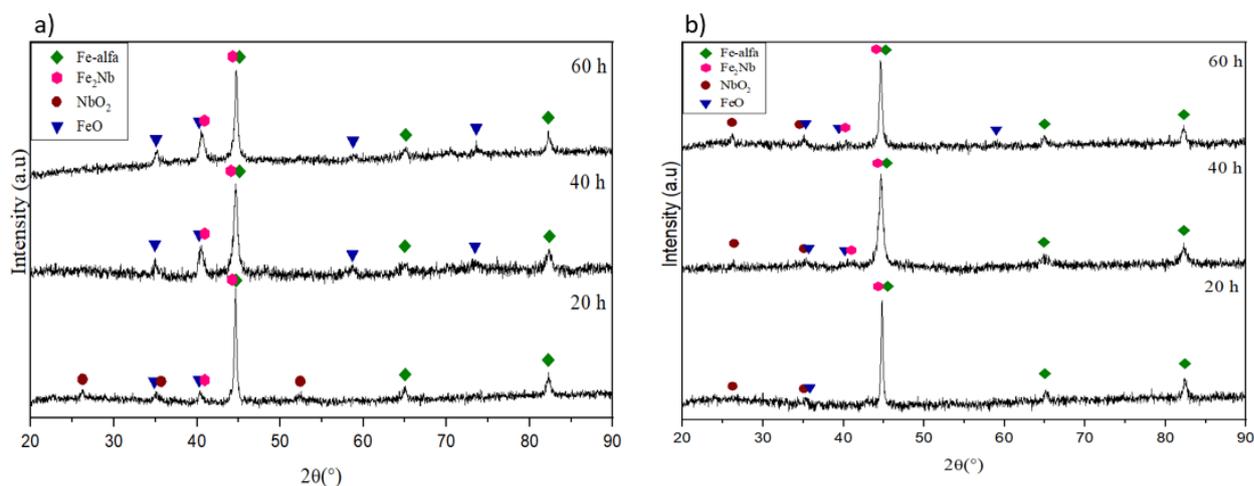


Figure 1. Diffractograms of Fe15Nb at.% phase after heat treatment at 600 °C (a) without PCA addition and (b) with methanol PCA.

### 3.2.2 Samples with heat treatment at 800 °C

Samples with heat treatment at 800 °C, Figure 2, presented in all conditions analyzed, the presence of Laves, Fe-alfa, NbO<sub>2</sub> and FeO phases.

In sample without PCA, Figure 2, it is possible to identify an intensity increase of Laves phase according to MA time and the no-identification of NbO<sub>2</sub> phase at the end of 60 hours of milling, phase that is present in the other times. The reduction of NbO<sub>2</sub> intensity demonstrates that during increase of intensity for Fe<sub>2</sub>Nb phase the whole available niobium portion was used, not remaining enough Nb for oxide formation (Figure 2a).

The analysis of methanol PCA sample, Figure 2b, demonstrates the Laves formation with less intensity when compared to free-PCA material. This fewer intensity is due to sharper oxidation, NbO, when compared to material without PCA, restricting available niobium portion for growth of Laves phase during heat treatment.

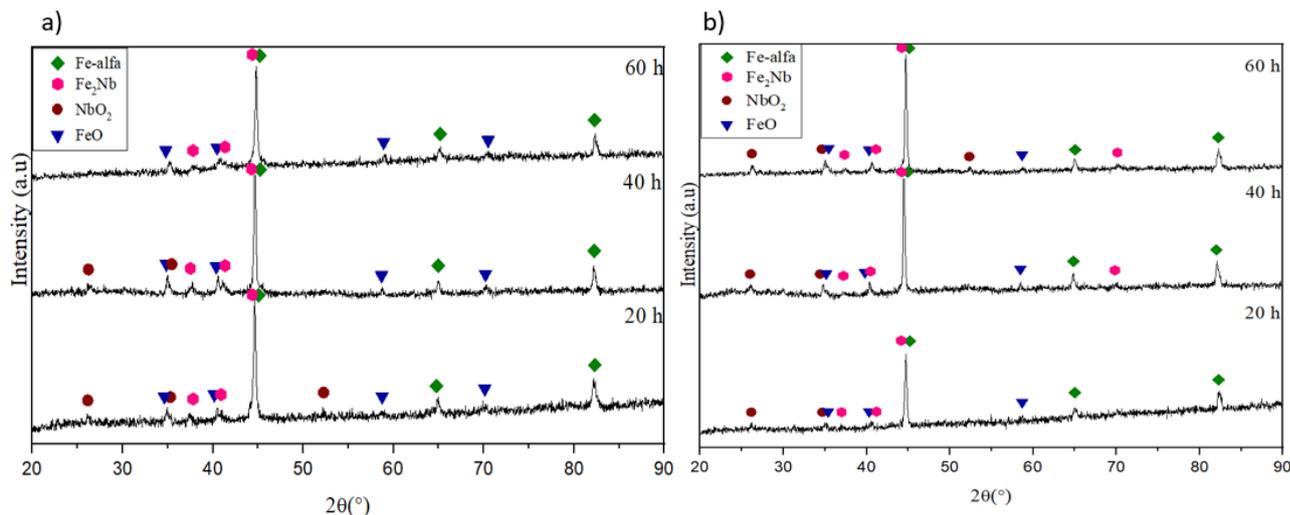


Figure 2. Diffractograms of Fe15Nb at.% phase after heat treatment at 800 °C (a) without PCA addition and (b) with methanol PCA.

### 3.2.3 Samples with heat treatment at 1000 °C

Diffractograms of Figure 3, without methanol PCA, allow the identification of Laves phase (Fe<sub>2</sub>Nb), Fe-alfa, FeO and NbO<sub>2</sub>. In both of the cases, it is possible to notice that interest phase, Fe<sub>2</sub>Nb, is formed and stabilizes after heat treatment, for all milling times.

It is possible to observe that in sample without PCA, for milling times of 40 and 60 hours, there is a separation of one of the Laves peaks, with more relative intensity when compared to all diffractograms before, Figure 3a.

It was also possible to identify it overlaid on main peak of Fe-alpha phase of  $2\theta = 44.66^\circ$ . For this area, there are two peaks of high intensity of Fe<sub>2</sub>Nb phase that, due to enlargement presented by Fe-alpha peak, they are found overlaid on itself. It was possible to verify a difference among preference crystal levels of Laves phase for these MA times.

The milling with methanol addition presents the same niobium oxide formation found in previous treatments. Such as in those cases, NbO<sub>2</sub> formation may be responsible for less Laves phase formation, once as described by Velez (2013), the fewer availability of Fe or Nb in the system restricts the intermetallic formation (Figure 3b).

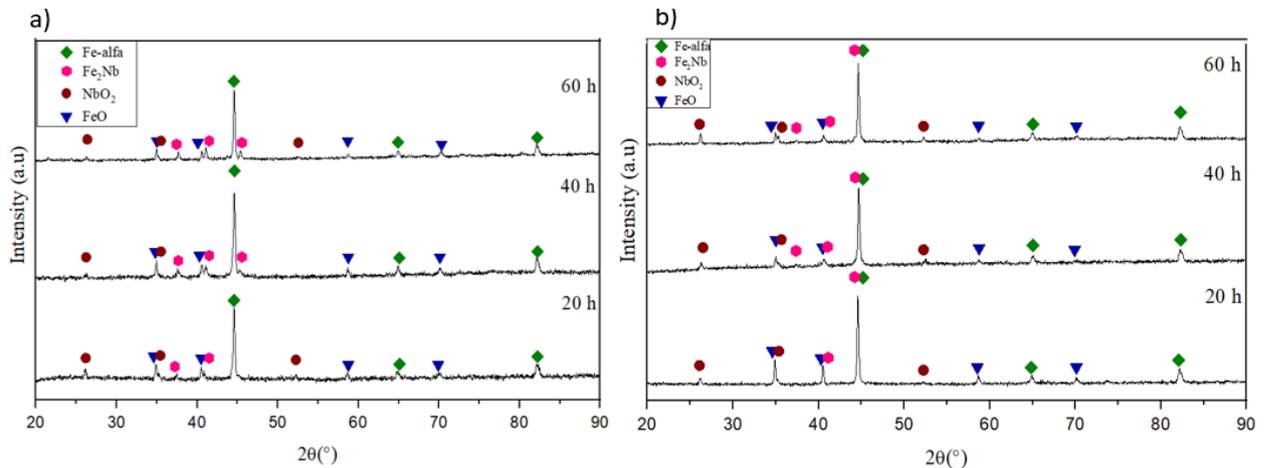


Figure 3. Diffractograms of Fe15Nb at.% phase after heat treatment at 1000 °C (a) without PCA addition and (b) with methanol PCA.

#### 4. CONCLUSION

During milling, it is possible to verify that the best results for Laves (Fe<sub>2</sub>Nb) phase derive from Methanol PCA samples, with formation in the beginning of milling process, but with amorphization at 60 hours.

Regarding thermal treatments, the best results for formation, crystallization and balance of phases showed up at 1000 °C. In this case, methanol remains as the most efficient, presenting larger formation and intensity for Laves (Fe<sub>2</sub>Nb) phase.

Granulometric and morphological analysis found the smallest particle average sizes, and fewer agglomerations formation for the material milled with methanol, both before and after heat treatment. It justifies better compressibility observed in these samples during compression and better densification after thermal treatment.

There were oxidations due to atmosphere contamination during milling process, caused by loss of sealing on jar or decomposition of control agent during MA. Better chemical affinity between O<sub>2</sub> and Fe or Nb restricted chemical bond between Nb and Fe, but it did not avoided Laves (Fe<sub>2</sub>Nb) phase formation.

#### 5. ACKNOWLEDGEMENTS

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