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OBTAINING OF Cu-Ni ALLOY POWDER FROM ELECTRONIC SCRAP BY CHEMICAL ALLOYING

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Abstract: Synthesis of Cu–Ni alloy powders from metal nitrate solution from solubilisation of electronic scrap was carried out. Combustion, ultrasonic mist combustion and ultrasonic pyrolysis processes were applied and Cu–Ni alloy powder was successfully synthesized by mist combustion and ultrasonic pyrolysis of nitrate salts in a reducing atmosphere. X-ray diffraction data showed that the copper and the nickel atoms were completely mixed. For the Cu–Ni alloy powder prepared by ultrasonic mist combustion, the powder used was a hollow sphere and consisted of nano-sized particles. For the Cu–Ni alloy powder prepared by ultrasonic pyrolysis, particles consisted of nano-scale particles loosely coagulated. The synthesis temperature was 800°C, which is much lower than the liquidus of a Cu–Ni binary system. Chemical alloying has many advantages: no crucible, ball or jar is needed; low synthesis temperature below the liquidus of the alloy system; no extraction step is needed; no cation contamination; direct synthesis of fine powder from metal salts and a simple and inexpensive process. The disadvantage is the contamination of organic elements from the solvent and the salt.

1. INTRODUCTION

The need for new materials having better characteristics increases and alloying is one of the promising techniques for developing new materials.

Cu-Ni alloys have difficult moulding properties, a high gas adsorption tendency, bias towards void and slag inclusions, low fluidity, etc. [1-3]. When alloys are made by moulding, large non-homogeneities and seggregations can also appear in the structure.

In order to obtain alloys, excavated raw materials are extracted to have pure elements and then mixed. Atomic scale mixing is a necessary step for making alloys and the most common and fundamental process is heating to a temperature above the melting point, for mixing in the liquid state. Another important method developed so far is a mechanical alloying technique, which mixes the raw material powders in the solid state using a high energy ball mill. Alloy powder and/or bulk are formed into the proper shape for the applications. Both alloying techniques of melting and mechanical alloying have an intrinsic problem stemming from the use of a container such as a crucible, jar, balls and so on. The use of a container inevitably results in the contamination of impurities into the alloy. Therefore, elimination of the container in the alloying process is very helpful to obtain the alloy composition targeted. Additionally, the alloying process always consists of the two processing steps of extraction and alloying. The combination of these two processes into a single process, which has not been tried until now, should have many economic and scientific advantages.

The synthesis of alloy powder using a metal salts solution has little chance of contamination because the synthesis process is carried out in the chamber space without any contact with the chamberwall.

Recently, Thury *et al.* [4] succeeded in making a silver–palladium alloy powder by aerosol decomposition below the melting point of a silver–palladium alloy. Thereafter, Evans *et al.* [5] synthesized a nanocrystalline Ni–Fe alloy powder by spray pyrolysis. Even though the synthesis of the alloy powders by aerosol decomposition or spray pyrolysis has many advantages, no further report was made for other alloy systems. Very recently authors noticed that the combination of self-sustaining combustion and aerosol pyrolysis will promote the decomposition of the metal salts and deepen understandings about direct alloying from a metal salts solution.

With ever-increasing quantities of electronic products becoming obsolete, the electronic scraps raise a serious environmental problem challenging both original equipment (electronic) manufacturers and recycling industries. These electronic scrap shares are seemingly insignificant when compared to the total weight. However, with the huge amount of obsolete end-of-life electronics each year, the lack of established methodologies capable of handling these increasing volumes of scraps gives rise to serious environmental problems [6].

The purpose of the present work was to develop synthesis process of a fine Cu–Ni alloy powder from electronic scrap by powder metallurgy methods.

2. EXPERIMENTAL PROCEDURE

Samples of electronic scrap, in the form of shredded printed circuit boards fragments from a PC computers waste, was obtained from Remat S.A., Romania. Components with contaminants (capacitors, batteries, etc.) were removed. For experimental use, these scraps were crushed by using cutting mill grinder and grounded to pass 0.1 mm sieves and, then were placed into dilute nitric acid solution, at 50-80 ^{o}C, to dissolve copper and nickel. The resulting solution was conventionnaly processed to produce an aqueous nitrate solution of Ni and Cu metals as a stock solution. The residue containing other metals was treated with aqua regia and filtered to recover other metals.

The precursor solution for self-sustaining combustion and ultrasonic mist combustion was prepared by adding twice the stoichiometric amount of glycine as a fuel to the above stock solution while, for ultrasonic mist pyrolysis, the stock solution was used as prepared. The self-sustaining combustion process was performed by heating the stock solution on a hot plate in open air. As soon as the water became fully vaporized, spontaneous combustion started by the burning of the metal salts and fuel. The precursor solution was continuously fed via an ultrasonic nebulizer operating at a frequency of 720 kHz. The mist of precursor solution was generated at room temperature. The droplets passed through a reactor held at 800°C. The synthesized powder was collected after cooling the furnace to room temperature. In order to reduce the metal oxides and suppress the oxidation of the metal elements, this process was performed in a reducing gas mixture of Ar + 4% H_2.

The composition of the recovered metal was determined by energy dispersive X-ray spectroscopy (EDS), while the crystalline phases of the as-synthesized powder were examined by using XRD (HZG-4C Carl Zeiss Jena, CuK_α radiation, Ni Filter). Moreover, the particle morphology was observed by scanning electron microscopy - SEM (Tesla BS-343).

3. RESULTS AND DISCUSSION

Figure 1, a) shows the X-ray diffraction (XRD) pattern of the powder synthesized by the self-sustaining combustion process of the nitrate solution of Ni and Cu metals in open air. The precursor solution was used by adding twice the amount of stoichiometric glycine as fuel to a prepared stock solution. It was revealed that the powder synthesized consisted of multiple phases of NiO, Cu_2O and CuO. The formation of the oxides indicates that the metal atoms decomposed from the metal nitrates and reacted with the molecular oxygen present in air, even though fuel was excessively added.

Figure 1, b) shows the XRD pattern of the powder synthesized by the ultrasonic mist combustion process of the nitrate solution of Ni and Cu metals. A precursor solution was used by adding twice the amount of stoichiometric glycine as a fuel to a stock solution prepared. Ultrasonic mist combustion was performed at 800◦C in a reducing gas mixture of

Ar + 4% H_2. The XRD pattern of the as-synthesized powder showed the diffraction peaks from a single phase of Ni–Cu alloy with a lattice parameter of a = 3.586 Å. This means that Ni and Cu atoms were well mixed at atomic level, i.e., alloyed. Figure 2 show the SEM micrograph of the Ni–Cu alloy nanocrystals. Holes were hardly observed in the shell of the hollow particles. However, it is not clear whether the surfaces of the hollowspheres are fully closed or not. The SEM micrograph shows the spherical particles with a size smaller than ~ 3 µm. The wide particle size distribution is a consequence of the mist's wide droplet size. The particles have rough surfaces resulting from fuel combustion [7]. The synthesized powder was pressed with a pressure of 200 MPa and polished for SEM–EDS analysis. The chemical composition of the powder analyzed by SEM–EDS was Ni = 30.41% and Cu = 69.59%, which is very close to the composition of the stock solution. The lattice parameter calculated by Vegard's law was a = 3.5826 Å for this composition. The lattice parameters used for the calculation were Cu = 3.61 Å and Ni = 3.52 Å [8]. The difference of the lattice parameter between the measured one and the calculated one from the chemical composition might be due to the presence of residual stresses.

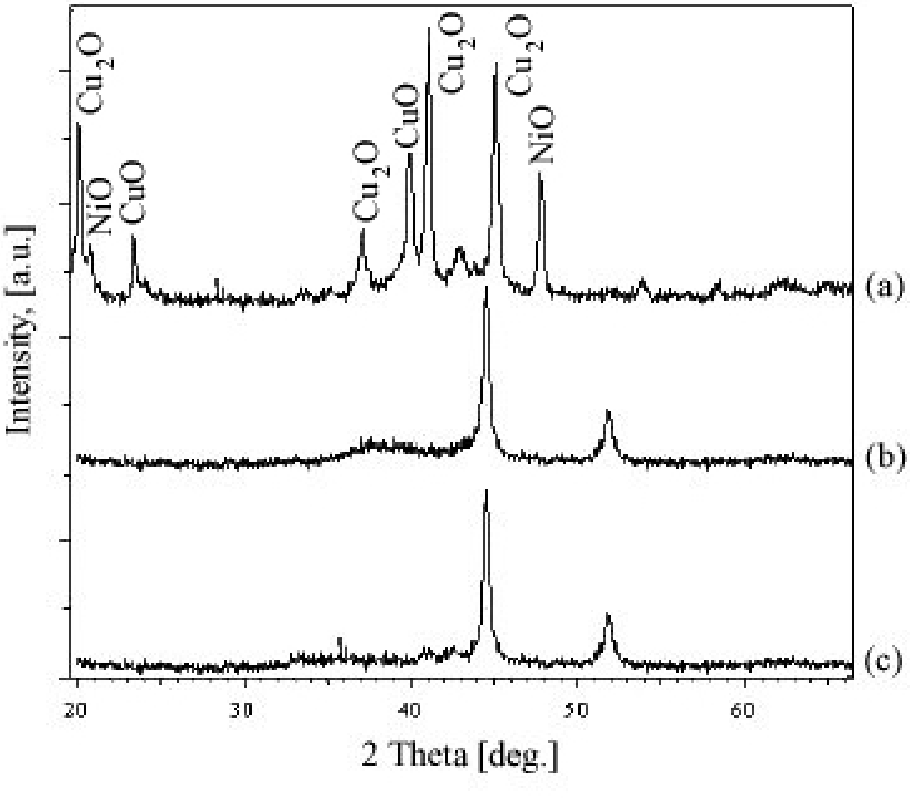

Figure 1. ***XRD pattern of the powder obtained by the self sustaining combustion process (a), synthesized by the ultrasonic mist combustion process (b) and synthesized by the ultrasonic mist pyrolysis (c) of the nitrate solution of Ni and Cu metals***

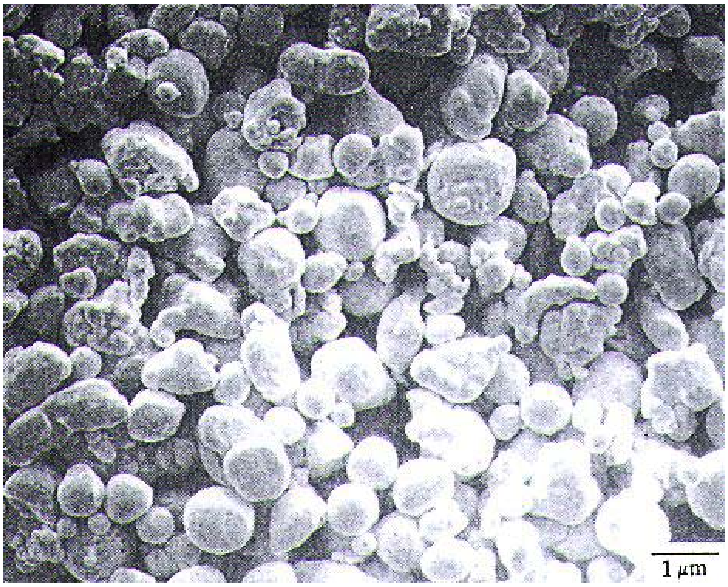

Figure 2. ***SEM micrograph of the powder obtained by the ultrasonic mist combustion process***

Figure 1, c) shows the XRD pattern of the powder synthesized by ultrasonic mist pyrolysis of the nitrate solution of Ni and Cu metals. The precursor solution was an aqueous solution of copper and nickel nitrate, prepared as a stock solution.

Ultrasonic mist pyrolysis was performed at 800°C in a reducing gas mixture of Ar + 4% H_2. The XRD pattern of the as-synthesized powder shows diffraction peaks from a single phase of Ni–Cu alloy with a lattice parameter of a = 3.577 Å. This means that Ni and Cu atoms were well mixed, i.e., alloyed. Figure 3 shows the SEM micrograph of the powder synthesized by the ultrasonic mist pyrolysis. The spherical particles with a size smaller than ~ 1.5 μm is observed. The particles have smooth surfaces because no fuel was used for the ultrasonic mist pyrolysis. From the diffraction patterns, it was revealed that the individual particles were polycrystalline.

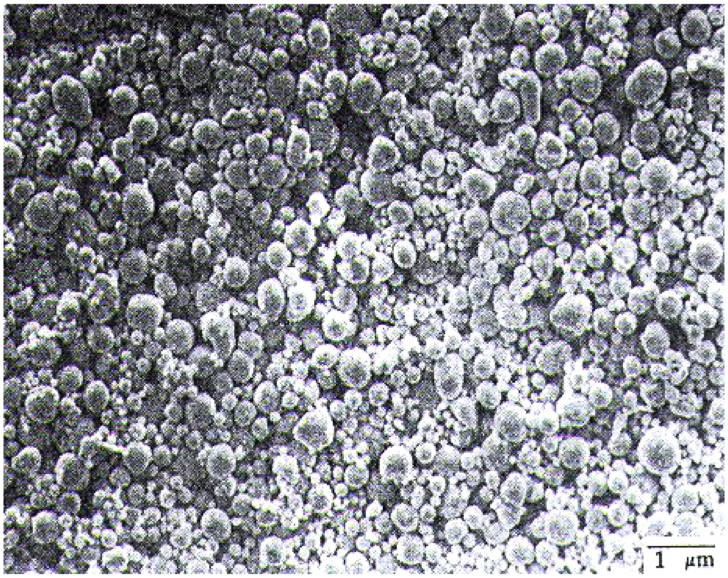

Figure 4. ***SEM micrograph of the powder synthesized by ultrasonic mist pyrolysis of the nitrate solution of Ni and Cu metals***

In order to alloy, different metal atoms should be thoroughly mixed at atomic scale. For alloying, the bonding between atoms should be broken and then mixed. In the solid state, the de-bonding of metal atoms hardly occurs and therefore thermal or mechanical activation processes should be involved in order to break the metallic bonding. Thermal energy makes the metals melt and mechanical energy can crush and/or compulsorily mix the metals. Therefore, sufficient thermal energy for melting and mechanical energy for the de-bonding of metal atoms are minimum requirements for the alloying methods developed until now. The melting temperatures of copper and nickel are 1083˚C and 1453˚C, respectively, and the melting temperature of the 70Cu–30Ni system is about 1240˚C [8]. It is rather surprising that alloying of the binary 70Cu–30Ni system occurred at a temperature much lower than the melting temperature (or solidus line). Mechanical alloying is to mix the metal powders constituting the alloy with high energy using a high-energy ball mill, and it has been known as a unique technique for obtaining alloys at low temperatures. High-energy ball milling mixes the metal atoms automatically. The alloying method suggested here contains no melting and mechanical mixing step in the process. This infers that, in the metal salts solution where the metal nitrates are completely mixed, metal salts are decomposed into metal atoms above the decomposition temperature of the metal salts and maintain their atomically mixed state down to room temperature. The process can be named chemical alloying because, in contrast to the mechanical mixing of metal atoms in mechanical alloying, the mixing of the metal atoms is accomplished chemically when the metal salts in a source solution are thermally decomposed. Copper nitrate and nickel nitrate decompose into CuO and NiO above 170˚C and 137˚C, respectively. NiO and CuO decomposed from nitrates will be reduced to Ni and Cu under a reducing atmosphere, respectively. Complete atomic level or nano-scale level mixing of the metal atoms might be possible if copper nitrate and nickel nitrate decompose simultaneously. Alloying might be accomplished by maintaining the atomic level mixing state or by sintering the Ni and Cu particles mixed at nano-scale. For both processes of ultrasonic mist combustion and ultrasonic mist pyrolysis, the hollow spherical nature of the powder synthesized infers that the formation of Ni–Cu alloy starts from the surface and proceeds inward. In the case of ultrasonic mist pyrolysis, the nano-scale small particles consisting of primary particles are loosely coagulated. But, for ultrasonic mist pyrolysis, SEM image shows that the secondary particles are fully sintered. Fuel combustion also accompanies a heat generation by an exothermic reaction which might assist the sintering and alloying of the Ni and Cu particles. The difference between the two processes is the presence of fuel. Therefore, it can be said that the fuel promotes fast instantaneous decomposition of nitrates in a whole droplet and sintering and alloying of the Ni and Cu particles. It is also expected that the presence of fuel lowers the oxygen partial pressure by consuming the oxygen and promoted the reduction of the metal oxides to metals.

The lattice parameter of a = 3.577 Å, for the powder synthesized by ultrasonic mist pyrolysis corresponds to the composition of Ni (36.67%)-Cu (63.33%) based on Vegard's law. The lattice parameters used for the calculation were Cu = 3.61 Å and Ni = 3.52 Å. Compared to the ultrasonic mist combustion, ultrasonic pyrolysis contains no fuel and the decomposition of metal salts may gradually occur from the droplet surface. Therefore, the decomposition of nickel nitrate might be faster than the decomposition of copper nitrate due to the difference in the decomposition temperature mentioned above.

As it appears above, the principle of chemical alloying is to synthesize a metal alloy directly from a stock solution of metal salts by decomposing the metal salts instantaneously into metal atoms. The metal atoms of the metal salts are atomically well mixed in the solvent. Explosive combustion in a small solution droplet may result in the simultaneous decomposition of nitrates even though there are some differences in the decomposition temperature. There is a temperature gradient from the surface to the center of the droplets and a volatile solvent, H_2O, begins to evaporate from the surface of the droplets. Combustion and/or pyrolysis start from the surface of the droplets and precede inwards. XRD and SEM observations support this hypothesis well. Chemical alloying has both advantages and disadvantages compared to melting and mechanical alloying because it is a distinct process of obtaining a metal alloy powder directly from a metal salt solution. The advantages are: no crucible, ball or jar is needed because the alloying occurs in a small droplet in chamber space; low synthesis temperature below the liquidus of the alloy system; no extraction step in order to prepare the starting pure metals is needed; no contamination except the elements present in the source because there is no contact with the process chamber; direct synthesis of fine powder from a metal salts solution and a simple and inexpensive process. The disadvantage is the contamination of organic elements from the fuel and the salt.

4. CONCLUSIONS

Cu–Ni alloy powders were synthesized directly from metal salts. Combustion, mist combustion and ultrasonic pyrolysis processes were applied and Cu–Ni alloy powder was successfully synthesized by mist combustion and ultrasonic pyrolysis of nitrate salts in a reducing atmosphere. XRD data showed that the copper and the nickel atoms were completely mixed. For Cu–Ni alloy powder prepared by mist combustion, the powder used was a hollow sphere and consisted of nanosized particles. For Cu–Ni alloy powder prepared by ultrasonic pyrolysis, particles consisted of nano-scale particles loosely coagulated. The synthesis temperature was 800°C, which is much lower than the liquidus of a Cu–Ni binary system. Chemical alloying has many advantages: no crucible, ball or jar is needed; low synthesis temperature below the liquidus of the alloy system; no extraction step is needed; no cation contamination; direct synthesis of fine powder from metal salts and a simple and inexpensive process. The disadvantage is the contamination of organic elements from the solvent and the salt.

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