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PHASE STRUCTURE AND MAGNETIC PROPERTIES OF INTERMETALLIC Cu-Ni ALLOY NANOPOWDERS SYNTHESIZED BY THE ELECTRICAL EXPLOSION OF WIRE

Cu-Ni composite nanoparticles were successfully synthesized by electrical explosion of wire (EEW) method. Cu-Ni alloy and twisted wires with various Ni contents were used as the feeding material for a 3 kV charging voltage EEW machine in an ethanol ambient chamber. The phase structure and magnetic properties of the as-fabricated samples were studied. It was established that the prepared powders after drying have a spherical form with the particle size is under 100 nm. XRD analysis indicated that the nanopowders consisted of binary Cu-Ni phases. Only pure phases of the intermetallic compound Cu-Ni (Cu0.81Ni0.19 and Cu3.8Ni) were observed in the XRD patterns of the samples. The synthesized intermetallic Cu-Ni alloy nanopowders reveal magnetic behaviors, however, the lower Ni content samples exhibited paramagnetic behaviors, meanwhile, the higher Ni content samples exposed ferromagnetic properties.

Keywords: Cu-Ni alloys, nanoparticle, phase structure, magnetism, explosion of wire

1. Introduction

Nanomaterials are known as the most important type of materials for science and technology due to their remarkable chemical, physical and mechanical properties. The nanomaterials with functionalities reveal the higher potential in applications than bulk materials. Copper (Cu) and nickel (Ni) nanopowders were widely used because of their good characteristics such as catalytic, electronic and magnetic properties. There are many studies reported that Cu-Ni alloys have interesting physical characteristics, good mechanical properties even under continuous loading and at elevated temperature conditions, and high resistance to corrosion and bio-fouling in many media especially seawater. Therefore, they were promising materials in electrical engineering, aircraft, automobile, building construction, and offshore industries [1,2]. In addition, the Cu-Ni alloys are also known for capable assembly of such materials. Thus, this well-considered alloy material is chemically stable, biocompatible and exhibits appropriate magnetic properties [3,4].

In term of the Cu-Ni alloys, bimetallic Cu-Ni nanopowders have attracted particularly considerable interest with their unusual properties [5-7] and their applications in conductive electrodes, plasmonics, dentistry and catalysis [4,8,9]. Due to the remarkable potential in use of the Cu-Ni bimetallic nanoalloys, many techniques have been conducted to synthesize bimetallic Cu-Ni nanoparticles including physical and chemical methods such as mechanical alloying [10], sol-gel [11], the hydrothermal method [12], microwave technique [3], and the microemulsion route [5]. The good results achieved by using these methods indicates that studies on the synthesis of Cu-Ni alloy nanopowders still attracted the attention of the scientists. However, it is also noted that they are high energy consumption, long time reaction, complex, toxic, and high-cost processes.

The Electrical explosion of wire (EEW) is known as a "top-down", physical method to fabricate the nanomaterials. EEW exhibited a simple, efficient and low-cost process for preparing and synthesis the powders of metal and alloy materials. In this work, the Cu-Ni nanoalloys were synthesized by EEW in liquid and systematically characterized their properties. Both Cu-Ni alloy wires and the twisted wires of Cu and Ni were used as charging materials for EEW process.

2. Experimental

Cu, Ni wires and Cu-Ni alloy wires were used as starting materials for fabrication of the nanopowders. All the wires used in this study were analytical grade obtained from Nilaco Corp., Japan, and they were used as the received materials without further purification. The Cu-Ni nanopowders were produced through the electrical explosion of wire in liquid method. This technique has been reported previously [13], therefore we would like to skip describing in this work. The experimental parameters of the EEW process in our study are presented in

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Table I. The samples were prepared with different mass ratios of Cu to Ni to obtain Cu-6Ni, Cu-12Ni, Cu-23Ni, and Cu-45Ni alloy nanopowders. In addition, the twisted wires of Cu and Ni were also exploded in EEW machine for investigation. The twisted wires were made with the ratio of Cu-55Ni and Cu-70Ni (Fig. 1).

TABLE I

Conditions of the explosion of wire in liquid process

Capacitance	30 μF
Charging voltage	3 kV
Wire diameter	0.1 ~ 0.3 mm
Wire length of one explosion	27 mm
Ambient liquid Ethanol	94%

For each explosion circuit, the initial wire with a length of 27 mm was fixed to the two electrodes then immersed into 500 ml ethanol in a stainless steel cylindrical chamber. A high-density current was passed through the solid wire which was located in the liquid via discharging of a 30 μF capacitor. Due to the deposit and the high rate of the electric energy injection on the wire, it was melted, evaporated and then plasma formed followed by a shockwave scattered to the ambient medium. The metal vapor was rapidly cooled down and finally, the nanopowders were formed and dispersed into the ethanol liquid. After the explosion, the obtained nanopowders were collected and taken out from the aqueous mixture by centrifuging and then dried under the vacuum condition to remove all of the liquid for further investigation. Phase characterizations of the prepared nanopowders were observed by using a Rigaku (Ultima IV) X-ray diffractometer (XRD). The XRD pattern was performed from 20^o to 80^o (2θ) with Cu Kα radiation (λ = 1.5406 Å). The scanning electron microscope (SEM) equipped with energy-dispersive spectroscopy (EDS), transmission electron microscope (TEM) were also used to determine the particle morphology and to confirm the size of the particles. The magnetic properties of the nanopowders were investigated with a vibrating-sample magnetometer (VSM) at room temperature.

3. Results and discussions

The morphology and shape of the Cu-Ni nanopowders prepared from the alloy wires by EEW in ethanol were observed by TEM analysis, the results were presented in Fig. 2. It could be seeming that the as-synthesized powders had a spherical form with the particle size less than 100 nm. From the TEM images, the particle size consists of big and small size particles with a tendency increasing in the amount of the small particle with the higher of Ni content in the initial wires. This is attributed to the higher melting point of Ni in comparison with Cu, and the better electrical conductivity of the large Ni content Cu-Ni wires to the small Ni content wires which is due to a higher in the electrical conductivity of Cu (~5.98 × 107σ (S/m) at 20^{o}C) to Ni (~1.46 × 107σ (S/m) at 20^{o}C). There are many particles with a twinned structure that were also observed in TEM micrographs of the obtained alloy nanopowders (Fig. 2, white arrow). Additionally, while investigating the morphology of the as-exploded alloy powders, we found that there were the layers of graphitic carbon covering the surface of the nanoparticles, Fig. 2(b). This was due to a large amount of carbon element diluted in the ethanol solvent in particular and in organic solvents in general. Interestingly, from TEM micrographs we observed few core-shell structure particles in the exploded Cu-45Ni sample, Fig. 2(a). The core-shell structure of metallic nanoparticles prepared by EEW has been mentioned in some previous reports [14], however, in this research that kind of structure was not popular, therefore, it needs to be studied further.

The structural phases of the exploded nanopowders were determined by X-ray diffraction analysis. The XRD patterns of the as-synthesized Cu-Ni alloy nanoparticles with different composition are shown in Fig. 3. It can be seen that all samples exhibited similar typical patterns with the presence of the three well-defined peaks at 34.4^o, 50.55^o, and 74.26^o (2θ) corresponding to (111), (200) and (220) planes of the cubic (FCC) Cu-Ni bimetallic alloy, respectively [3,10,12,15]. Thus, these peaks were in an intermediate position in relation to the reflections of

Fig. 1. The twisted wires of Cu and Ni wires were used in study

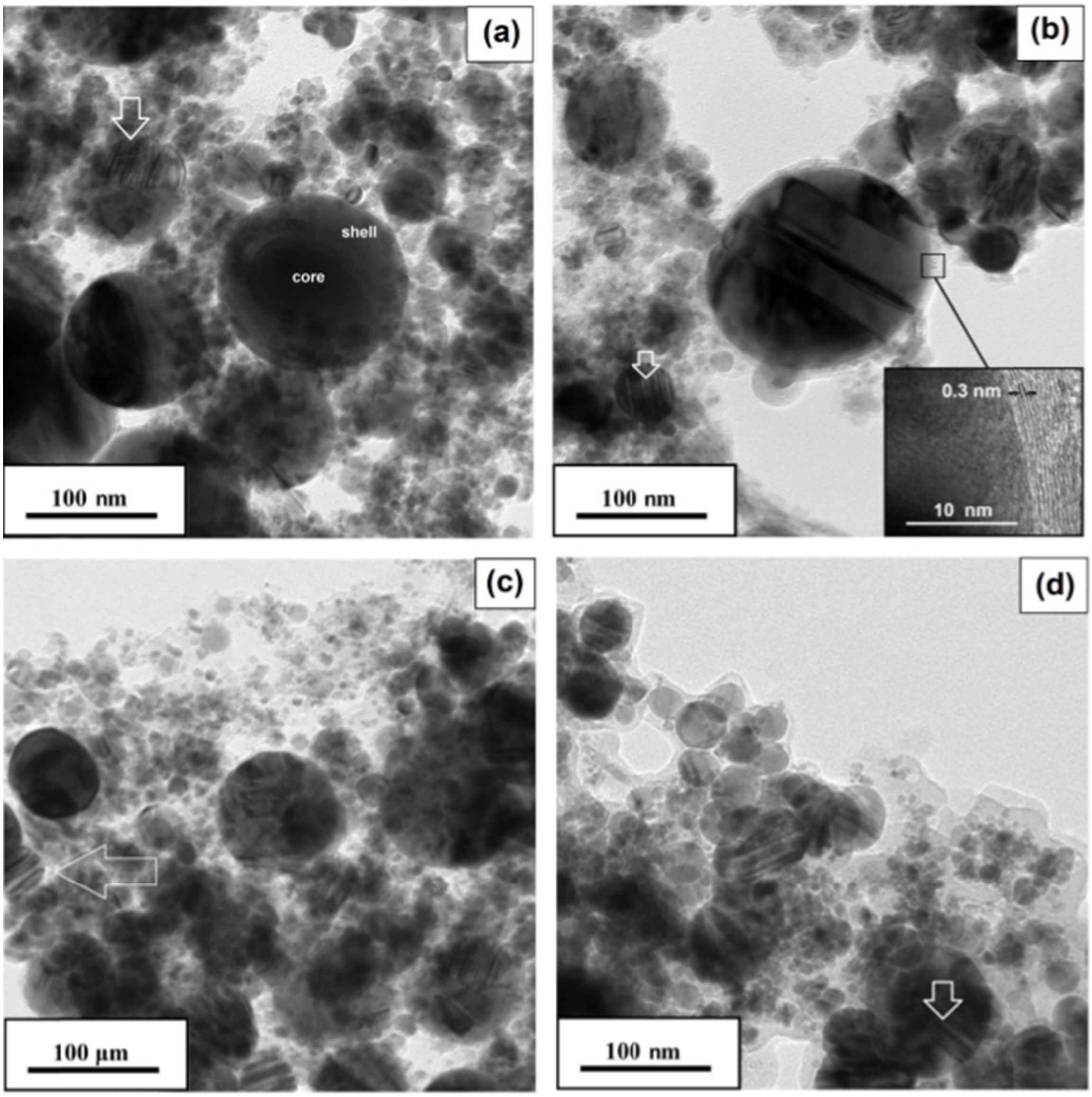

Fig. 2. TEM images of the alloy nanopowders (a) Cu-6Ni, (b) Cu-12Ni, (c) Cu-23Ni and (d) Cu-45Ni fabricated by explosion of the Cu-Ni alloy wires

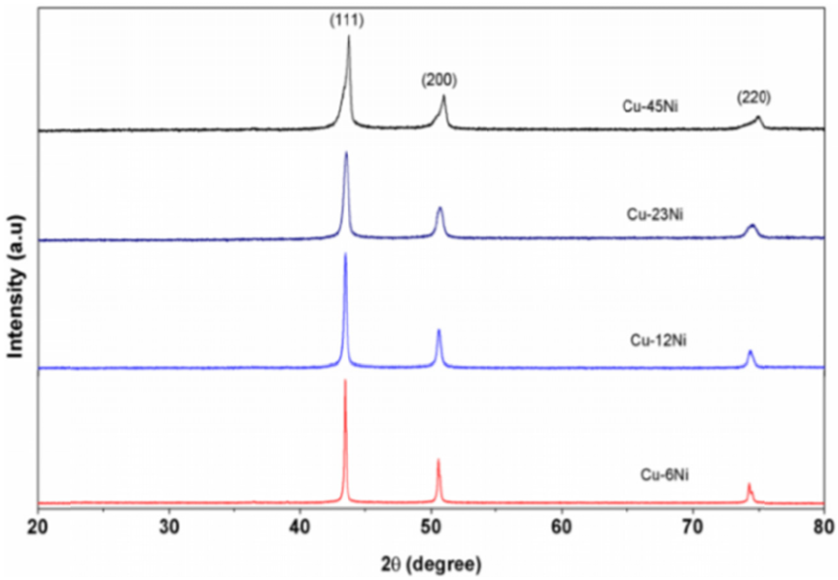

Fig. 3. XRD patterns of the Cu-Ni alloy samples prepared by EEW in ethanol

face-centered cubic crystalline structure phases: Cu0.81Ni0.19 (JCPDS# 47-1406) and Cu3.8Ni (JCPDS# 09-0205) corresponding to the intermetallic compounds in the Cu-Ni system [16]. Moreover, no signals of pure copper, pure nickel or other oxidation phases were observed in the diffraction patterns demonstrates that a pure Cu-Ni solid solution of binary compound nanopowders with a face-centered cubic crystalline structure was completely fabricated by the explosion of the initial alloy wires in the ethanol condition.

$$d = 0.98\lambda / \beta \cos\theta \quad (1)$$

where: d is the crystallite; λ is the X-ray wavelength; θ is the Bragg diffraction angle; β is the full width at half maximum (FWHM).

From XRD diffraction patterns, it could be seen that when Ni content in the alloy nanopowder increased, the peaks broaden slightly with the tip of the peaks shifted a bit to the right side [17] and the intensity of peaks decreased also. These results proved the formation of the Cu-Ni solid solution due to means of the diffusion and the substitution of Cu by Ni which have the same crystalline structure, ionic radius electronegativity and identical valence [10,15]. The average crystallite size was estimated using Scherrer's formula [18] given in Eq. (1) and summarized in Table II. The results reveal that the average crystallite size decreases with increasing the Ni content and in a good agreement with the TEM results.

In our study, the explosion of the twisted wires which were made of individual Cu (1.0 mm, 2.0 mm in diameter) and Ni (2.5 mm in diameter) wires with the twisted number of 6 turns in the nominal span length of 27 mm were also conducted. The Ni content in twisted wires was calculated equally to the Cu-55Ni (sample A) and Cu-70Ni (sample B) alloy wires. As shown in the TEM image in Fig. 4, the as-synthesized particles from the twisted wire exhibited a spherical form with the particle size under 100 nm and the average crystallite size was estimated at about 20 nm. Moreover, the EDS spectrum and EDS mapping (the insert part in Fig. 4) show that there are two components (Cu and Ni) which were observed in each particle and the distribution of them are uniform in the powder samples. In addition, the XRD pattern presents only the typical reflections correspond to the phases of the bimetallic Cu-Ni [12,16]. These results are totally similar to the Cu-Ni nanopowders fabricated from the commercial Cu-Ni alloy wires which have mentioned above indicating that the bimetallic Cu-Ni nanoparticles could be synthesized by the explosion of the twisted wires in ethanol as well.

TABLE II

Crystallite size of Cu-Ni alloy nanopowders fabricated from EEW of alloy wires

Cu-Ni alloy particle	Crystallite size (nm)
Cu-6Ni	45
Cu-12Ni	33
Cu-23Ni	20
Cu-45Ni	19

Magnetic properties of the obtained nanopowders were investigated at room temperature using a VSM with an applied field -20,000 Oe ≤ H ≤ 20,000 Oe. Fig. 5 shows their magnetic hysteresis loops of the as-synthesized nanopowders. It was found that the nanopowders exploded from alloy wires exposed the hysteresis loops of ferromagnetic material with high coercivity (Hc: 1000 ~ 1100 Oe) and the saturation magnetization values

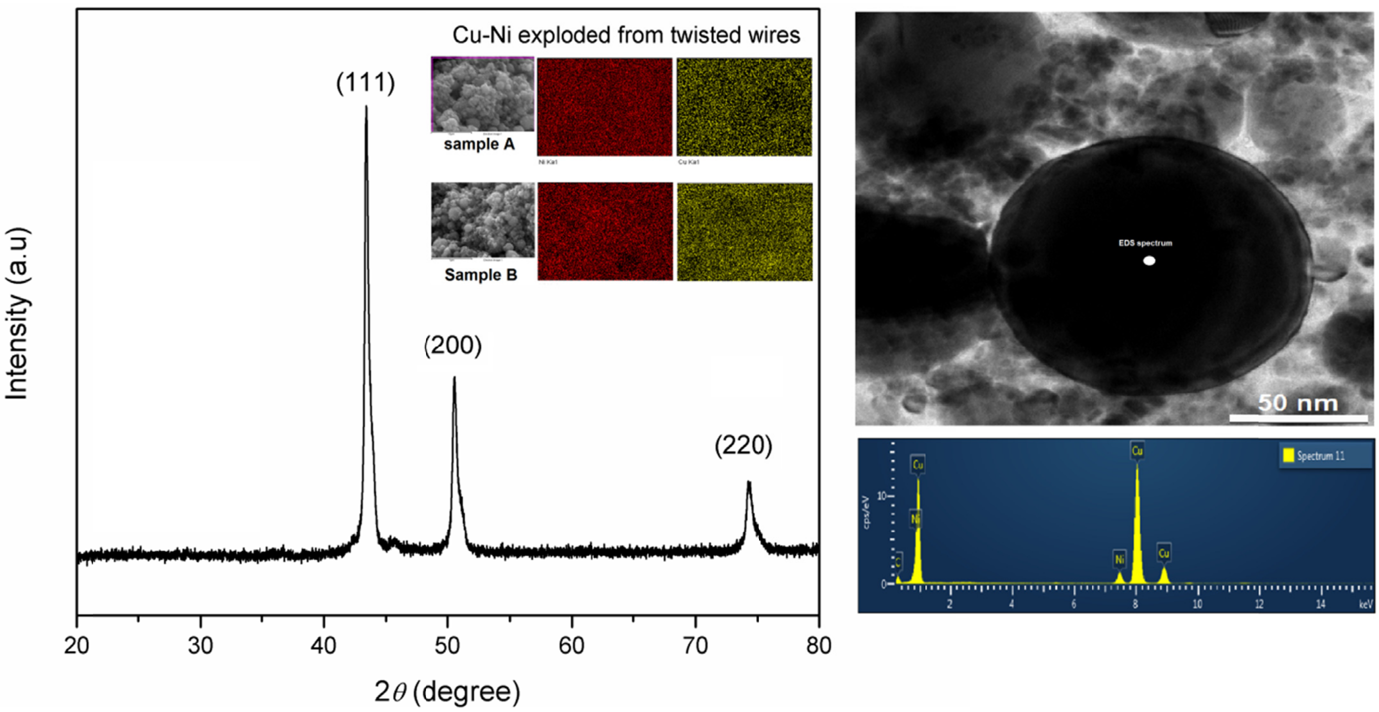

Fig. 4. XRD pattern (with the EDS mapping in the insert part), TEM, and EDS spectrum of the Cu-Ni powders synthesized by exploding the Cu-70Ni twisted wires in ethanol

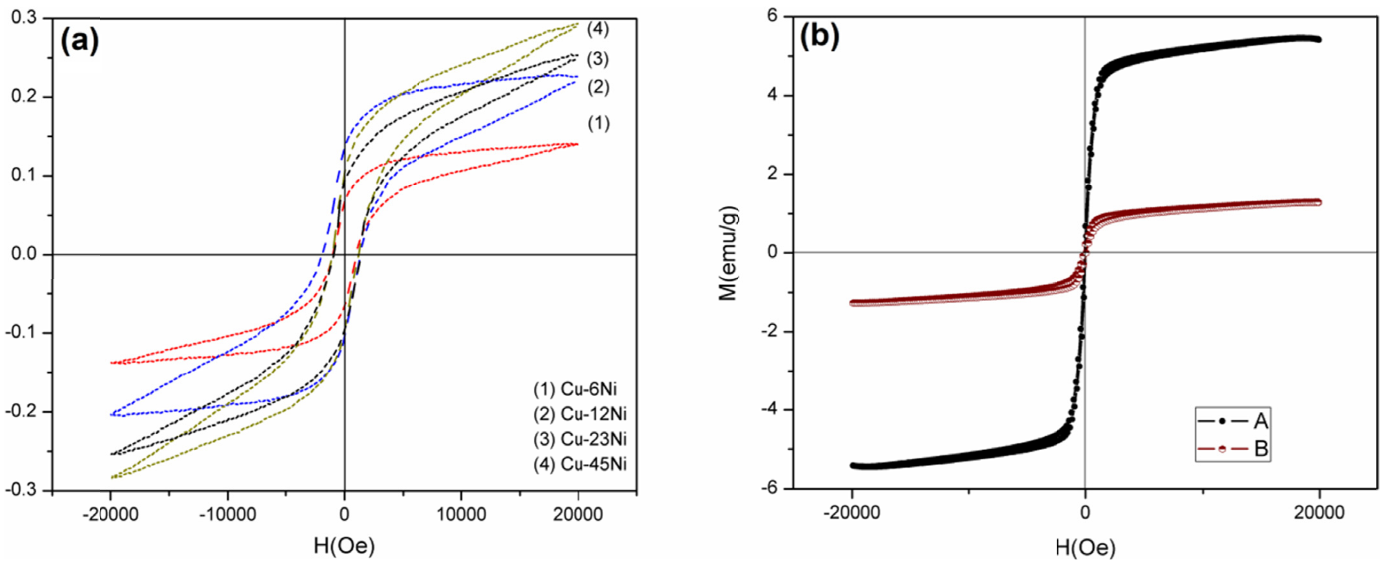

Fig. 5. Hysteresis loops of the as-fabricated nanopowders by explosion of (a) Cu-Ni alloy wires; (b) Twisted wires (A_Cu1.0 mmNi2.5 mm and B_Cu2.0 mmNi2.5 mm)

increased with the increase of the Ni content [3,19]. Thus, the Cu-6Ni alloy nanopowder shows magnetization of about 0.15 meu/g, meanwhile, those values are about 0.225 emu/g, 0.25 emu/g, and 0.3 emu/g for Cu-12Ni, Cu-23Ni, and Cu-45Ni, respectively (Fig. 5(a)). Contrastingly, from Fig. 5(b), the nanopowders prepared by exploding the twisted wires exhibited the behavior of a ferromagnetic material with the much higher values of saturation magnetization (about 1.2 emu/g for A specimen and 5.5 emu/g for B specimen) and lower in coercivity values (57.343 Oe for A and 109.71 Oe for B). It is noted that Cu is a diamagnetic material but Ni is a ferromagnetic one, therefore, with the inclusion of Ni in the Cu-Ni alloy nanoparticles resulting in the change in magnetic properties from diamagnetic to ferromagnetic in nature.

4. Conclusions

The intermetallic Cu-Ni alloy nanopowders were successfully synthesized by the explosion of Cu-Ni alloy wires and the twisted wires in ethanol. The as-synthesized nanopowder exhibited the spherical shape with twinned structure and the particles size is under 100 nm. There was a very thin graphitic layer covering the particle and a few core-shell structural particles were formed. The XRD results demonstrate that only the pure phases of the Cu-Ni intermetallic compound presented in the nanoparticles and the crystalline phase of the obtained Cu-Ni alloy nanopowders retained the cubic structure for all the compositions and the average crystallite size decreased from about 45 nm to 20 nm and maintained at about 20 nm with the increase in the Ni content. The magnetization of the as-fabricated nanopowders by the explosion of Cu-Ni alloy wires shows paramagnetic properties, meanwhile, the alloy particles synthesized by the explosion of twisted wires exposes ferromagnetic properties with much higher saturation values and lower in coercivity values. All of the samples show a tendency of increasing in saturation magnetization and decreasing in coercivity with the increase in the Ni content in the Cu-Ni alloy nanopowders.

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