	Advanced Ceramics Progress	**Research Article**

Electro-Synthesis of Cu-Nb Nanocomposites; Toward Novel Alloying of Immiscible Bimetals

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PAPER INFO	ABSTRACT
	Immiscible metals due to their inherent specs are insoluble over the steady state. Developing an innovative approach to this issue would be fascinating and challenge the overriding rules. Herein, we proffer the principles of synthesis of Cu-Nb nanocomposites using electrochemical deoxidation route. This method consists of the cathodic electrolysis of the nanoparticles Cu-Nb_2O_5 through the molten salt electrolyte medium; which lead to the oxygen-free nanocomposites following the reduction of Nb_2O_5 and atomic translocation of Cu/Nb. Analysis of as-synthesized specimens by X-ray diffraction implies the Nb_2O_5 is reduced into Nb and all reflections of Cu are shifted to low-angles. Moreover, elemental analysis by energy dispersive spectrometry (EDS) illustrates the high solubility of Nb in Cu and Cu in Nb structure, which their crystallinity is consistent with the XRD. These findings confirm the electro-synthesis is a key technique for reduction of nanometer oxides, the substantial increase of solubility, and nano-alloying of immiscible metals.

1. INTRODUCTION

Recent progress in nanoscience has led to the great breakthroughs in materials field, broad foundation in nanomaterials, and processing technologies[1-7]. The overall aim of the synthesis and upscaling of nanomaterials to macro-products fulfilled through direct manipulation of atoms and molecules are the emergence of novel nanostructures[8-12]. The nanotechnology capabilities open up exciting new prospects for designing the monolithic materials from immiscible metallic elements[13-17], that is the main subject in designing of alloys. The solubility of elements in bulk phases commonly limited to equilibrium states on the extent which is defined an element might dissolve in another structure. Based on the Hume-Rothery rules[18,19], synthesis of the homogeneous bulk alloys from immiscible metals infeasible and increment one of the elements lead to the formation of a new phase. Since the optimum performance in mixed phases cannot be gained; hence, the development of synthesis methods is inevitable for improvements of the solid solubility[20-22].

Cu-Nb belongs to an important class of bimetals with innate special properties[23-26]. It presents a large immiscibility gap according to its equilibrium phase diagram. Therefore, Cu and Nb cannot be alloyed by conventional methods. Although many methods have been developed to process Cu-Nb nanocomposites, controlled synthesis of these materials remains a major challenge.

The Nb solubility in Cu structure is indeed extremely limited to a maximum of 0.28% in 1095°C and lower than 0.1 at% at room temperature. The Cu solubility in Nb structure is appreciably higher, up to 0.9% at 1675 °C [27,28]. While Cu-Nb compounds are certainly the most common functional materials owing to their excellent features such as thermal stability, mechanical strength, and superconductivity[24, 26-30]. However, and these are particularly true for reinforced Cu based on Nb and relies on well-defined architectures (e.g. 2D nano-laminate composites, nano-rod reinforcement, and nanoparticulate nanocomposites)[29-32].

The remarkable research has been conducted to design and fabrication. However, the controlled synthesis of these materials is generally a major challenge[33-39].

Due to the great importance of F.F.C. process[39,40] in the field of purifying and extracting, further developments are obtained to produce some of the alloy particles (e.g.

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Tb_4O_7, SiO_2/Si, Nb_3Sn, , TiNb, NbSi and $CeNi_4Cu$ [40-48]) by using electrochemical deoxidation. But so far did not report the synthesis of bulk nanocomposites through this method. Recently, Shokrvash and et al. [49] reports a new approach for electrosynthesis of metal-matrix nanocomposites by electro-deoxidation method. In this report, we describe the successful synthesis of Cu-Nb nanocomposites by an electro-deoxidation method based on referene 49. We designed and synthesized Cu-Nb nanocomposites via cathodic deoxidation of a nanometric $Cu-Nb_2O_5$ precursor in a molten NaCl-CaCl$_2$ electrolyte. Structural analysis of protype product revealed the embedment of Cu and Nb within the bulk nanostructures of Nb and Cu, respectively. Homogenized nanostructures with nanocomposite architecture and significant solubility of Nb in Cu and Cu in the Nb lattice were identify.

2. EXPERIMENTAL

The nanoparticles of Nb_2O_5 and Cu product of Merck are used to yield Cu-Nb nanocomposites. Firstly; the exact weight of Nb_2O_5 has been ground in a high-energy mill. The milling of Nb_2O_5 powder was carried out at different times (2, 5, 8, 15, 30 and 45 min). After grinding, powders were collected and analyzed by zeta analyzer and the particle size was determined. The mean diameter of Nb_2O_5 after 45 minutes of grinding reaches to 90.3 nm. The blends $Cu-Nb_2O_5$ nanoparticles, the starting material for the reduction process, with desired weight ratios are obtained via higher energy milling.
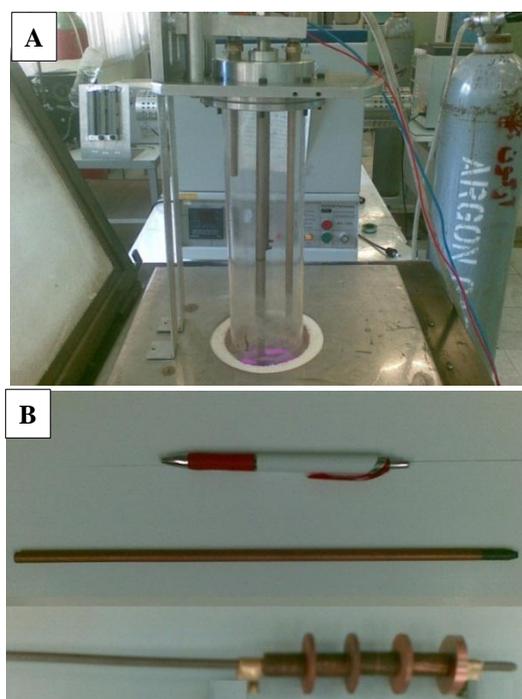

Figure 1. (A) Electrolysis apparatus set-up, (B) anode and cathode electrodes

Three sets of $Cu-Nb_2O_5$ prepare and each with 5, 10 and 15 at% Nb. The electrolysis apparatus for the synthesis of Cu-Nb, originally designed to systematic electro-deoxidation of the nanoparticulate $Cu-Nb_2O_5$ (Fig. 1A). The anode electrode made up compact pure graphite and cathode electrode is assembled $Cu-Nb_2O_5$ specimens (Fig. 1B). The eutectic composition of NaCl-CaCl$_2$ is selected as electrolyte. The preparation of electrolyte includes preheating at 150°C for half an hour and then heating to 350 °C for One hour and maintain at this temperature with the aim of complete evaporation of the water content of calcium chloride. After preparing the specimens, electro-synthesis experiments carried out in the molten salt electrolysis system. The direct potential (dc) is keep constant at 3.1, 3.0 and 2.9 volt. Using in situ current-time measurements with the various weight ratios of Cu/Nb_2O_5 approximate duration of the reduction and atomic transition to be estimated.

The characterization and phase composition of raw and synthesized materials are determined through a Philips pw3710 x-ray diffractometer. Morphology and chemical composition of phases are investigated by Mira 3-XMU Field Emission Scanning Electron Microscope (FESEM) equipped with energy-dispersive x-ray spectrometry (EDS). The atomic force microscopy (AFM) studies of surface topography, phase imaging, and lateral force microscopy are perform with auto probe park scientific instrument.

3. RESULTS AND DISCUSSION

Since the goal of this investigates is to develop, practically electrochemical deoxidation to the synthesis of Cu-Nb nanocomposites. The scheduled experiments performed by cathodic electrolysis of $Cu-Nb_2O_5$ precursor.
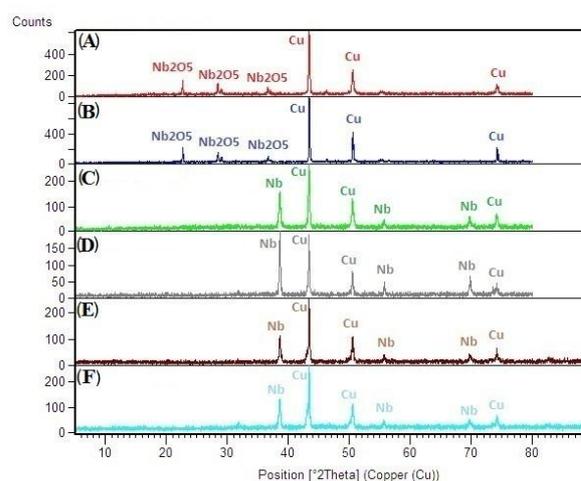

Figure 2. XRD pattern of Cu-29.38wt% Nb_2O_5, (A) powdered and (B) sintered and before electrolysis, (C, D, E and F) 4 and 5 h electrolysis, applying voltage 2.9 V at 850 °C

The exact identification of the as-synthesis specimen supplies by XRD at different times. Fig. 2 shows the XRD patterns of Cu-29.38% Nb_2O_5 before electrolysis, four and five h electrolyzed at 2.9 V in 850 °C. The XRD pattern before electrolysis shows main peaks (001), (200), (201) of Nb_2O_5 and (111), (200), (220) of Cu (respectively, data take from JCPDS 37-1468 and JCPDS 85-1326). While only Cu and Nb phases are detected after four h electrolyzes, and no peaks of the surplus or trace phases. (Fig. 2C, D). The XRD patterns cross-sectional cut of specimens with 4 and 5 h electrolyzes (Fig. 2E, F) exhibit Nb_2O_5 phase was fully reduce into Nb (data matched with JCPDS 35-0789), in which the positions are consistent with an oxygen-free content and all reflections of Cu are fixed. By exploring analyzing, XRD patterns of products, which extracted at various

times up to 5 h can be inferred all of the reflection are shift to small angles and broadened.

XRD patterns after 4- and 5 hours electrolysis exhibited broadening of peaks (Fig. 3 (D), (E) and (F)), where the crystallite size of Cu (111) were estimate using the Xpowder-12 software. (Fig. 3(E) and 1(F) top right insert). The spectra were fitt using a Scherrer function and any disparity between the measured Cu (111)-2θ position and simulation as a linear offset for the reflections from the corresponding data. A new peak arises at 43.19° after 5 hours electrolysis and its position is wholly different from the strongest peak of (111) Cu and unrelated to compounds in the Cu–Nb–O system, which was exposed to X-rays with high intensity. This peak typically indicates a new phase and strong evidence to the ordering of Cu-Nb compounds.
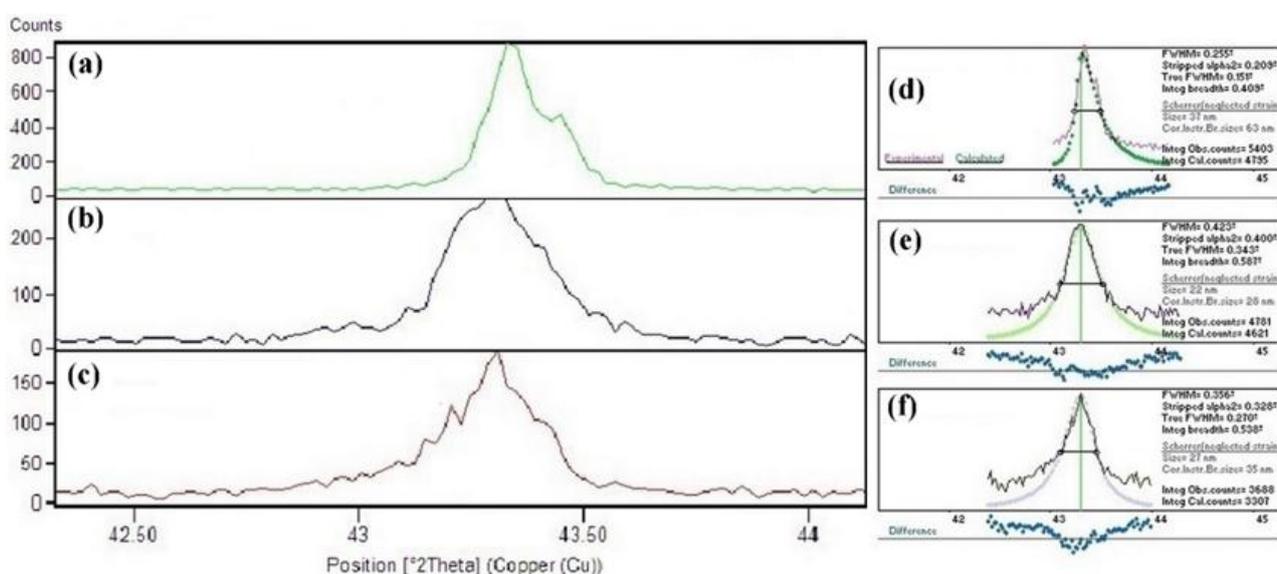

Figure 3. (A), (B), and (C) The peak of Cu (111)-2θ position, (D), (E), and (F) measured and simulation as a linear offset for the reflections from the corresponding data

Morphologic analysis of the Cu-Nb bulk nanocomposite was perform by FESEM imaging (Fig. 4A). The FESEM images represent the development of in-grain and nano-nano nanocomposites architecture and show the reality of the phase distribution and complicated structure, including spherical nanometer particles in the matrix (Fig. 4B). The homogeneous structure (Fig. 4C), uniformity distribution of particles, and intertwined grains with an average diameter less than 100 nm.

Energy-dispersive x-ray (EDS) map used to determine the elemental composition of individual points with

nanometer size of the imaged area(Fig. 5A). EDS performed for spatially-resolved elemental analysis of matrix, niobium reinforcement and the boundary of phases. The EDS spot analysis carries out in two distinguish Nb-containing phase (red region) and Cu-matrix (green region). Figure. 5B shows the EDX spectra of Cu and Nb phase. The ratio of the peaks is in good agreement with elemental composition. The EDS analysis of specimens which 4 h electrolyze significant higher solubility of Cu in Nb (9.75 wt% or 10.59 at%) and Nb in Cu (6.72 wt% or 2.59 at%) structure.
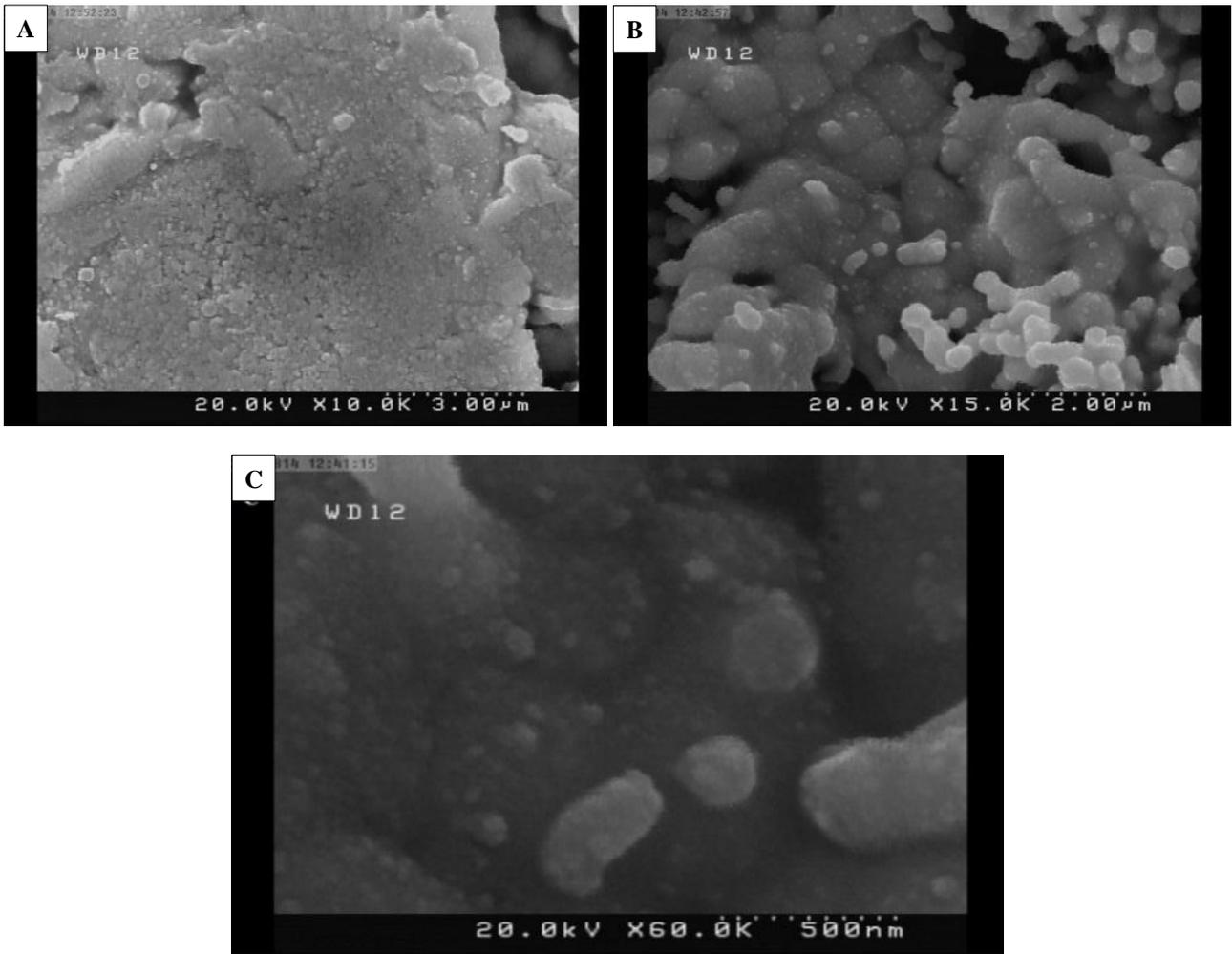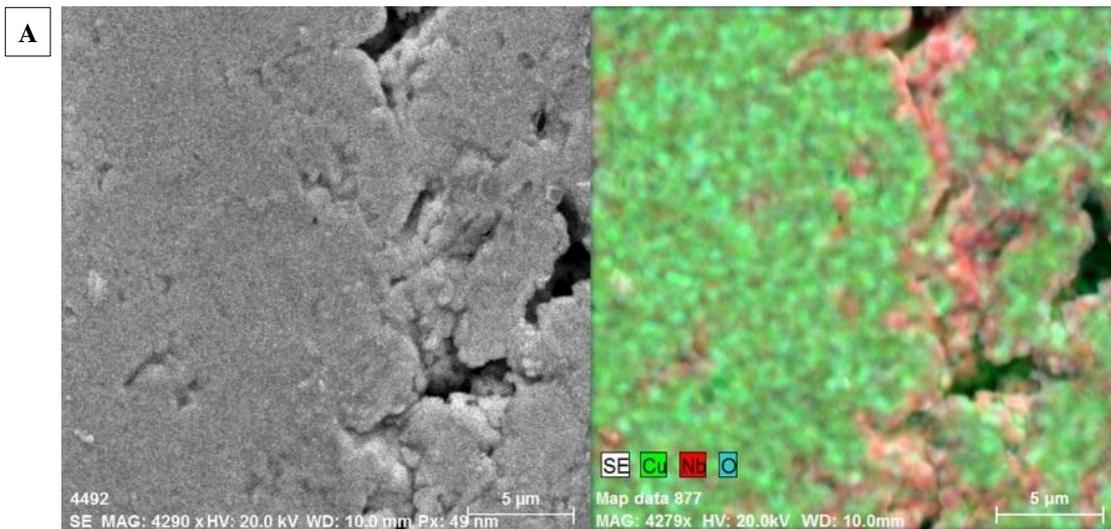
Figure 4. (A). FESEM secondary electron detector image of as-synthesize Cu-20.5% Nb, (B). ×15000 magnification of as-synthesize Cu-20.5% Nb, and (C) ×60000

HV: 20.0kV   Puls th.:4.33kcps

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El AN  Series    unn. C  norm. C Atom. C Error (1 Sigma)
                  [wt.%]  [wt.%]  [at.%]           [wt.%]
------------------------------------------------------------
Nb 41  L-series   25.42   49.31   36.75             1.03
Cu 29  K-series   24.86   48.22   52.54             0.91
O  8   K-series    1.27    2.47   10.70             0.79
------------------------------------------------------------
       Total:     51.55  100.00  100.00
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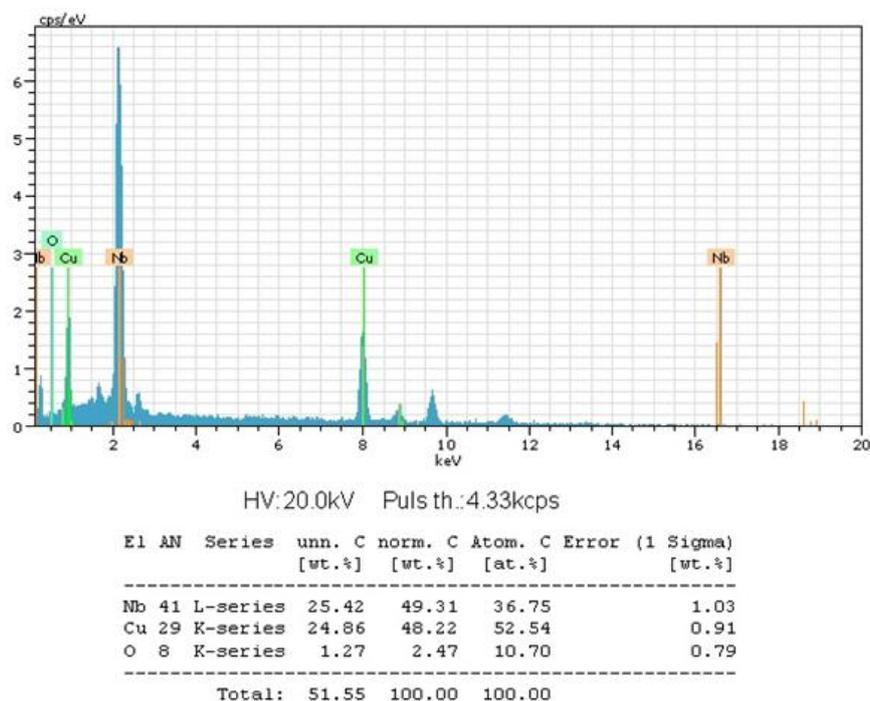
Figure 5. (A) EDS map of Cu matrix (green dots) and Nb reinforcement (red dots) (B) EDS spectra of Cu-Nb nanocomposite

Further, the lateral force microscopy allows obtaining high-resolution scanning of surfaces and topographic images were record as chemical distribution. Hence, high-sensitivity, chemical component reconstructions of samples are possible with the LFM, so is used for accurate perception of phase distribution (Fig. 6A). The experimental LFM image shown in Figure 6B, to obtaining compositional contrast with high-resolution nanometer-scale and the phase distribution.

Using the LFM technique, the map of the phase distribution of Cu-Nb nanocomposites is construct with nanometer resolution (Fig. 6C). This map detects the significant large contrast difference between the phases, as they exclude regime, which the contrast between the phases is reversed. As indicated in figure 6B, Nb was grow as nanowires and have a rough surface and perfect taper mode. The roughness (RMS) value is obtained 500 nm (Fig. 6D), which higher than the size of particles coming from the milling.

4. DISCUSSION

The aforementioned analyzes reveal the electro-synthesis of nano-metric Nb_2O_5 precursors is a short time and lower temperature fabrication method. Homogenized nanostructures with nanocomposite architecture and significant solubility of Nb in Cu and Cu in the Nb lattice were identify. Based on XRD

findings, the duration of the full synthesis of Cu-Nb is 4~5 hour using the nano-sized Nb_2O_5. By comparing, this is much less than deoxidation process of micron-size Nb_2O_5 (24~48 hour) reported by Yan[48] which was synthesized by the same method. Furthermore, Song *et al.*[50] successfully prepared metallic Nb from Nb_2O_5 by electro-deoxidation and estimate that the NbO_2 is reduced to NbO after 12 hours.

In contrast, our data show the electrolysis process would be complete in 5 hours. The XRD exhibits three relatively broadened reflections of Nb and Cu due to the effect of solubility of Cu/Nb. The main peaks of Nb and Cu phase, after 4 and 5-hour electrolysis reveal the removal of oxygen from the niobium oxide and solubility of Cu/Nb in each other's.

The EDS spectrum is show in figure 5 where it is clear that the solubility of Cu in Nb nano-phase in equilibrium with Cu matrix is much larger than for Nb bulk-phase. These results utterly evident the nano-alloying of Cu-Nb, which is one order of magnitude greater than the equilibrium grades. Furthermore, based on XRD data the formation of the peak near (111) of Cu and far from the (100) of Nb indicates a new phase with the saturation of Nb in the structure of Cu. The mutual dissolution of Cu/Nb shows the local electric field in the Cu/Nb nano-array is a force amplification for rapid migration of atoms. However, the growth of Nb nano-wires may experience a self-assembling process of the local electric field enforces during electrochemical reactions.
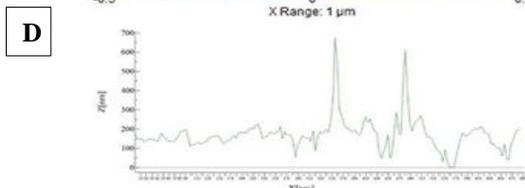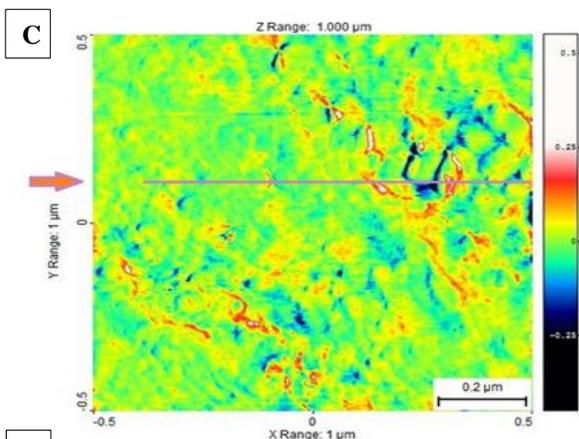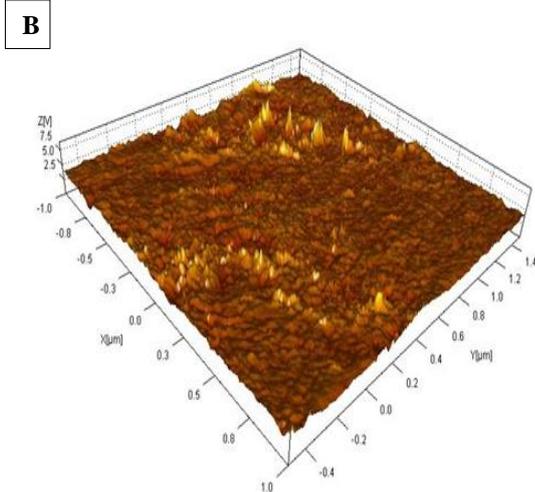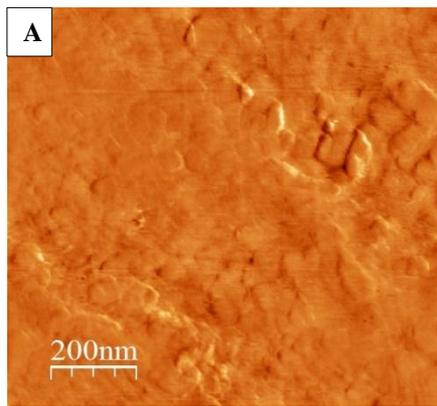
Figure 6. (A) 2D LFM, (B) 3D LFM image of Cu-20.5%Nb nanocomposite, (C) LFM map of Cu-20.5%Nb, and (D) topological height values along the arrow

It seems mechanism of formation of Cu-Nb nanocomposite by electro-synthesis consists two-step; the early stage is reduction of Nb_2O_5 and formation of non-stoichiometries Nb_xO_y and second the interdiffusion of Cu/Nb simultaneously with the gradual removing of oxygen. Structural defects (oxygen ion vacancy) in non-stoichiometry niobium oxide, largely affect the rate of electrochemical reduction and interdiffusion of Cu/Nb as the key points of the electro-synthesis. It is noteworthy that the non-stoichiometry layers of Nb_xO_y prior to bond formation are crucial. As the embodiment in figure 7, the distribution of electrons in Cu/Nb_xO_y nano-arrays impose the local electric field, towards the copper region.
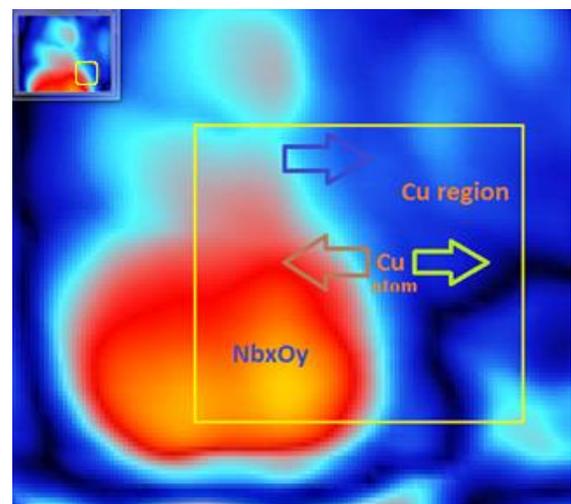

Figure 7. Schema of Cu-Nb_xO_y boundary and influential forces on Cu atom (The blue arrows show the electric field, brown arrows wind force direction, and green arrows direct force); where pale blue area virtually has been alloyed

This event leads to secondary reactions during the reduction of niobium oxide. Copper ions due to thermal fluctuations and local instabilities, exposure to scattering of electrons move in the opposite direction of electric field. The electric field on Cu/Nb_xO_y causes a significant increase in reduction of Nb_xO_y and the interaction between the ions of Cu and Nb. Thereby continuously both phenomena at the nanometer scale take place and leads to binding of particles and formation of the nanocomposite.

5. CONCLUSION

Current attempts focused on electro-synthesis and characterization of Cu-Nb nanocomposites by using nanoparticulate oxide precursors. The investigation suggests the electro-deoxidation is a reliable technique for the synthesis of Cu-Nb nanocomposites. The structural analysis of the obtained product revealed rapid reduction of Nb_2O_5 to Nb and the embedment of Cu

and Nb within the bulk nanostructures of Nb and Cu, respectively. The EDS analyses represents the high solubility of Cu in Nb nano-phase and Nb in Cu and mutually nano-alloying of Cu/Nb. The crystallinity of Cu and Nb-rich phase based on XRD is recognizable. The nano-alloying of Cu/Nb proves the diffusion-driven hypothesis can be rule out, to clarify the electro-deoxidation phenomena. Therefore, a new mechanism is propose for electrolysis synthesis of CuNb nanoalloys. Briefly, a new strategy is introduce for the electrolysis synthesis of immiscible Cu-Nb compounds which generalizable to the broad range of immiscible metals.

6. ACKNOWLEDGMENTS

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