

## Chapter

# Copper Bimetals and Their Nanocomposites

*Hussein Shokrvash, Rahim Yazdani Rad, Abouzar Massoudi and Reza Shokrvash*

## Abstract

This chapter deals with the study of the electrolysis synthesis of copper matrix nanocomposites developed for the fabrication of nanoparticulate Cu-bimetals. In this chapter, we describe the successful synthesis of Cu matrix nanocomposites by the electro-deoxidation method. We think that this approach will make it possible to realistically integrate a series of copper-bimetals. This study makes a significant contribution to the literature because this method opens novel opportunity to the design of nanocomposite materials. Particularly, this opens up prospects for designing the new materials from immiscible metallic elements, which is the main topic in designing of alloys as well as materials science progression.

**Keywords:** copper bimetal, immiscible metals, nanocomposites, nanoalloys, electrosynthesis

## 1. Introduction

Copper is widely used for electronic and thermal devices due to its excellent electrical and thermal conductivity, as well as corrosion resistance and ease of fabrication [1]. Its application is limited due to poor mechanical properties and high coefficient of thermal expansion [2, 3]. Along with rapidly growing technologies, demand for new materials which could meet the technological needs quickly increases. Therefore, scientists are looking for materials that are able to meet the new demands presented by operating conditions in the high-tech applications [4–7].

Some of optimal properties are the high strength-to-weight ratio, high conductivity, and thermal stability. Traditional commercial Cu alloys can achieve these functions but show limitations which include lower specific strength and high density which impact negatively on structural applications. The Cu bimetal is the foundation of high-strength materials without any compromise in electrical conductivity. They are becoming a research focus on how to extend the solubility of immiscible metallic elements in copper which will increase the strength and without losing conductivity.

The solubility of elements in bulk phases commonly limited to equilibrium states, which is defined as an element might dissolve in the structure of the metal. Since the optimum performance in multiphase materials cannot be gained, the development of synthesis methods is inevitable for improvements of the solid solubility [8–12].

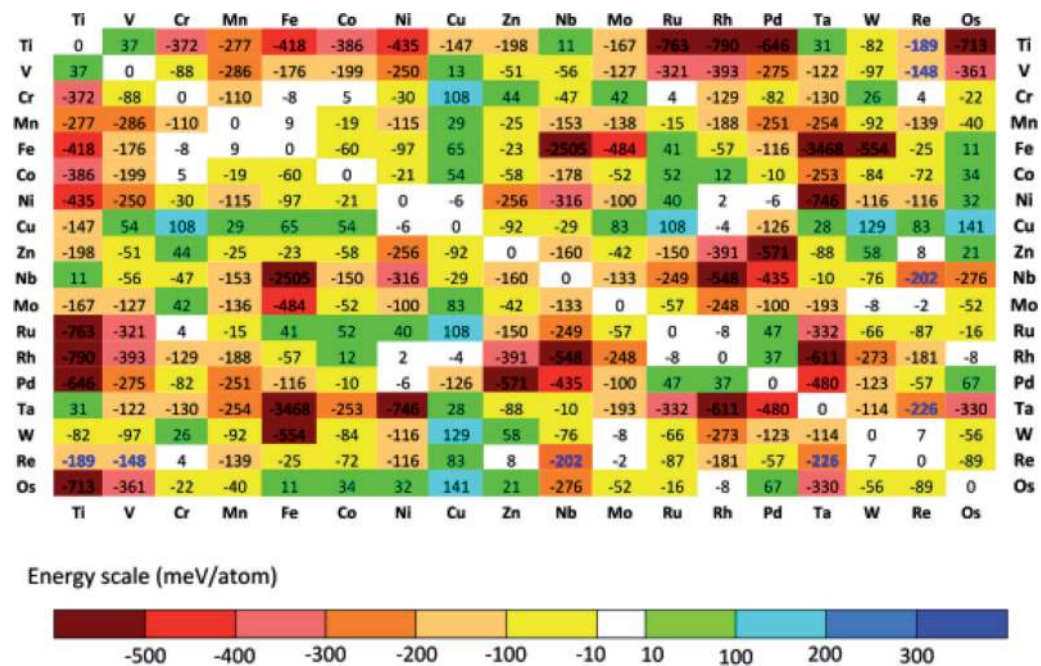
Recent progress in nanoscience has led to the great breakthroughs in the material fields and broad foundation in nanomaterials and processing technologies [13–17].

The synthesis and upscaling nanomaterials to bulk products fulfilled through direct manipulation of atoms and molecules with using of new approaches and precise assembling which leads to the emergence of novel multi-component nanostructures. The capabilities of nanotechnology open up exciting new prospects for the design of monolithic materials from immiscible elements which have a positive enthalpy of formation [18–22].

## 2. Aspect of thermodynamics

As a thermodynamic principle, all binary systems are divided into two groups: those with positive heat and those with a negative heat of formation. The negative enthalpy of formation symbolizes a mutual solubility of elements [23]. The same applies to the intermetallic compounds. If one or more intermetallic compounds occur in the phase diagram, or if there is a significant solid solubility between the given elements, an enthalpy of negative detection is expected. If none of the conditions are satisfied, it is expected to be positive enthalpy [24]. **Figure 1** shows collections of immiscible binary systems which have a positive enthalpy of formation. Based on the Hume-Rothery rules [26], synthesis of the homogeneous bulk alloys from immiscible metals infeasible and increase one of the elements leads to the formation of a new phase.

Cu bimetals are the most important immiscible binary systems used in magnetic, mechanical, thermal, and energy systems. The strength of copper increased by adding nonsoluble elements at the expense of electrical conductivity. This can be mitigated by choosing the alloying elements with little or no solubility in copper



**Figure 1.** Enthalpy matrix. Calculated enthalpies of formation of the lowest-energy structures of binary compounds relative to phase separation into pure elements. The numbers in bold blue font have been calculated with respect to the solid solution (with the permission of Troparevsky, M. C. [25]).

at thermodynamic equilibrium state which will increase the strength without any reduction in electrical conductivity. Niobium (Nb) and molybdenum (Mo) with bcc crystal structure are elements which satisfy the above criteria. The Cu-Nb and Cu-Mo bimetals are an advanced class of materials offering superior performance and defined by a unique structure, precisely engineered to overcome the limitations of bulk materials.

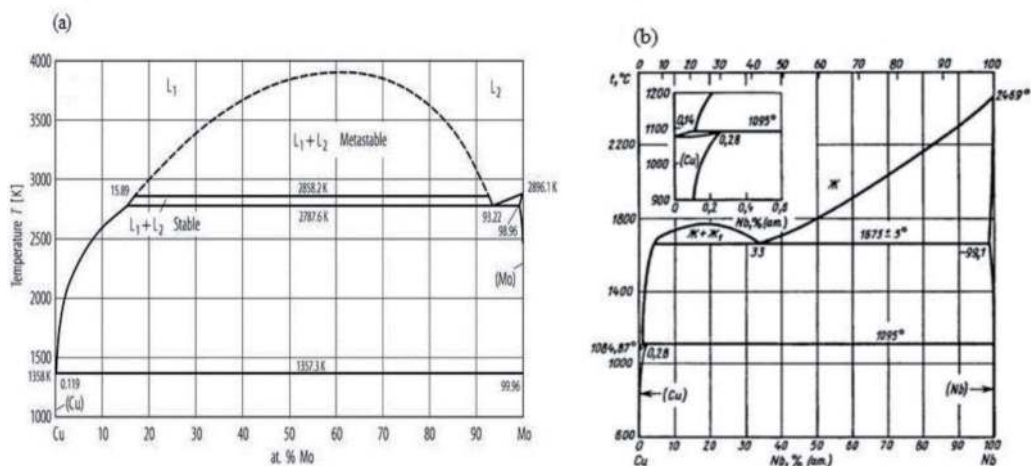
Thermodynamic data for reliable predictions of liquidus, phase fraction, and equilibrium and non-equilibrium solidifications behavior is required, because it is difficult to obtain these information from enthalpy of formation. The equilibrium phase diagrams of Cu-Mo and Cu-Nb are shown in **Figure 2**.

The Cu-Mo system has a very limited terminal solid solutions and the eutectic reaction  $\text{Cu}_{(L)} + \text{Mo}_{(L)}$  at  $1083.4^\circ\text{C}$  and the monotectic reaction  $2515^\circ\text{C}$  [27].

In the Cu-Nb system, Nb is soluble into the structure of Cu less than 0.1% at room temperature and up to 0.98% at  $1095^\circ\text{C}$ . The Cu dissolution in the Nb structure is about 0.1% and up to 0.975% at  $1675^\circ\text{C}$ . In this system, there is also a tendency for clustering in a liquid state due to the transformation of the peritectic reaction with 0.87% of Nb at  $1095^\circ\text{C}$  [28].

The Cu-Nb and some binary systems of Nb were studied by Ablitzer [29]. He showed that the diffusion rate of Cu-Nb was greater than Nb/Nb. These studies showed no interdiffusion of Cu-Nb or partial diffusion in Cu-Nb pair at  $1000^\circ\text{C}$  for 14 days. These results show that iron, cobalt, and nickel diffuse abnormally fast in niobium, whereas the latter displays no curvature (on an Arrhenius plot) in self-diffusion (Eq. (1)). Analysis of all available data for impurity diffusion in niobium shows that the solidus rule proposed by Roux and Vignes is completely quantitative as regards both activation energies and diffusion coefficients [30]:

$$\begin{aligned}
 D_{\text{Nb}/\text{Nb}} &= (0.81 \pm (0.57 \ 0.30))e^{-\left(\frac{94900 \pm 1400}{RT}\right)} \\
 D_{\text{Cu}/\text{Nb}} &= (0.00 \pm 0.00 \ 0.00)e^{-\left(\frac{000000 \pm 0000}{RT}\right)} \\
 D_{\text{Fe}/\text{Nb}} &= (0.14 \pm (0.08 \ 0.05))e^{-\left(\frac{70300 \pm 1400}{RT}\right)} \\
 D_{\text{Co}/\text{Nb}} &= (0.11 \pm 0.05 \ 0.04)e^{-\left(\frac{65600 \pm 1200}{RT}\right)} \\
 D_{\text{Ni}/\text{Nb}} &= (0.077 \pm 0.02 \ 0.016)e^{-\left(\frac{63100 \pm 800}{RT}\right)}
 \end{aligned} \tag{1}$$



**Figure 2.**  
 The equilibrium phase diagrams of (a) Cu-Mo and (b) Cu-Nb [27, 28].

### 3. Fabrication techniques

Copper bimetals consist of immiscible metals with notably different melting points and are attractive due to the unique combination of their mechanical, electrical, and physical properties. It has been shown that the non-equilibrium supersaturated solid solutions can be achieved in Cu-based binary system by mechanical alloying (MA) [31, 32] rapid solidification [33, 34], and thin-film deposition [35, 36]. The fabrication of Cu-based binary system such as Cu-(Nb, Cr, W, Fe, etc.) has been reported by mechanical alloying. Despite the positive heat of mixing the alloy constituents, the complete dissolution of the minority phases into the copper fcc lattice was observed for each specimen after 16 hours of MA.

Apart from the importance of Cu-Nb system due to the outstanding properties and applications in various fields, a major restriction of this system is the immiscibility of elements in each other. Therefore, Cu and Nb do not form any alloys by conventional bulk processing techniques. These issues have been addressed in researches related to the synthesis of Cu-Nb composites. Dupouy et al. [37] have presented a method for production of nanocomposites from these materials. In this method, Nb rod was placed in the Cu tube, and the nanostructured composite was produced by drawing. Extended results of investigations into these materials are contained in the studies carried out by Funkenbusch et al. [38] as well as Hangen and Raabe [39]. However, it has been shown that non-equilibrium supersaturated solid solutions can be achieved in Cu-Nb system by mechanical alloying, rapid solidification, thin-film deposition, and accumulative roll bonding.

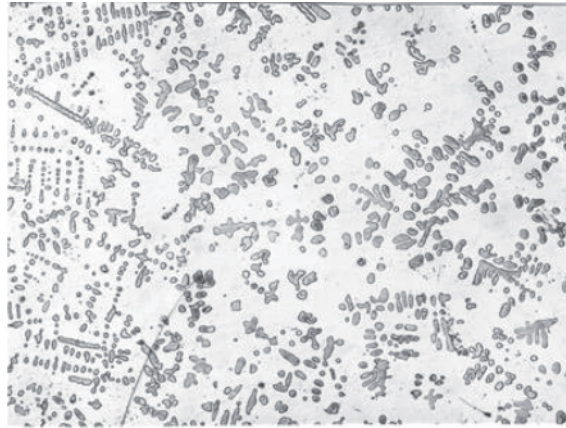
### 4. Microstructure and properties

The multidisciplinary properties of Cu-Nb materials require a coordinated, collaborative, and focused approach in addressing the immiscibility challenge. The mutual solubility of Nb and Cu is negligible, less than 0.1% for Nb in Cu lattice and 0.9% for Cu in Nb lattice near room temperature. Whereas, there are great prospects for application and their superb roles, which have ultimate tensile strength over 750 MPa, and electrical conductivity of 65% IACS and resistivity of  $1.7241 \mu\Omega \text{ cm}$  [40–45].

Zeik used rapid solidification technique and showed high volume fraction of Nb-Cu multiphase which is distributed within a Cu-rich matrix containing Nb-rich dendrites [46]. Gluchowski used pure Cu as matrix, and fine particles of second phase with dimensions at the level of 100 nm has been observed on the borders of matrix grains [47]. Being a non-equilibrium method, film formation by sputtering deposition could result in improvement of the solid solubility, intense changes within the defect density, the formation of metastable phases (pseudo-alloys), and changes within the microstructure of alloy films. Research studies have documented the wide variety of copper-niobium nanocomposites, exhibiting the enhanced properties such as thermal stability, mechanical strength, superconductivity, and irradiation resistance (**Figure 3**) [48–53].

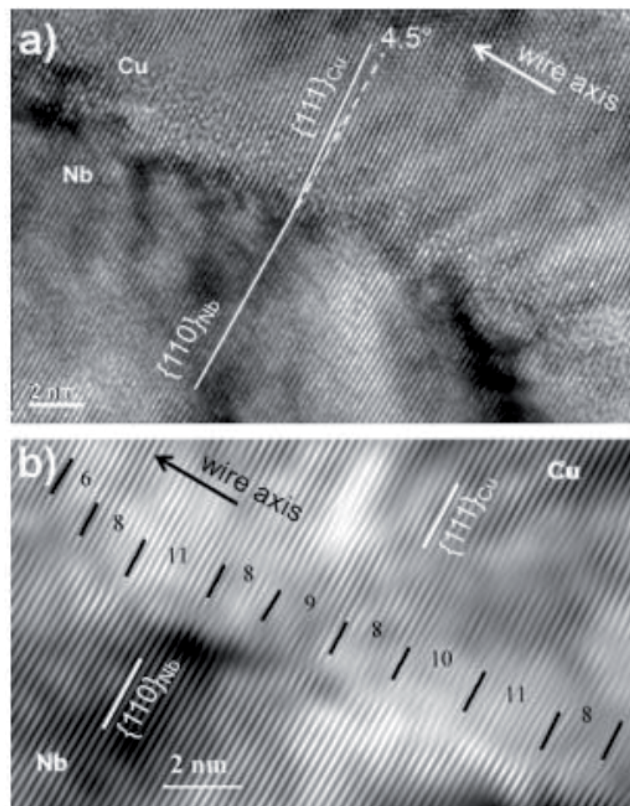
The fabrication of pseudo-alloys by nanoparticles has been reported for different Cu-based binary systems such as Cu-(Nb, Cr, Fe, W, Ru, etc.). One way to strengthen copper is to add immiscible metallic elements such as chromium and niobium elements to form supersaturated solid solution [31, 47], which is subsequently heat-treated to form high-strength copper alloy with fine dispersed metallic particles.

Excellent mechanical properties and good electrical conductivity are outstanding features of copper-niobium compounds. Other important features of copper-niobium compounds are superconductivity and its use in superconductor wires [49–54].



**Figure 3.**  
*The microstructure of copper-niobium coarse-grained particles is copper-rich and niobium-rich compounds dispersed in amorphous phase [46].*

Cu-Nb nanocomposites have been produced with severe plastic deformation (SPD) process. The Cu-Nb composition plays a significant role in the mechanical properties of these materials. The copper-niobium interface has been studied with high-resolution transmission electron microscopy (HRTEM). Although copper and niobium have poor mechanical bonds prior to the process, they are produced with strong bonds after plastic deformation. In **Figure 4** the regular interface  $\{111\}$  Cu// $\{110\}$  Nb is shown with a thickness of 2 nm along the wire axis [52].



**Figure 4.**  
*HRTEM image shows the Cu-Nb interface. It is observed that a regular interface of  $\{111\}$  Cu// $\{110\}$  Nb is formed along the wire axis with thickness of 2 nm [52].*

Mara and co-workers investigated nanoparticle nanocomposites of Cu-Nb with thicknesses of 5 and 40 nm with magnetic sputtering techniques [54]. They observed the growth of layers was consistent with the planes of {111} Cu//{110} Nb and with the constant control of uniform growth of the nano-layers.

The experiments are given by three-dimensional Cu-Nb nanocomposites in which nano-sized drops of niobium are immersed into a copper matrix. The structure consists of coarse phase of copper and niobium-rich compounds, which are scattered throughout the amorphous phase. Degtyarenko showed such systems being superconducting even at Nb content lower than a percolation threshold, but its properties in comparison with the granular one fabricated at slow melt cooling have a distinction in kind [55].

The transport properties in this system are strongly affected by the size and proximity effects but free from a complicating anisotropy factor. In comparison with it, Degtyarenko et al. evaluated the Cu-Nb composites with a micron-scale structure. Samples of the first type represent the tapes prepared at extremely fast cooling of Cu-Nb melt. The niobium drops and spacing between them have a measure of about 10 nm, and the drops are immersed into the Cu matrix with low content ( $\sim 1$  at%) of Nb. The system is similar to a granular superconductor, but its structural sizes are less than coherence lengths of the materials forming it.

The copper-rich or niobium-rich phases exhibit a positive resistance coefficient (TCR). In the Cu-90Nb composition, the first transition temperature is superconducting ( $T_C \sim 4.5$  K). The amorphous film exhibits high room temperature resistance as well as negative TCR, and the transfer of superconductivity is dependent on the amorphous phase composition (Figure 5) [55].

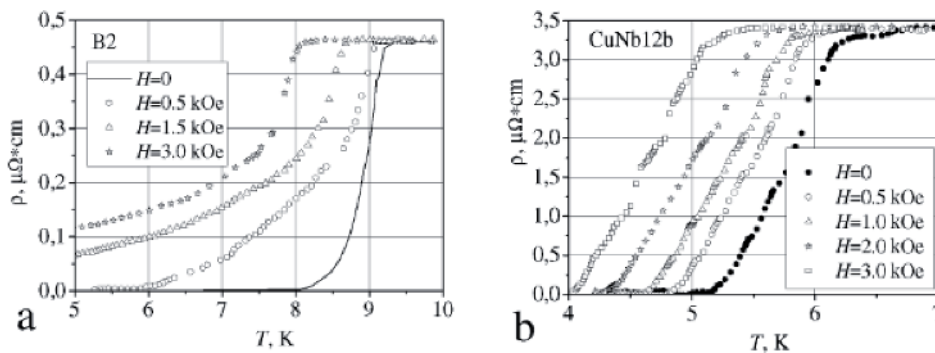


Figure 5.

The temperature dependence of the resistivity in the vicinity of the superconducting transition of the slow cooled (a) and quenched (b) samples [55].

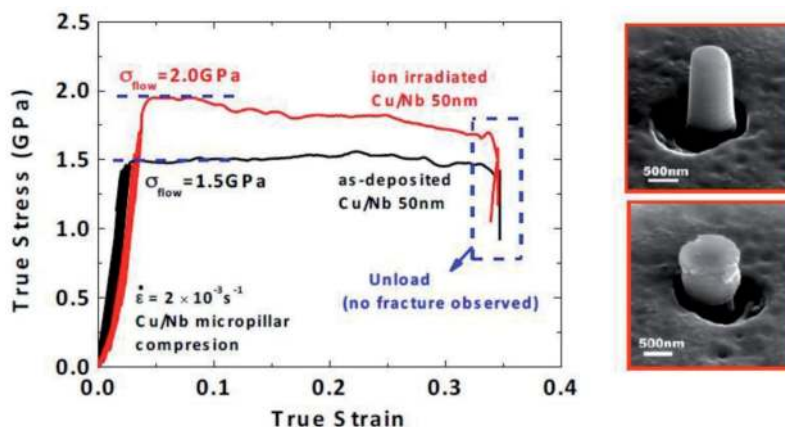


Figure 6.

The stress-strain diagram of Cu-Nb composite which is true in different circumstances [56].

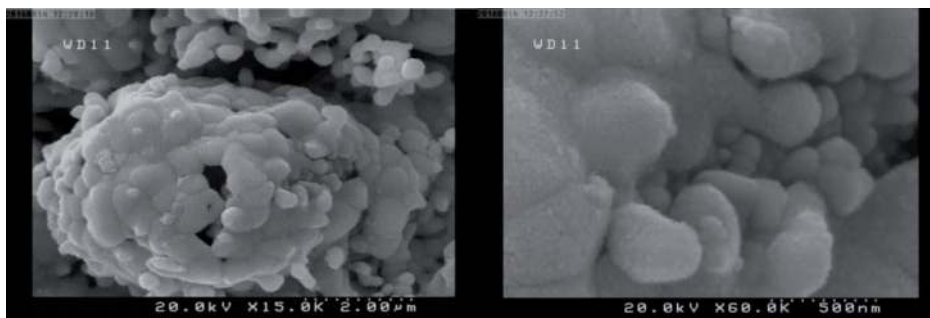
Beyond the ability of conductance, superconductivity, and thermal stability, Cu-Nb nanocomposites also enable extraordinary and unusual mechanical properties after exposure to radiation [56]. The effect of radiation on mechanical properties of Cu-Nb thin-film nanocomposites was investigated by Li et al. [56]. To perform these tests, a pressure on the specimens was performed by designing micrometer diameter specimens. He described the effects of radiation on compressive strength and a slight reduction of the plastic strain, while a failure phenomenon was observed at the applied maximum strain (**Figure 6**).

## 5. New approaches

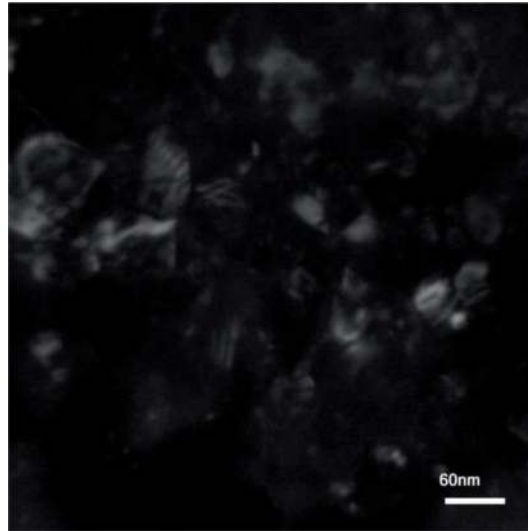
Early success in manufacturing Cu-Nb bimetallics at scale have come as three-dimensional nanocomposites. At this scale, Shokrvash et al. [57] lined the Cu-Nb bulk nanostructure with a metal oxide precursor ( $\text{Nb}_2\text{O}_5$ ) and Cu. These studies describe the successful synthesis of Cu-Nb nanocomposites by the electro-deoxidation method. Structural analysis of the obtained products reveals rapid reduction of  $\text{Nb}_2\text{O}_5$  to Nb and the embedment of Cu and Nb within the bulk nanostructures of Nb and Cu, respectively. The authors have elaborately discussed the electrochemical route to process Cu-Nb composites. The solubility of Cu in Nb could be enhanced through this technique. They have adopted different characterization techniques to show the solubility, structure, and morphology of Cu-Nb composites synthesized by the electrochemical route. The oxygen-free nanostructured materials could be processed using this technique. This investigation deals with the study of the electrolysis synthesis of Cu-Nb nanocomposites, and developed to fabrication of nanoparticulate bulk materials with equilibrium processes to delivering improved electrical conductance (**Figures 7 and 8**) [58].

It has been proven in the Cu-Nb system that the immiscibility can be overcome and direct alloying can be realized between the constituent elements by a local electric field between the boundaries of nanoparticles [58]. The mechanical properties of as-synthesized materials have been investigated by nanoindentation testing. The indentation hardness and modulus have been measured using a maximum load of 10 mN with a loading rate of 20 mN/minute and holding and unloading rate 20 mN/minute. The acquisition of data from five tests presented the ultimate strength for Cu-14%Nb and Cu-22%Nb nanocomposites ranging 4.42–4.82 GPa [59].

In these research, thermodynamic and kinetic model has been established for direct alloying between Cu and Nb, based on electromigration theory. Particularly, this opens up prospects for designing the new materials from immiscible metallic elements, which is the main topic in designing alloys as well as materials science progression.



**Figure 7.** FESEM image of Cu-22%Nb representing the composite structure (images by secondary electron mode) (with the permission of Shokrvash [57]).



**Figure 8.**  
*The dark field TEM image of Cu-22%Nb nanocomposite (with the permission of Shokrvash [57]).*

## Author details

Hussein Shokrvash<sup>1\*</sup>, Rahim Yazdani Rad<sup>2</sup>, Abouzar Massoudi<sup>2</sup> and Reza Shokrvash<sup>3</sup>

1 Research Center for Nanotechnology and Nano-Devices (RCNN), University of Maragheh, Iran

2 Materials and Energy Research Center, Iran

3 Electronics, Telecommunication Department, Civil Aviation Technology College, Tehran, Iran

\*Address all correspondence to: hshokrvash190@gmail.com

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