A Theoretical Framework for Design and Validation of in situ Composite Manufacturing Techniques

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Abstract

In situ composite manufacturing techniques can improve the bond between the matrix and reinforcements in a composite material. This is achieved by creating the reinforcements within the matrix through the reaction of precursor materials, which form the desired phases. Thermodynamic data and simulation tools can be used to validate the process and design variables, saving time and resources. The aim of this study is to apply a theoretical framework developed by the authors to the development of a Fe-NbC *in situ* metal matrix composite. The framework involves using Gibbs free energy and dissociation criteria of reinforcements to validate the feasibility of the composite system and to assess composite formation kinetics and microstructural features based on the driving force and diffusion of elements in raw materials. Here, we demonstrate the application of these tools to the development of a Fe-NbC composite, starting from validating the feasibility to selecting between elemental powders, solid solutions, and intermetallics to achieve the desired microstructure.

Keywords: in situ composites, computational thermodynamics, powder metallurgy

Introduction

An *in situ* composite is a type of composite material where the reinforcement phase is generated within the matrix during the processing of the composite itself, rather than being added separately. This method involves a chemical reaction between the raw materials, leading to the formation of the reinforcement phase directly in the matrix. The advantage of this approach is that it ensures a more uniform distribution of the reinforcement particles, enhances the bond between the matrix and reinforcement, and can lead to improved mechanical properties. This method also allows for greater control over the microstructure of the composite, making it possible to tailor properties to specific requirements [1].

The premise of forming *in situ* composites depends on the reaction between the raw materials to form the final microstructure of the composite. This, in turn, requires that the phases of the desired material have lower free energy than the initial system. A preliminary thermodynamic analysis of the system can be a powerful decision-making tool in the design of *in situ* composites, as it allows not only to assess the feasibility of these composites but also to understand the transformations involved in a system tending to a specific equilibrium state [2]. Also, it is possible to select from the available raw materials and estimate the diffusion of elements between them, which in turn provides information about the final microstructure. Consequently, thermodynamic data and CALPHAD-based software are powerful tools for designing and optimizing these composites. This facilitates the analysis of raw material combinations and the estimation of solid-state diffusion of elements, providing valuable insights into the resulting microstructure and supporting better decision-making [2].

The aim of this article is to enhance the likelihood of achieving the desired microstructure by analyzing and understanding the underlying thermodynamic phenomena that influence it. Some tools in the framework developed in our review [2] have been applied to an Fe+NbC composite prepared by our group. Brazil is responsible for approximately 90% of the world's niobium production; however, most of this substance is used as a microalloying element in steels. Developing a new material with a high niobium content and high added value could positively impact this sector of the Brazilian industry. Niobium carbide (NbC) is a high-hardness material that has been successfully used as a reinforcement in metal matrix composites [3]. We intend to use the experimental results to illustrate the decision-making steps and demonstrate the success of our methodology in obtaining the material based on the proposed framework

Theoretical Framework

The framework we developed is summarized in Fig. 1. Our framework is designed to be modular and flexible, allowing for the selective application of criteria based on the specific requirements of the system under investigation. While some criteria were applied to this particular system, not all were necessary, relevant, or feasible. This also illustrates how it can be adapted to various scenarios, optimizing the development process for *in situ* metal matrix composites.

Firstly, an analysis was conducted to validate a composite as a viable candidate for *in situ* powder metallurgy, using Gibbs free energy

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minimization and low reinforcement dissociation as criteria. Then, potential raw materials were discussed based on the probable reactions and the resulting microstructure. These reaction possibilities were evaluated through the thermodynamic and kinetic characteristics of the systems.
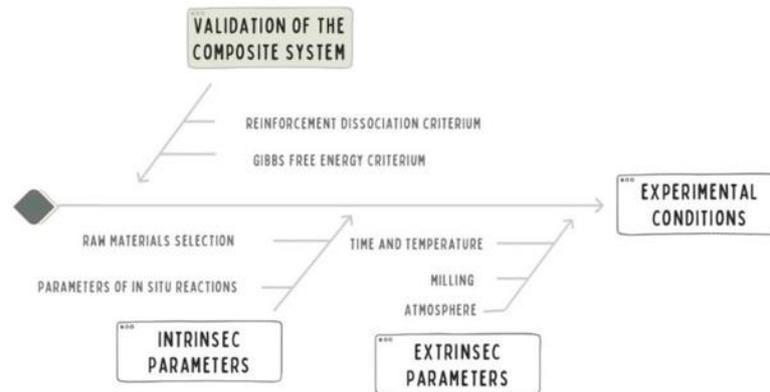

Fig. 1: Flowchart summarizing the parameters covered in our review, which can be used to guide the design of experimental conditions for manufacturing *in situ* composites using powder metallurgy [2].

Concept

Gibbs Free Energy Reduction Criterion

The first step in designing our *in situ* composite was to analyze whether the desired reaction is thermodynamically possible. It is important to highlight that, for *in situ* composite formation, it is not enough for a single phase to have high thermal stability and low Gibbs free energy, but the entire set of phases in the composite — that is, the matrix and reinforcement combination — must be stable in each other's presence. This is why it is not enough to analyze the free energy of formation of niobium carbide. Ternary diagrams of the Fe-Nb-C system can be used for this purpose; however, it is necessary to analyze different isotherms to verify if the desired structure is stable in the processing temperature range.

For this reason, simulating the equilibrium of the system at various temperatures using computational thermodynamics is very useful. If the phases of interest — iron matrix and NbC reinforcement — are stable at equilibrium, all combinations of raw materials tend to transform accordingly. To this end, a simulation of the Fe-NbC pseudobinary diagram was made (Fig. 2).
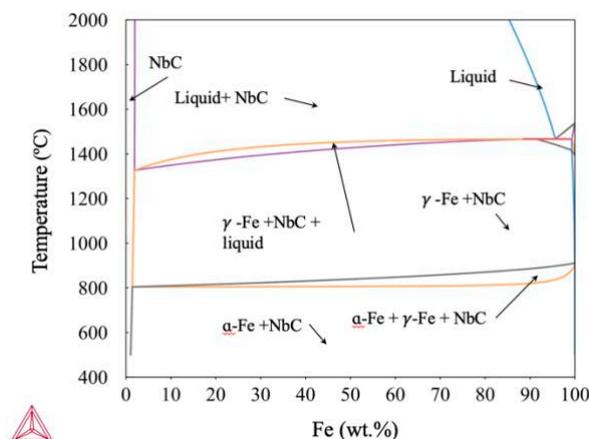

Fig. 2: Fe-NbC pseudobinary diagram. The unidentified fields in the upper right corner correspond to mixtures of ferrite, austenite, and liquid phase.

Fe-NbC pseudobinary analysis confirms that except for contents below ~1 wt.% Fe or NbC, the most stable form of a system containing iron and stoichiometric amounts of Nb and C at 1:1 is a mixture of iron phases — alpha, gamma, or delta, depending on the temperature — and niobium carbide. In the Fe-NbC system, a liquid phase forms at slightly lower temperatures than 1500 °C due to the presence of carbon in solid

solution in iron. This diagram has a eutectic at ~1450 °C for ~95 wt.% Fe. In other compositions, although both carbon and niobium become more soluble in liquid iron, complete decomposition of the reinforcement phase is not identified for Fe contents below ~85 wt.% at any temperature below 2000 °C.

Dissociation Criterion

Besides the reduction in Gibbs free energy, it is also interesting to analyze the number of Nb and C atoms dissolved in the matrix at equilibrium. The solubility limit is reached when the molar free energy of the solid solution equals the molar free energy for the compound formation.

It is worth noting that, for ex situ composites, there must be some solubility between the matrix and the reinforcement because generally, ceramics do not exhibit good wettability with metals, thus, for interfacial bonding to occur between the two, diffusion between the materials is necessary.

When composites are forming *in situ*, this is not an issue, and low dissociation of ceramic particles in the matrix helps ensure that the desired amount of reinforcement can be formed during sintering; otherwise, part or all of it would remain dissolved in the matrix. Moreover, low dissociation helps ensure that the microstructure remains stable even if the material is subjected to high temperatures, as it guarantees the presence of reinforcement under these conditions. The increased solubility of Nb and C atoms also promotes the coalescence of NbC particles. Solubility of carbides is less than 1% in any region of the solid phase fields of the pseudobinary in Fig. 2. When a liquid phase is present, densification tends to be improved, but NbC solubility increases markedly, resulting in accelerated reinforcement coalescence. Balancing densification in a material containing numerous barriers to diffusion, such as NbC, is challenging. Therefore, a suitable compromise in the sintering temperature must be found so as to be high enough to allow for proper densification but not so high as to cause excessive coalescence of the reinforcing particles.

Raw Material Selection

After confirming that the matrix and reinforcement set — i.e., Fe + NbC — is a promising *in situ* composite, the raw materials that will be used to form it must be selected. Depending on the starting powders, different diffusion paths may occur during sintering, and the resulting microstructure will vary accordingly. This affects the reaction rate, reinforcement size, and — even for *in situ* reinforcements — whether there will be defects at the interface. Therefore, an intelligent selection of raw materials implies not only cheaper powders and processing but also a potential increase in matrix-reinforcement interface bonding and refinement of particle size distribution. Some types of reactive systems that can form the targeted composites in this work are commented on below.

Elemental Powders: A + B + C → A + BC

In this system, the microstructure is determined by carbon diffusion, which has a much higher diffusion coefficient ($2.91E^{-10}$) compared to niobium ($1.17E^{-13}$) in iron. Carbon diffuses toward the elemental Nb to form NbC three orders of magnitude faster than niobium can diffuse in iron to form a solid solution. In other words, before interdiffusion between iron and niobium can occur, the carbon has already diffused to the niobium and formed the carbide. As illustrated in Fig. 3, this results in the formation of NbC where the Nb powder particles used to be, rather than NbC nucleating within the iron matrix as a precipitate. Consequently, the particle size, distribution, and surface will closely resemble the initial niobium powder particles. Thus, the adhesion between the matrix and the reinforcement depends on the densification of the iron around the NbC particles, as they do not nucleate within each other but form side by side, potentially leading to weak interfaces. Also, after a layer of NbC is formed around the Nb particle, the reaction rate may be retarded by the diffusion of carbon across it. It is possible to use extremely fine niobium powder to form fine carbides; however, processing fine powders (below 1 µm) is complex and leads to issues such as agglomeration and low flowability, in addition to being more expensive. Milling an elemental powder mixture could help improve particle adhesion and reduce size.
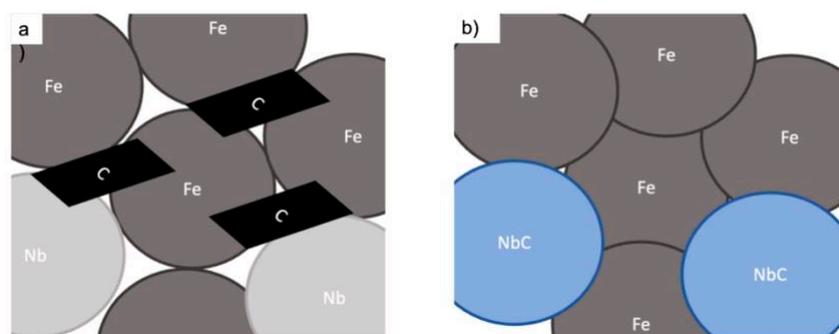

Fig. 3: Diagram representing a) the use of elemental powders of Nb, Fe, and C b) after sintering, where NbC particles have a size similar to the initial elemental Nb powder.

Less Stable Compounds: AB + C → A + BC

Instead of elemental raw materials, less stable compounds can be selected to obtain Fe + NbC composites. In Fig. 4, there is a Fe-Nb phase diagram that illustrates the possible intermetallics.
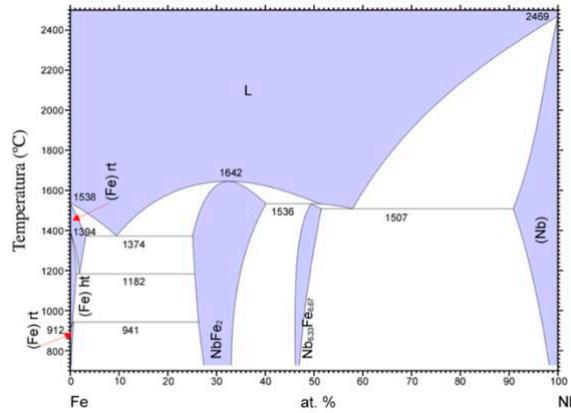

Fig. 4: Fe-Nb phase diagram [4].

In this strategy, it is not possible, however, to design an arbitrary amount of reinforcement, as the fraction of NbC is defined by the stoichiometry of the FeNb and Fe_2Nb compounds. Thus, although this composite system contains more than two chemical elements, there is only one degree of freedom that defines the volume fraction of the reinforcement unless additions of other powders are made, which would result in reinforcement-free zones. From the pseudobinaries of the intermetallic FeNb and Fe_2Nb, respectively Mu and Laves phases, with carbon, it is possible to prove that there are ranges in carbon contents that promote the formation of a composite powder containing only a ferrous matrix and NbC reinforcements. These contents are summarized in Table 1. The pseudobinary diagrams can be found in Fig. 5.
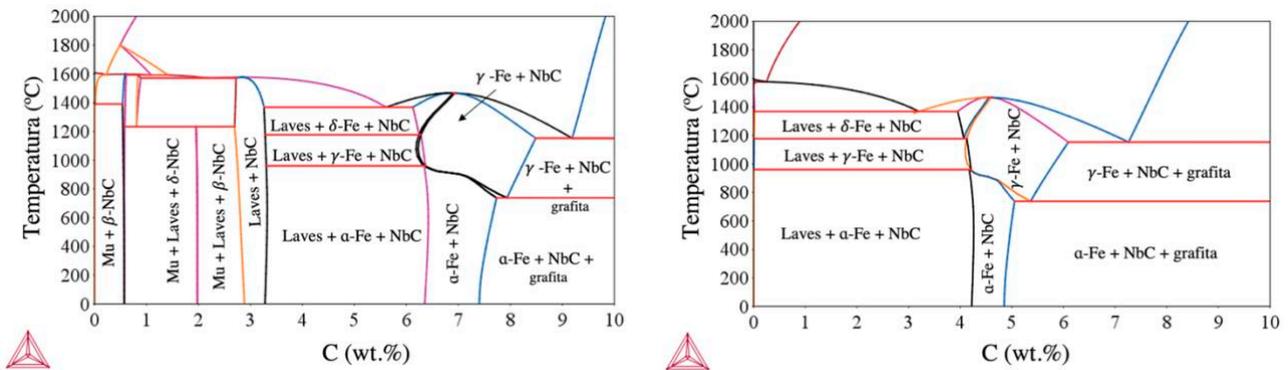

Fig. 5: a) FeNb-C pseudobinary diagram b)Fe_2Nb-C pseudobinary diagram.

Those pseudobinaries can also be used to determine the graphite content to be added: by exceeding the amount of carbon predicted by the diagram it is possible to form pearlite or a cast iron matrix.

Table 1: Carbon contents required for complete conversion of intermetallics into composites.

Diagram	Carbon content for composite formation (wt.%)
Fe_2Nb - C	4.9-5.7
FeNb - C	6.5-7.5

From the elemental powder analysis, it can be concluded that for the precipitation of reinforcements within the matrix, niobium would need to be homogeneously distributed in the iron beforehand. This is why using Fe(C) + Nb would have a similar result to elemental powders. In FeNb + C or Fe_2Nb + C systems, niobium carbide forms by the reaction of carbon with niobium located within the lattice of intermetallic particles,

precipitating NbC and iron, while niobium is gradually depleted from the intermetallic. In this case, a single ferroniobium particle can give rise to multiple carbides, and the size of the carbides is determined not only by the initial particle size but also by nucleation and growth within the matrix, as illustrated for Fe_2Nb particles in Fig. 6.
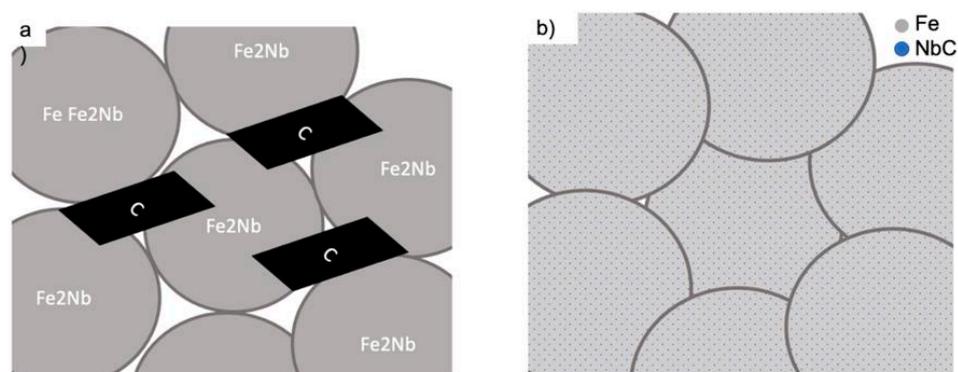

Fig. 6: Diagram representing a) the use of Fe_2Nb powders and graphite (C) and b) Fine NbC particles formed from precipitation within the lattice after sintering.

From a thermodynamic standpoint, precipitate formation occurs by heterogeneous nucleation at lattice defects, resulting in their destruction. By nucleating on the defect, there is a reduction in the system's free energy, favoring the formation of the new phase. The larger the defect (free surface > grain boundary and phase interfaces > stacking fault > dislocations > vacancies), the greater the driving force and, therefore, the lower the nucleation barrier. Therefore, when ΔG decreases due to temperature reduction, less potent (but more numerous) sites become viable — in other words, nucleation can occur at dislocations, vacancies, or even homogeneously — and consequently, the number of stable nuclei increases. Thus, for a fixed volume of precipitates, particles will be finer in *in situ* reactions occurring at lower temperatures. Therefore, while high temperatures and long reaction periods may increase the speed of *in situ* reactions, they also favor the nucleation of larger reinforcements and promote coalescence kinetics. In this reaction system, it is necessary to select a temperature that allows the reaction to be completed within the stipulated time while minimizing carbide coalescence. Moreover, the literature indicates that the reaction between FeNb and Fe_2Nb and carbon is slow because it occurs only at the surface, without diffusion within the intermetallics [5]. Reducing the particle size to increase the reaction surface area is therefore expected to enhance the reaction rate. These parameters were studied experimentally to analyze the effect of temperature on the obtained reinforcement particles and the *in situ* reaction time.

Solid Solution: A(B) + C $\rightarrow$ A + BC   and A(B + C) $\rightarrow$ A + BC

Similarly to the previous section, if Nb is dissolved in Fe, niobium-based precipitate nucleation and growth will occur as the *in situ* reaction between niobium and carbon proceeds within the lattice. In this case, the maximum reinforcement content is subject to niobium's solubility in iron, which is less than 1 wt.% in almost the entire solid state, as can be seen in the Fe-Nb phase diagram in Fig. 4. This solubility may, however, be increased by creating supersaturated solutions out of equilibrium using techniques like mechanical alloying. Those possibilities were not included in our experimental scope due to limitations in our infrastructure and the cost implications of such a process, which render it less feasible from a technological standpoint.

Atmosphere

In the context of powder metallurgy (PM), powders, including compacted green bodies, have a surface-to-volume ratio significantly higher than bulk materials. Consequently, even if reactions with the atmosphere are limited to the surface, they can substantially impact sintering kinetics and degrade the properties of the composite.

During the sintering process, various chemical reactions involving gaseous phases occur. When designing *in situ* composites, it is necessary to consider that undesirable reactive elements can originate from the sintering atmosphere. For composites reinforced with intermetallics, as well as carbides, borides, and nitrides, it is essential to prevent oxidation by selecting the sintering atmosphere conditions. This is because oxidation can affect not only the matrix but also the metal reinforcement precursors, potentially transforming them into oxides instead of the desired phases.

It is possible to analyze the susceptibility of different raw materials to oxidation using thermodynamics. Fig. 7 demonstrates that intermetallic compounds have a lower tendency to oxidize than pure niobium. This also supports the choice of intermetallics. Based on the purity of the gas that is available to us, pure niobium can oxidize above 1200 ºC. Furthermore, it is worth mentioning that the carbide has higher Gibbs free energy of formation than oxide. This means that niobium oxidation can occur even when it has already been transformed into composite powder.
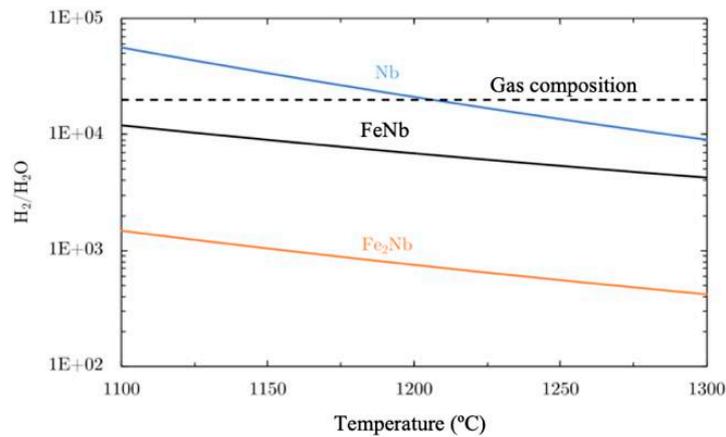
Fig. 7: Dew point of Nb in its metallic form, in the FeNb compound, and in the Fe$_2$Nb compound. The calculation was based on the purity of the gases used in our laboratory, which is grade 5.

Experimental Validation

Our composite, which was selected based on our thermodynamic assessment of the system, was produced from the reaction of Fe$_2$Nb with 6.5 wt.% graphite powders, which were mixed and sintered at 1250 ºC for 1h. The composite microstructure is displayed in Fig. 8a). We obtained a composite with a pearlitic matrix and more than 50% by weight of NbC, which, despite its high porosity of 16.5%, exhibited a microhardness of 952 HV. After sintering, no oxides were detected, and the low Nb content allowed for a greater mean free path between particles, which is expected to enhance the composite's toughness. The Fe$_2$Nb powder used is fine, with an average diameter of 3.5 µm, and the minimum temperature required to complete the reaction was 1150°C for 1h. However, the best densification was achieved in the presence of a liquid phase at 1250°C, within a region between the solidus and liquidus lines of the ferrous matrix.

To illustrate the effect of the precursors, we selected another example for comparison. An iron matrix composite found in the literature 6) was obtained from the reaction of elemental powders of carbon, niobium, and iron. The elemental powders were milled in a planetary mill at 100 rpm with milling times of 5, 10, 15, and 20 hours and a ball-to-powder ratio (BTP) of 10:1. The samples were compacted at 600 MPa and sintered at 1300°C in an argon atmosphere. The composite microstructure is displayed in Fig. 8b) As previously mentioned, milling the elemental powder mixture can help improve particle adhesion and reduce size. However, as reported by the authors, 20 hours of milling did not allow for the dissolution of carbon and Nb, and the resulting compacts, after sintering, had a hardness of 124 HV, while those milled for 5h had a hardness of 102 HV after sintering, which is low even for low-alloy steel.

Although the two cannot be directly compared due to differences in reinforcement quantity and matrix carbon content, it is clear that the strengthening potential of the second approach was much more effective. Comparing the SEM images of both approaches are shown in Fig. 8 we can demonstrate that, although thermodynamic equilibrium favors the formation of NbC and Fe in both systems, the resulting microstructures are significantly different. The mean free path and carbide size is one order of magnitude larger in Fig. 8b) and there is a larger number of pores, particularly at interfaces and within carbides.
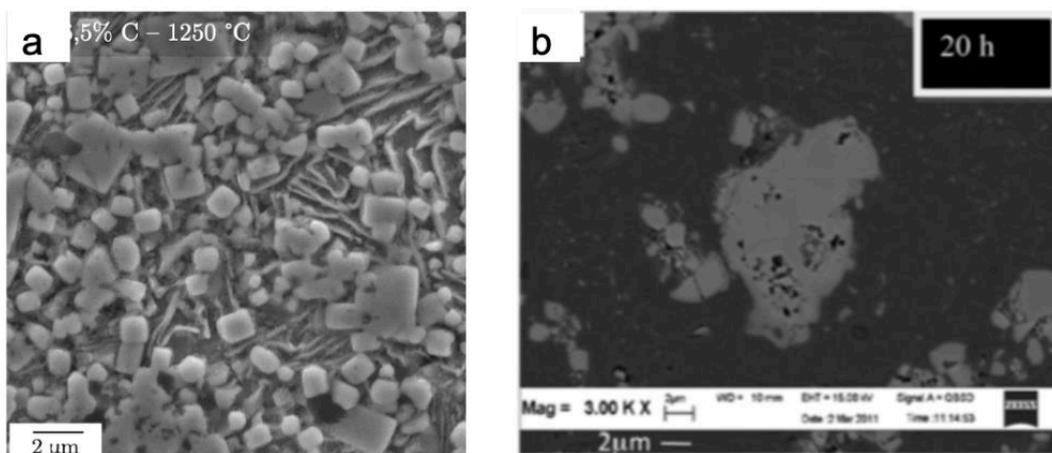

Fig. 8: a) composite made from Fe$_2$Nb and b) a composite made from elemental Nb and Fe [6], which exhibited inferior properties.

Conclusion

This study aimed to illustrate the application of a theoretical framework for *in situ* metal matrix composite development, particularly for powder metallurgy. By using thermodynamic principles, we validated the composite system and assessed composite formation kinetics and microstructural features based on the equilibrium simulations and an analysis of the diffusion of elements in raw materials. Our experimental results illustrated the decision-making steps and demonstrated the success of our methodology in obtaining the material based on the proposed framework.

Acknowledgements

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