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# Microstructural Evolution of the Refractory WCuNi Metallic Alloy

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**Abstract**

Science and technology of materials are widely interested in the development of new alloys involving tungsten due to its large applicability to the domain of nuclear material transportation. Tungsten is a refractory material and it has many applications in the nuclear industry due to its mechanical properties and excellent cross-section for thermal neutrons, being widely used for shielding of high-energy radiation. Some of the main elements added to tungsten forming alloys are Nb, Cr, Cu, Fe, Ni, Mo, Co, Sn, Ti, and Ta, which are responsible for modifications of the physical and chemical properties of the resulting alloy, interfering on the attenuation of gamma radiation. The main goal of this paper is to present a refractory alloy based on tungsten with embedded infiltrating elements like copper (Cu) and nickel (Ni) and characterize the microstructural evolution of different sintering process during its formation. Such a refractory alloy is submitted to the following characterization process: X-rays diffractometry, thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), scanning electron microscopy, and energy dispersive spectroscopy. The diffractometry exhibit typical standard results for the precursor powders: W, Cu, and Ni demonstrating high degrees of purity accordingly to the crystallographic determined parameters. The TGA for the powder W demonstrated thermal stability until 360 °C, after an increase of mass due to the process of oxidation. The DSC analyze present two endothermal processes at temperatures 350 °C and 450 °C. The microstructural evolution of WCuNi samples presents the absence of oxidation, homogeneous morphology and stability of the binary phase α–β (W and CuNi respectively) for different sintering. These results shall be taken into consideration for future works, particularly on the study of shielding and gamma radiation attenuation.

**Graphic abstract**

**Keywords** Microstructure · Tungsten · Alloy · Characterization

## 1 Introduction

Seeking the improvement of the quality of human health treatments is a worldwide permanent concerning. In this matter, nuclear science occupies a particularly important position on the production and control of radioactive and radio-nuclear substances necessary to attend the growing demand for specific drugs to be employed on the diagnosis and treatment of multiple forms of cancer. There exist a high demand worldwide for those products. Particularly, in Brazil the government started a project called Brazilian Multi-purpose Reactor (BMR) that is responsible for the production of molybdenum $Mo_{99}M$. The current demand for safe packing systems that can be used for transportation of such radioactive substances is intense, therefore fully justifying the search for new materials [1].

Different researches related to the microstructural evolution of metals and alloys are being carried on to obtain new composites presenting improved physical–chemical properties when compared to pure materials [2], which can be modified by introducing different concentrations of other elements, either in interstitial or substitutional positions [3, 4]. The introduction of punctual defects in the pure material directly contributes to modify its crystallographic parameters, causing segregation and/or formation of other

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crystalline phases. Modifications or transformations of the microstructure material directly contributes to change their mechanical properties in terms of resistance, ductility, tenacity, and fragility. These modifications can be produced by the diffusion of new elements through hot lamination and sintering [5].

Tungsten is a very interesting and particularly special material when shielding of radiation is important. It is a refractory metal [6, 7] having a large affinity with oxygen, particularly when interacting at an open atmosphere and submitted to temperatures between 327 and 400 °C, forming trioxide of tungsten or $WO_3$, but oxidation at high temperatures also occur [8].

For this paper, a new alloy made of tungsten as the matrix element with copper and nickel as infiltrating materials is studied, it is named WCuNi [9]. The principal idea is to obtain a refractory material suitable for shielding of gamma radiation and free of oxidation. The construction of such an alloy is characterized by two major roles. Copper is fundamental during the process of fusion as it provokes the complete diffusion of nickel inside the matrix of tungsten, agglutinating these materials and forming a homogenous alloy. Nickel is essential to inhibit the oxidation of tungsten. In this paper, some results of the microstructural evolution for this composed material are presented.

## 2 Sample Preparation

The samples used for characterization are constituted of tungsten powder within different concentrations of Ni and Cu as infiltrating elements. All powders used for this work are nominally 99.9% pure. In order to obtain these samples the following steps have been previously considered:

- Pure tungsten powder with the appropriate size of particles, in the order of 135 µm has been acquired;
- Separation of a set of different infiltrating samples, Ni and Cu;
- The powder of precursors have been weighted using a stoichiometric scale to obtain the correct amount of composition for each sample;
- The samples have been pressed with a charge on the order of 200 MPa, using a matrix holder sample that allows obtaining samples with 1.2 cm diameter and 0.8 height;
- These samples were separated and submitted to the sintering process in the sequence.

### 2.1 Sintering And Measurements Processes

The sintering step was realized accordingly to the composition of the processed alloy. A furnace with a temperature limit of 1600 °C has been used, set to a heating ramp of 50°/min and two different plateaus at 1200 °C and 1400 °C, respectively. For this system, the cooling is not controlled so the temperature drop is exponential. The furnace is coupled to a gas system in order to keep a constant and controlled flow of argon as a function of the temperature during the sintering process. The system also allows the possibility of applying a continuous reducing-atmosphere flow of argon and 5% of hydrogen [10].

Thermogravimetric analysis has been performed on the powder form of the composite after every step of the sample processing. The temperature ramp was set to 10 °C/min from room temperature up to 900 °C, under Argon atmosphere, in order to determine the mass variation as a function of time and temperature.

DSC analysis was realized using the same increase rate of temperature as described in the previous paragraph, i.e., 10 °C/min from room temperature up to 550 °C in order to observe the endothermic and exothermic processes. The thermogravimetric analysis help to determine some of the WCuNi samples sintering parameters [11].

In order to verify possible changes in the composite microstructure and phase changes during the sintering processes, X-ray diffraction (XRD) measurements have been performed. The introduction of interstitial elements induces local distortion in the matrix and can cause changes in the lattice parameter of the structure. The resulting diffractograms were analyzed using a mineral database software through a literature consultation of Hanawalt and Fink methods, comparison of results with the standards produced by the Joint Committee for Powder Diffraction System (JCPDS) of the International Center for Diffraction Data (ICDD), and by a refinement of Rietveld's method.

After each step to process and sintering samples, they were submitted to measurements for the analysis of its microstructural evolution. Micrographs were obtained through scanning electron microscopy (SEM) measurements to identify the current phases on the sample to observe its morphology, i.e. the formation and the contour of the grains, to evaluate the density of porous, and to analyze the possible formation of intermetallic phases. In the sequence, measurement of energy-dispersive X-ray spectroscopy (EDS) was obtained to provide both qualitative and quantitative analysis of the present elements in the samples of WCuNi.

## 3 Results and Discussions

The results presented in this paper are discussed after each separated technique has been employed to characterize the sample obtained from mixing tungsten (W), copper (Cu) and nickel (Ni), resulting in a composite called WCuNi. The sintering process described previously provides consistent stable samples. The principal goal in this report is to show and discuss the characterizations that follow below, which shall help the analysis of how convenient this composite may become for applications in all fields involved with materials of nuclear radioactivity.

### 3.1 Thermogravimetric Analysis

Figure 1 shows the mass gradient as a function of the tungsten powder temperature (W) used as the matrix for the metallic composite. The sample stability is noticeable between room temperature and approximately 380 °C when the mass starts increasing exponentially increase until T = 760 °C, after which it still increases but linearly. This augmentation of the mass is attributed to some residual contamination of the furnace atmosphere, together with some eventual gas impurity, and is certainly due to the high degree of chemical affinity between the tungsten and oxygen.

In Fig. 2a TGA measurement is exhibited for the copper (Cu) powder, which is used as the infiltrating element of the metallic composite. The mass of copper is plotted as a function of the temperature and its value is stable between room temperature and 500 °C approximately. A linear increase of the mass as a function of the temperature starts to occur after 500 °C. In this case, the linear coefficient is higher than the coefficient previously obtained for tungsten. Such an increase of the mass is again associated with residual impurities present into the furnace and eventual impurities of the gas. The chemical affinity between copper and oxygen is certainly responsible for the observation of this effect.

In this case, the analysis of TGA allowed evaluating the results obtained for the samples after they are submitted to a sintering process above 1250 °C. The isolated elements undergo a process of oxidation at low temperatures. When copper and tungsten are mixed, the oxidation process disappears. This effect can be explained by two simultaneous effects: the efficiency of the sintering process, which occurs under a high gas flow applied during the heating ramp, and by the stoichiometric balance between W-Cu, which minimizes the chemical affinity with oxygen.

### 3.2 Analysis of the Differential Scanning Calorimetry—DSC

The DSC measurements of the powder W, which was used as the matrix for obtaining the metallic WCuNi composite, are exhibited in Fig. 3. Two endothermic peaks are clearly identified in the graphic, the first one occurring at 360 °C while the second one appears at 450 °C. These endothermic peaks represent an increase of the chemical reaction enthalpy that can be associated with the process of oxygen absorption by the tungsten.

The endothermal peak observed at 180 °C is unconventional. It probably indicates an error regarding the measurements due to either some instrumental variation or due to a matter with the sample. It is not impossible that an issue occurred with the furnace heating at that point or even that some uncontrolled internal atmosphere happened during the preparation. On the other hand, this specific endothermic peak might also be associated to the sample through a

**Fig. 1** Characteristics curve representing the TGA of tungsten powder, i.e., the metallic mass variation as a function of the temperature

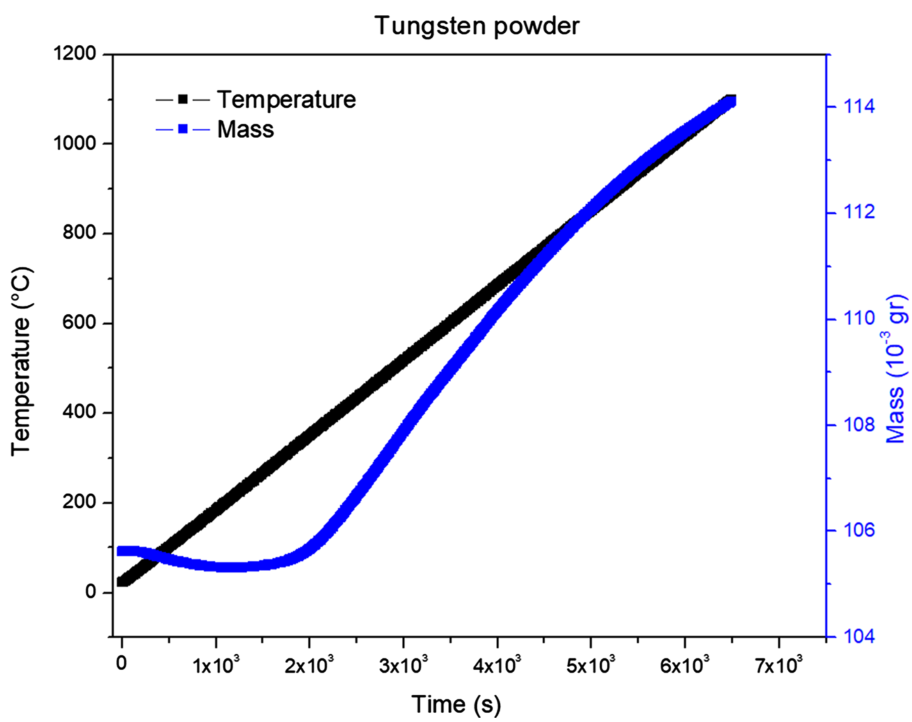


**Fig. 2** TGA measurements showing the variation of the Cu powder as a function of the temperature. Copper is the precursor for the composite WCuNi

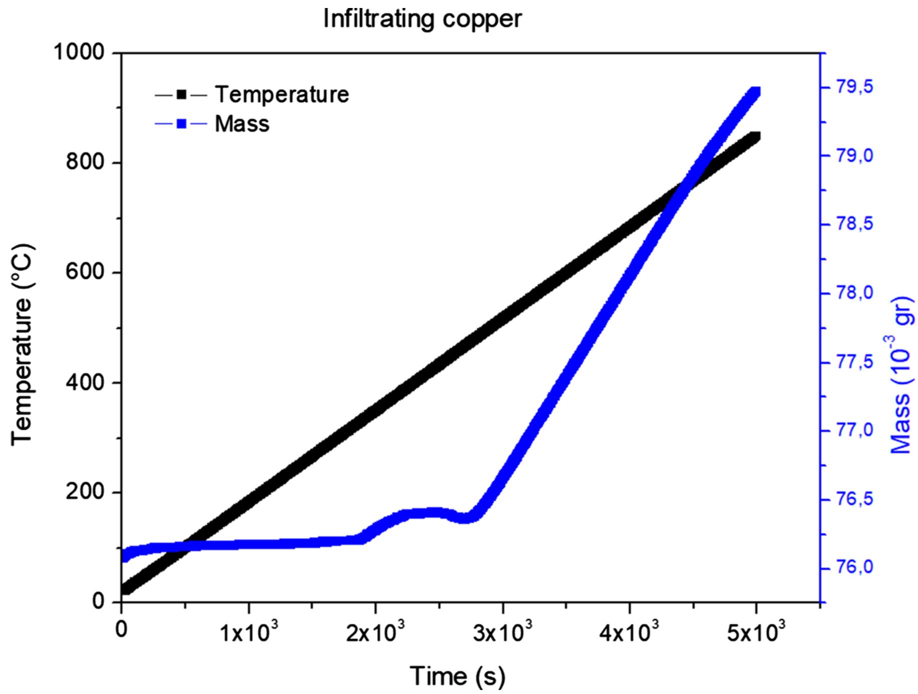
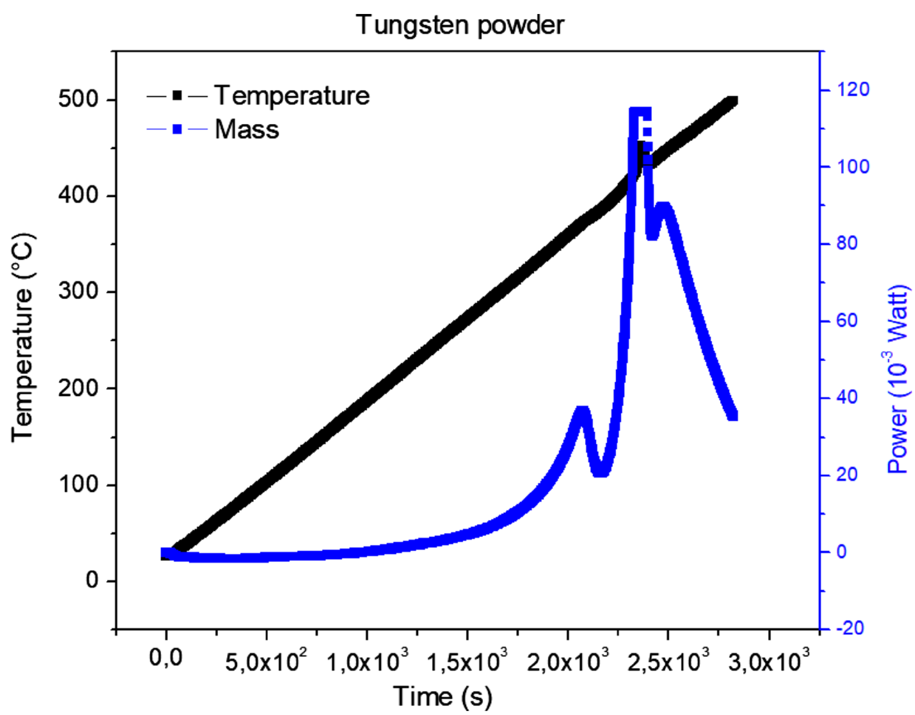



**Fig. 3** DSC results obtained for the tungsten powder, which is the matrix for the WCuNi composite




problem with the size of the particles or, eventually, with the solubility of gases released internally, or due to the reaction heat and the thermal conductivity of that sample [12].

Measurements of DSC have also been performed for the copper powder, which is used as the infiltrating element to obtain the metallic composite WCuNi. The result is exhibited as a graphic in Fig. 4, exhibiting again two endothermic peaks, with the first one occurring now at 100 °C while the second happens at 350 °C. These endothermic peaks represent again an increase of the chemical reaction enthalpy. The first endothermic peak is probably due to the enthalpy reaction between the copper and the water molecules that are present in the sample. The second endothermic peak can be associated to the enthalpy

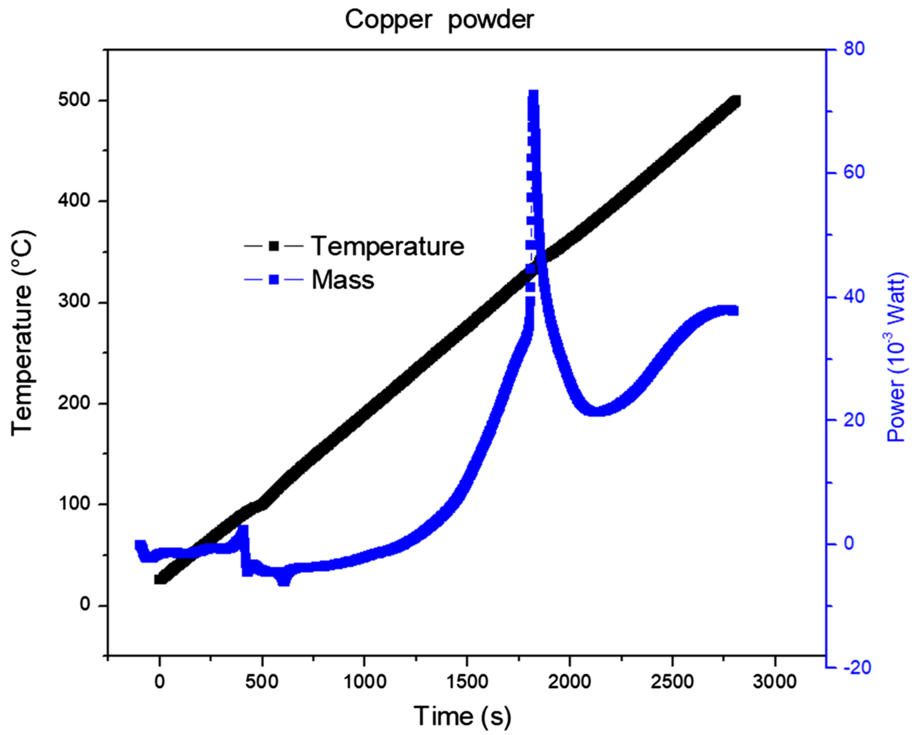



**Fig. 4** DSC results obtained for the copper powder, which is used as a precursor of the WCuNi composite

process of the chemical reaction attributed to the absorption of oxygen by the cupper.

These results obtained after the DSC measurements of tungsten and copper powders were used in the determination of the sintering parameters, principally to establish the gradient of the inert gas flow, searching to minimize all processes of oxidation of the metallic composite samples.

### 3.3 Diffractometry and Fluorescence of X-rays

Measurements of X-rays diffraction for the tungsten powder have been done and are exhibited in Fig. 5. The peak intensities are characteristic of a body cubic centered (BCC) crystal structure and their variation allows the identification of Muller indexes.

Patterns of X-ray diffraction (XRD) obtained for the powder of copper, which has been used as infiltrating

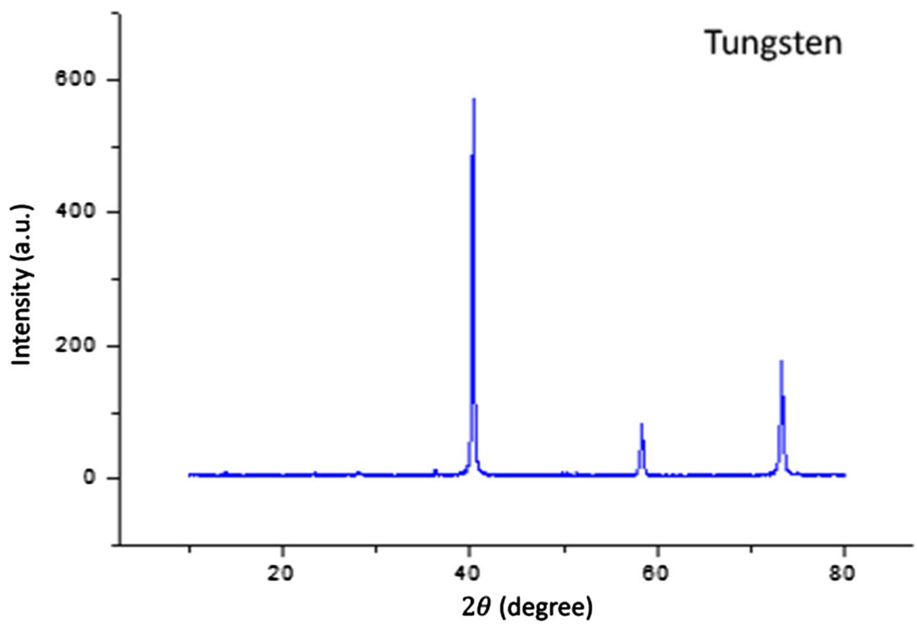



**Fig. 5** The spectrum of X-rays diffraction obtained for the tungsten powder used to form the metallic composite WCuNi

element to form the metallic WCuNi alloy, are exhibited in Fig. 6. The observed peaks are typical of an FCC crystal cell structure.

Results for the X-ray diffraction of Nickel powder, which has also been used as infiltrating element to form the WCuNi alloy, are exhibited in Fig. 7. The variation of the observed peak intensities is consistent with an FCC crystal cell structure.

From the results presented in Figs. 5, 6 and 7 the principal crystallographic parameters for those powders have been determined and are exhibited in Table 1.

The previous analysis of X-ray for the W, Cu and Ni precursors showed that the physical properties of the elements used to form the composite are entirely within the standard values of the international reference data. This is a guarantee that the purity of elements is preserved, i.e., they are free of oxides, nitrites and/or hydrates, which would potentially

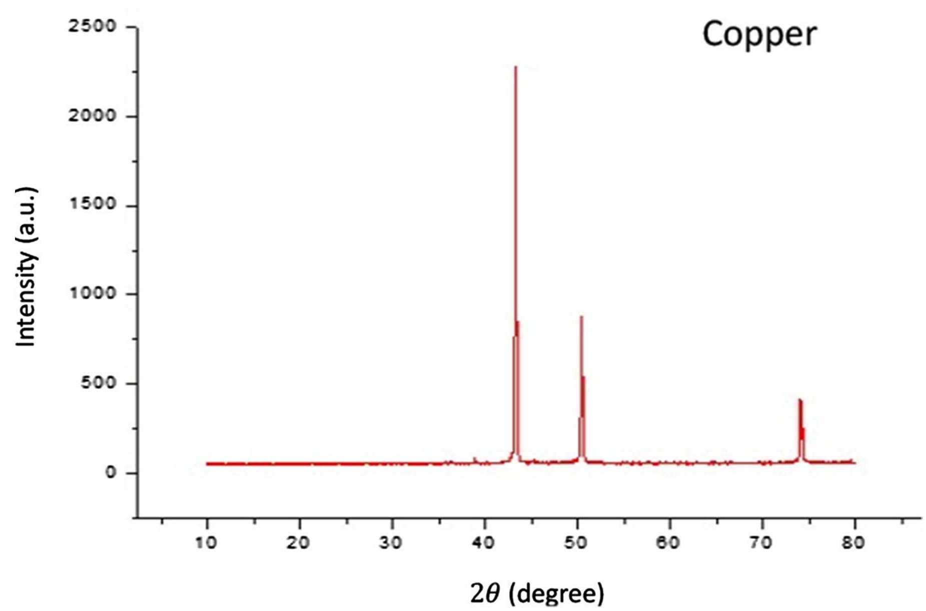



**Fig. 6** The spectrum of X-rays diffraction obtained for the copper powder used to form the metallic composite WCuNi

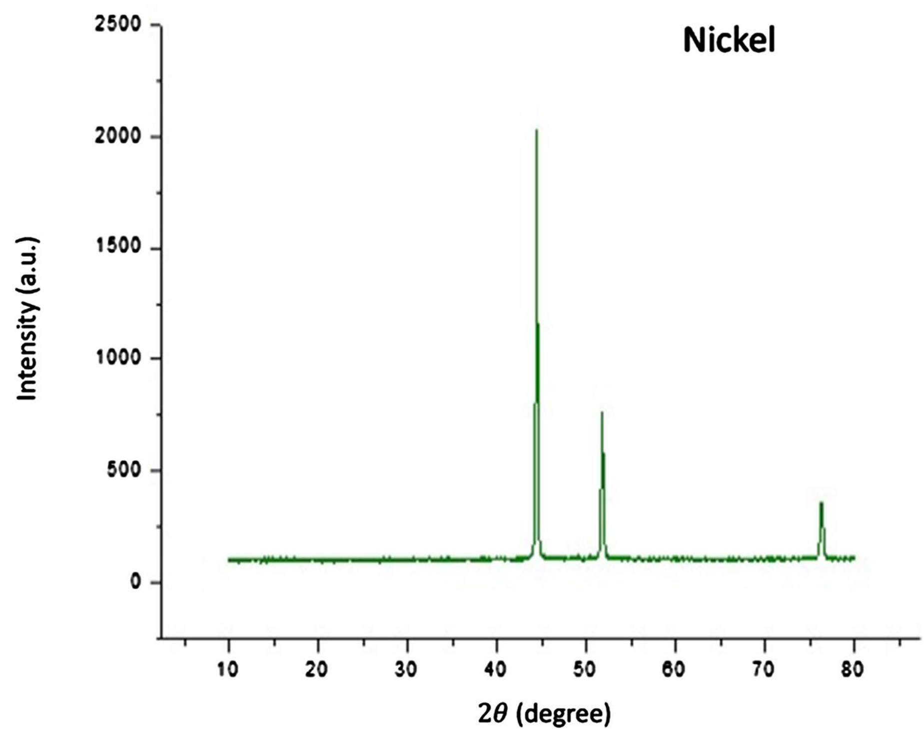



**Fig. 7** The spectrum of X-rays diffraction obtained for the nickel powder used to form the metallic composite WCuNi

**Table 1** Principal crystallographic parameters for tungsten (W), copper (cu) and nickel (Ni)

| 2-Theta | D-spacing (Å) | h k l | Intensity | Lattice parameter (Å) |
|---|---|---|---|---|
| *Tungsten (W)* | | | | |
| 40.339 | 0.2234 | 110 | 338 | 0.3160 |
| 58.338 | 0.1580 | 200 | 43 | 0.3160 |
| 73.247 | 0.1291 | 211 | 95 | 0.3162 |
| *Copper (Cu)* | | | | |
| 43.292 | 0.2088 | 111 | 1305 | 0.3616 |
| 50.422 | 0.1808 | 200 | 513 | 0.3616 |
| 74.070 | 0.1279 | 220 | 305 | 0.3617 |
| *Nickel (Ni)* | | | | |
| 44.430 | 0.2037 | 111 | 1128 | 0.3528 |
| 51.781 | 0.1764 | 200 | 465 | 0.3528 |
| 76.306 | 0.1246 | 220 | 158 | 0.3526 |

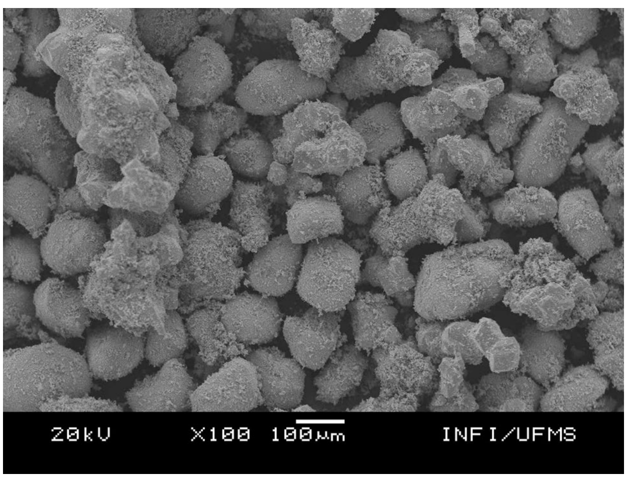



**Fig. 8** Micrograph image obtained for the tungsten powder using SEM

modify the physical–chemical properties of the resulting composite.

### 3.4 Analysis of microstructural evolution—SEM

The chemical elements used to form the composite have been observed with the help of a Scanning Electron Microscope (SEM) and typical results are exhibited in this session. All samples were exposed in the form of powder, in the same way as used during the X-ray characterizations. SEM micrographs of tungsten, copper and nickel powder that were later used to form the composite are separately discussed below.

A representative micrograph of tungsten powder is exhibited in Fig. 8. Tungsten has been used as the principal matrix element to form the WCuNi composite. Such a micrograph

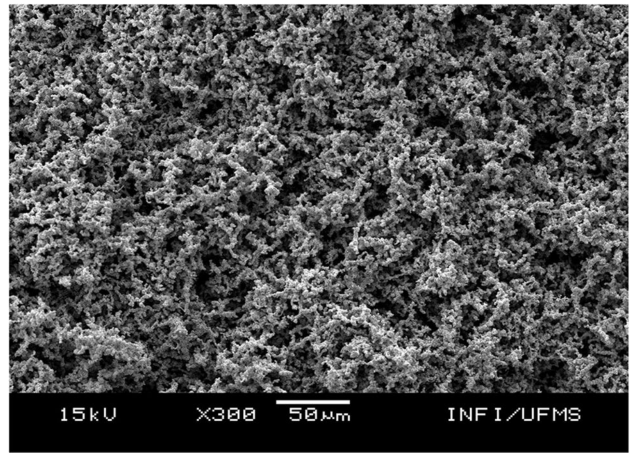



**Fig. 9** Micrograph image obtained for the nickel powder using SEM

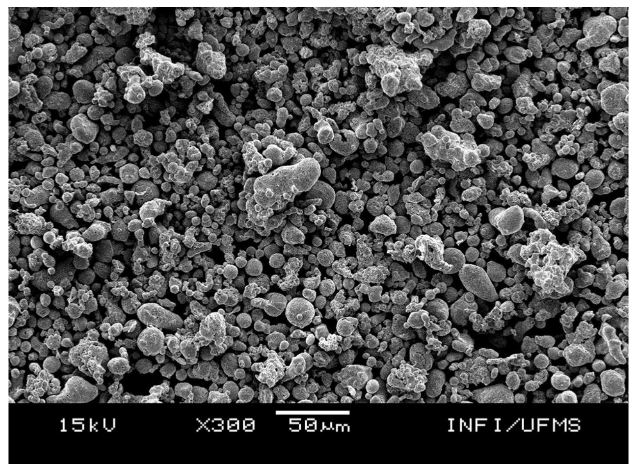



**Fig. 10** Micrograph image obtained for the copper powder using SEM

shows the morphology of tungsten constituent particles before grinding the mixed powder that will form the composite. The geometry of these particles is spherically symmetric and uniform in their sizes.

A typical micrograph for nickel powder is exhibited in Fig. 9, which was used as an infiltrating element to form the composite. In this case, the particles present irregular sponge-shaped geometries and uniform distribution along with the sample.

The micrograph exhibited in Fig. 10 shows the result of SEM obtained for the copper powder, which was later used as infiltrating material to form the composite. The copper particles exhibit geometry with spherical symmetry in the order of 10 mm and a noticeable non-uniformity along with the sample.

The next image, Fig. 11 shows a micrograph of the composite after the grinding process using a ball mill to form a

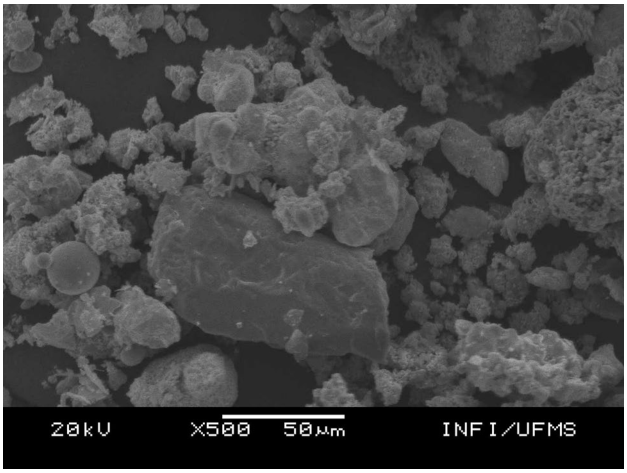



**Fig. 11** Micrograph image obtained for the W20C3Ni composite powder using SEM

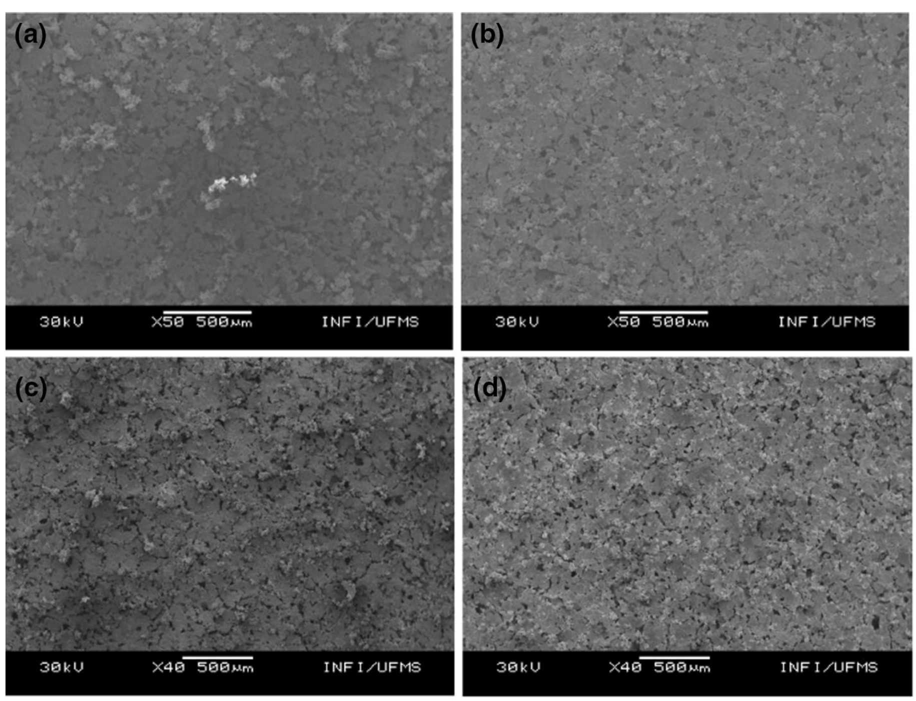
W20Cu3Ni metallic powder sample. It is possible to observe the homogeneity and uniformity of such a powder composite that was obtained. In the sequence, this powder is initially taken to a pressing process and later submitted to a sintering process.

Therefore, the standard composite analyzed in this paper is formed by alloying tungsten, copper and nickel to form a W20C3Ni composite. The sintering process is temperature-dependent and in order to study its influence in the final sample, different samples have been analyzed. In the next sequence of micrographs, the studied composite is represented in the Fig. 12a–d for the same sintering process but at the temperature of 1,250 °C, 1,300 °C, 1,350 °C, and 1400 °C respectively. The first clear resulting evidence extracted from this sequence is the sharp decrease in the alloy porosity level as the sintering temperature increases. This effect is attributed to the most effective thermal diffusion process of Cu and Ni among the W particles occurring when the temperature is raised. This observed decrease in porosity is followed by an increase in the density and the homogeneity of the samples. It is also possible to notice in the micrographs the W phase as well as the Cu–Ni intermetallic phase. Regarding the WCuNi alloy, the alpha (α) phase is associated with tungsten only while the beta (β) phase represents the binary alloy made by copper and nickel, or CuNi.

Based on the current micrographs it can be concluded that these samples are homogenous. The images present a certain level of whitishness on the occurrence of oxides, which is certainly not the case. Mapping of the sample during the EDS measurements is important, however, such photos of the region under analysis were not taken due to the limitations of the employed software.

Figure 13 is equivalent to the previous micrograph but obtained at a deeper depth, in the order of 500 ×. The sample is the same W20Cu3Ni composite and the sequence was obtained for the following sintering temperatures: 1250 °C, 1300 °C, 1350 °C, and 1400 °C respectively exhibited in Fig. 13a–d. Attentive observation of these results indicates a steady decreasing of the alloy porosity level as a function of the sintering temperature raise. This effect can be attributed to the process of thermal diffusion of Cu and

**Fig. 12** Micrographs taken in the SEM for the pressed W20Cu3Ni samples sintered at different temperatures: **a** 1250 °C, **b** 1300 °C, **c** 1350 °C and **d** 1400 °C respectively



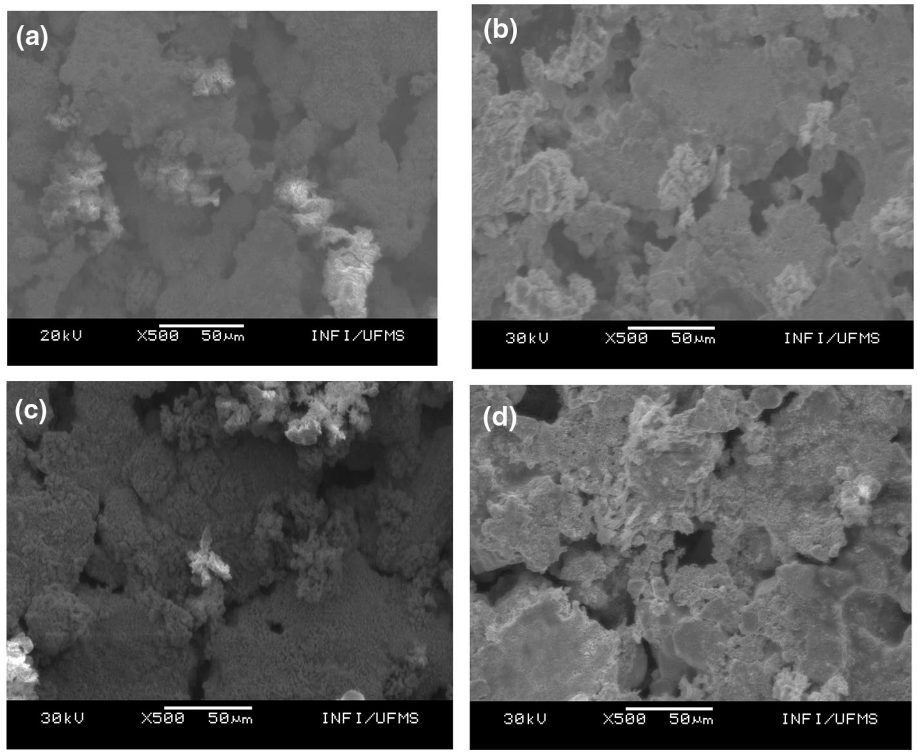



**Fig. 13** Micrographs taken in the SEM for the pressed W20Cu3Ni samples sintered at different temperatures: **a** 1250 °C, **b** 1300 °C, **c** 1350 °C and **d** 1400 °C respectively. The scanning resolution was set to 500 ×

Ni among the W particles due to the growth of the chemical reaction enthalpy and that is coherent with the thermal analysis results.

The reduction of the porosity is a direct contribution to the increase of the sample density and homogeneity. It is possible to notice in these micrographs of Fig. 13 the α-W and intermediary β-Cu–Ni phases, as well as the complete absence of oxides and nitrides, proofing that these are excellent results when compared to other equivalents specific scientific literature (Fig. 14).

The final set of analyses was obtained from the characterization of energy-dispersive X-ray spectroscopy, or EDS of the W20Cu3Ni metallic composite sintered at four different temperatures between 1250 and 1400 °C. It is qualitatively possible to infer from these spectra that the higher intensity peaks are associated with the concentration of W, while the peaks with smaller intensities are attributed to Cu and Ni. These results show that there is neither formation of oxides nor of nitrides after the sintering process. This conclusion is completely coherent with the analysis of the respective micrographs after the sintering processes.

These results clearly indicate that the set of parameters previously described and chosen to operate the sintering of the metallic composite WCuNi are particularly interesting. The fact that all micrographs, as well as the EDS analyzes, show that there are not oxides neither nitrides inside the sample is a solid indication for the sample quality, proving that the proposed goal has been achieved accordingly.

## 4 Conclusion

This paper intends to report the sintering of a metallic composite based on the mixed of three specific elements: tungsten (W), copper (Cu) and nickel (Ni) aiming at a high degree of both homogeneity and uniformity. Since nickel works as an excellent inhibitor of tungsten oxidation, the achievement presented in this work lies in the ability to use a precursor easily melted, such as copper, to promote the homogenous proximity of both.

An extensive series of physical characterization has been exhibited to help the different analyses concerning the quality of the sintered sample. Thermal analyzes present relevant information regarding endothermic and exothermic processes that are attributed to the chemical enthalpy reactions of the W, Cu and Ni precursors during the sintering. The analysis obtained from the X-ray diffractometer proved the stability of crystal structures of the composite components, showing that tungsten accommodates in a BCC cell while the Cu and Ni are arranged in FCC cells.

A series of scanning electron microscopy (SEM) results showed that all metallic refractory samples obtained as described are free of oxides after the sintering process for all temperatures that have been tested, which were 1250 °C, 1300 °C, 1350 °C, and 1400 °C. These results also confirmed the stability of the α-W and β-CuNi phases. The showed spectra of X-ray dissipative energy (EDS) qualitatively confirmed the composition stoichiometry of the

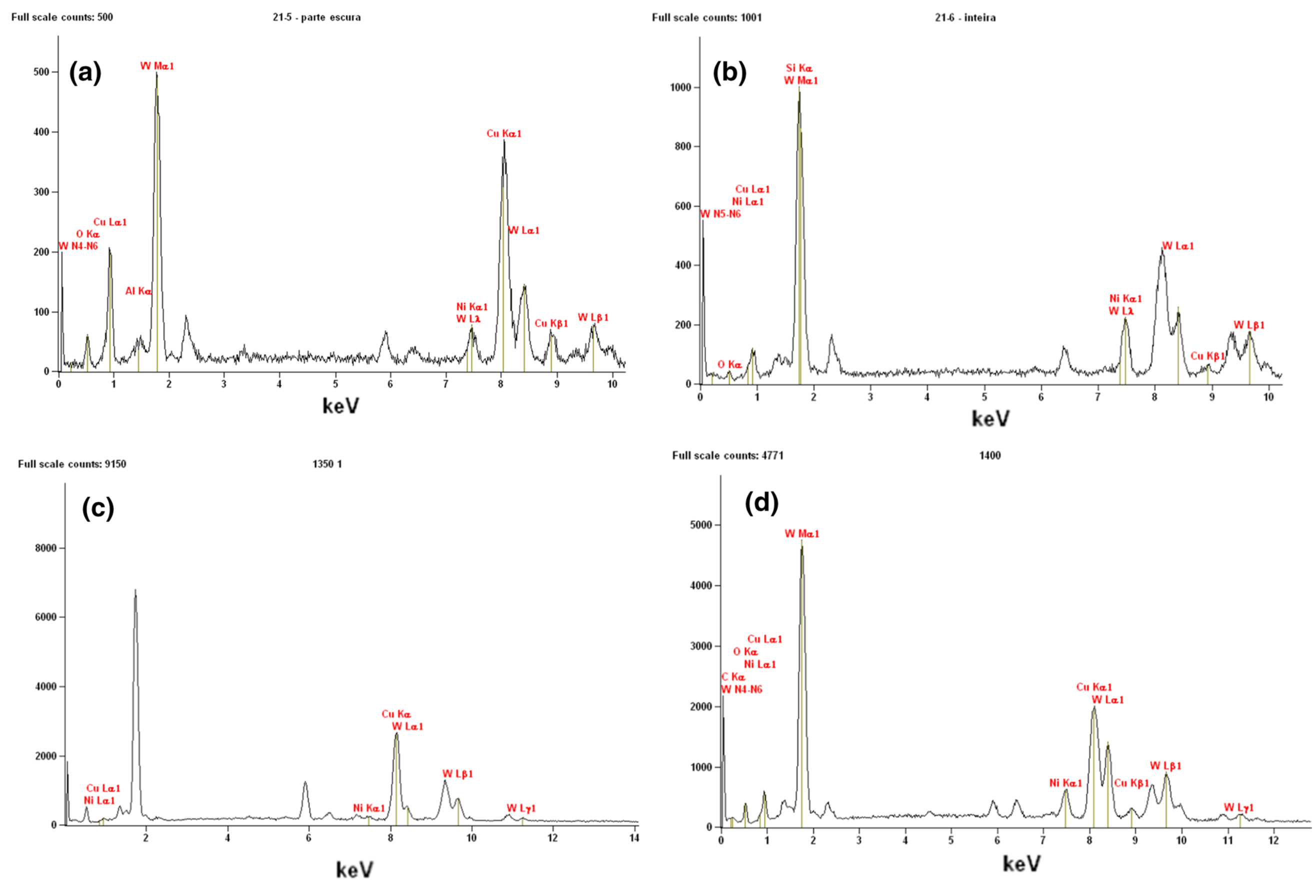



**Fig. 14** EDS spectrum for the W20Cu3Ni metallic composite obtained after sintering the powder solution at four different temperatures: **a** T = 1250 °C; **b** T = 1300 °C; **c** T = 1350 °C; and **d** T = 1400 °C, respectively

obtained metallic composite, in complete accordance with the equivalent results acquired from the SEM.

Therefore, the metallic composite that has been obtained presented an excellent degree of physical homogeneity; as well as of uniformity of its granulometry; and of phase consistency. This report demonstrated the possibility of using the refractory metallic alloy indicated as W20Cu3Ni on future studies devoted to building a receptacle to transport radioactive materials. The results presented here motivate new investigations to study the shielding and the attenuation coefficient of gamma radiation trough such an alloy in order to construct a packing system to transport materials of high nuclear activity.

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