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A Review on NiTiCu Shape Memory Alloys: Manufacturing and Characterizations

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ABSTRACT

Shape memory alloys have the thermoelastic phase transformation, known as shape memory characteristics, which make them be used in wide technological applications compared to other alloys. Ni-Ti based SMAs compared to the other families have more applications especially in the biomedical field since they have high biocompatibility, high strain recovery, flexibility, and antirust. In this work, the studies conducted for NiTiCu SMAs were reviewed. Additionally, different manufacturing techniques used by researchers have been explained. Different characteristics of the alloys have been clarified and compared with some other families.

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1. Introduction

Shape Memory Alloys (SMAs) are a special type of material, in which they have some features that make them distinguishable from the other alloys. The most highlighted properties are shape memory and high damping compared to the other materials. SMAs can be deformed by external stress, however, they can back to their original form after heating to a certain temperature. Besides, shape memory is an ability of SMAs that has two types, that classified into Superelasticity (SE) and shape memory effect (SME) [1-3]. Thus, these behaviors have made SMAs be used in wide application areas such as the automotive [4, 5], aerospace [6, 7], engineering [8], industrial [9], and medical field such as dental, orthopedics, vascular, and neurological [10]. Also, SMAs have two different phases which are known as austenite and martensite with various physical characteristics and crystal structures [11-17]. Generally, the austenite phase (parent phase) is more stable in the high temperature with a cubic crystal structure. While, the martensite phase (product phase) which martensite phase appeared at low temperature, has a lower hardness compared to the austenite phase.

Although SMAs have several different types, only three families including NiTi-based, Cu-based, and Fe-based, have more commercial applications [7, 18-21]. NiTi-based SMAs have attracted the attention of researchers and various industries such as medical applications because they have high biocompatibility [22], high strain recovery [23], flexibility, and antirust [24]. It has been reported that the additional elements to NiTi alloy have a significant impact on its shape memory effect (SME) [25-27]. Cu is one of the elements which they have the positive effect to improve the physical properties of Ni-Ti alloy, for example, the substitution of Ni with Cu in a NiTi alloy can improve the SME by reducing its transformation hysteresis, diminishing the high sensitivity of transformation temperatures to chemical structure, and growing fatigue life [28]. Nam et al. stated that the temperature hysteresis of NiTiCu was decreased by increasing the amount of Cu, and the phase transformation of the alloy changed from one step ($B2 \rightarrow B19'$) to a two-step ($B2 \rightarrow B19 \rightarrow B19'$) thermoelastic phase transformation [29]. Also, Mercyer and Melton [30] investigated the replacement of Ni with Cu caused a significant shift in the temperature of transformation.

This review focused on NiTiCu shape memory alloys. Different characterizations and manufacturing techniques have been explained. The advantages of these alloys and the recent findings of researchers have been demonstrated. This article also deals with the existing gap in this area, which makes an opportunity for new researches.

2. Fabrication Of Ni-Ti-Cu Shape Memory Alloy

There are several different methods for manufacturing shape memory alloys, each of which changes the characterization of the alloy. In this review, we focused on the most common methods used by researchers to prepare NiTiCu SMAs. Also, we explained the working principle and the benefits of these techniques.

2.1. Powder Metallurgy Method

Powder metallurgy (PM) or powder sintering, is one of the most common methods that are using in the formation process of metals and metal alloys. PM technique is useful for giving some particular shapes and sizes [31]. The size of powder particles used in the PM technique generally is in µm or nm [32].

Figure 1 demonstrates the schematic diagram of the PM technique. The process consists of three major steps, including fabrication of powders (Figure 1a), compacting and molding (Figure 1b), and (c) merging the powders into a solid element under high pressure and temperature (Figure 1c). In the first stage, the raw material puts in a narrow hole under a high pressure of argon gas to create a tinny liquid stream and cooled down the material with a high cooling rate of 106 °C/sec. In the second stage, the produced powders are mixed and injected into the container under high pressure to form a shape near the final product. In the third stage, which is called hot isostatic pressure (HIP) or sintering, the compacted shape of powders consolidated and diffusion bonded under high pressure (1000-45000 psi) and temperature (1100-1300 °C). An alloy component is obtained with a fine grain structure that is practically free of porosity. In the HIP process, the vacuuming process is more important to avoid the oxidation process [32, 33]. Atiyah et al. used the powder metallurgy technique to produce Ni-Ti-Cu SMA samples. The XRD result showed that the main (Ni-Ti) samples have three phases at room temperature, including NiTi monoclinic phase (martensite), NiTi cubic phase (austenite), and Ni_3Ti hexagonal phase (second phase). Also, after adding Cu by 2.5, 5, 7.5, and 10 wt.%, (CuNi2Ti) intermetallic compound has appeared, moreover, the porosity percentage was decreased by increasing pressure.

On the other hand, Cu addition had a reverse impact on the porosity ratio while the transformation temperatures were decreased [34]. Lucaci et al. used the same technique to produce NiTi, NiTiFe, and NiTiCu alloys. They found that the samples have two different solid solutions which were (NiTi and Ni_3Ti). The Ni-Ti-Cu alloys with shape memory characteristics have to be treated thermally to improve their phase transformation [35].

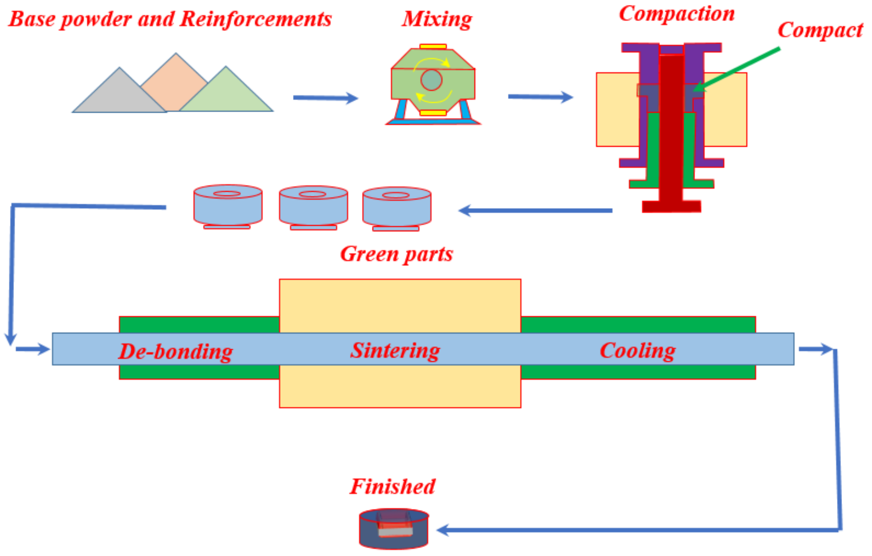

Figure 1 Schematic diagram of the powder metallurgy (PM) method [32]

2.2. Vacuum Induction Melting Process

Vacuum Induction Melting (VIM) It is one of the most widely used methods that can be used for the fabrication of SMAs especially for Ni-Ti alloy, where the metal elements are melted by an energy source produced by electromagnetically induced in the vacuumed area. The induced electromagnetic produces a permanent magnetic field, which consequently generates an electrical current (eddy current) that converted to heat energy. A pellet of compacted powders melts rapidly inside the furnace with air-tight water-cooled steel (Figure 2) [36]. Then the alloy cooled and re-melted several times to homogenize the alloy. The alloy produced by VIM has high homogeneity and low production cost compared to the other fabrication methods [37, 38]. Nam et al. used VIM to the fabrication of Ni-Ti-Cu and they found that the temperature hysteresis of NiTiCu was decreased by increasing the amount of Cu. Also, they reported that the transformation in the equiatomic NiTi changed from one step (B2 → B19′) to a two-step (B2 → B19 → B19′) phase transformation by adding Cu into the NiTi SMA [29]. Likewise, Bricknell et al. fabricated Ni-Ti-Cu SMA by the same process, and they obtained that the sample in which the Cu content is more than (30 wt.%) showed a high-temperature phase with the CsCl crystal structure and when it cooled this high-temperature phase transforms to monoclinic martensite phase by the same morphology and lattice parameters as the binary Ni-Ti alloy [39].

2.3. Vacuum Arc Melting

Arc Melting is a secondary melting technique for melting metals– typically to manufacturing alloys such as Ni-Ti shape memory alloys. The technique has a high chemical and mechanical homogeneity [40].

The source of heating is an electric arc struck that placed between two tungsten electrodes and a sample. The pellet is placed in a crucible in the copper hearth **(**Figure 3). The VAR's chamber is vacuumed and then filled with argon gas to avoid the oxidation process. Also, the remelting process in the VAM technique is performed to improve the homogeneity of the alloy [41]. The temperature of VAM can be reached up to 2000 ℃. In some VAM devices, more than one sample can be produced by one evacuation process, however, this multi-sample production is not recommended for samples that have different compositions because when a sample is heated it may evaporate, therefore this process make contaminants for the rest of samples. Since the device contains some crucible with different volumes, so samples with 15g to 80g can be produced. VAM has three main parts that include a power source (TIG 600Amp), a chiller, and a vacuum part. The vacuum part can be vacuuming the system by the vacuum pump about $10^{-6} mbar$, and the chiller part cools both cupper hearth and the electrodes by the cold water. After the melting process, the melted alloy solidified and to producing the high compositional homogeneity the melting-solidification process repeated several times [42, 43]. Tatar et al. Prepared Ni-Ti-Cu SMA samples using the VAM process, they reported that the crystalline size was decreased by adding Cu, while the temperature hysteresis was increased [44]. Also, Tsuji and Nomura used the arc melting technique to produce Ni-Ti-Cu alloys, where Cu additions were chosen as (6-9%). They found that the transformation temperatures of orthorhombic to monoclinic (exothermic process) were decreased after Cu-additive [45].

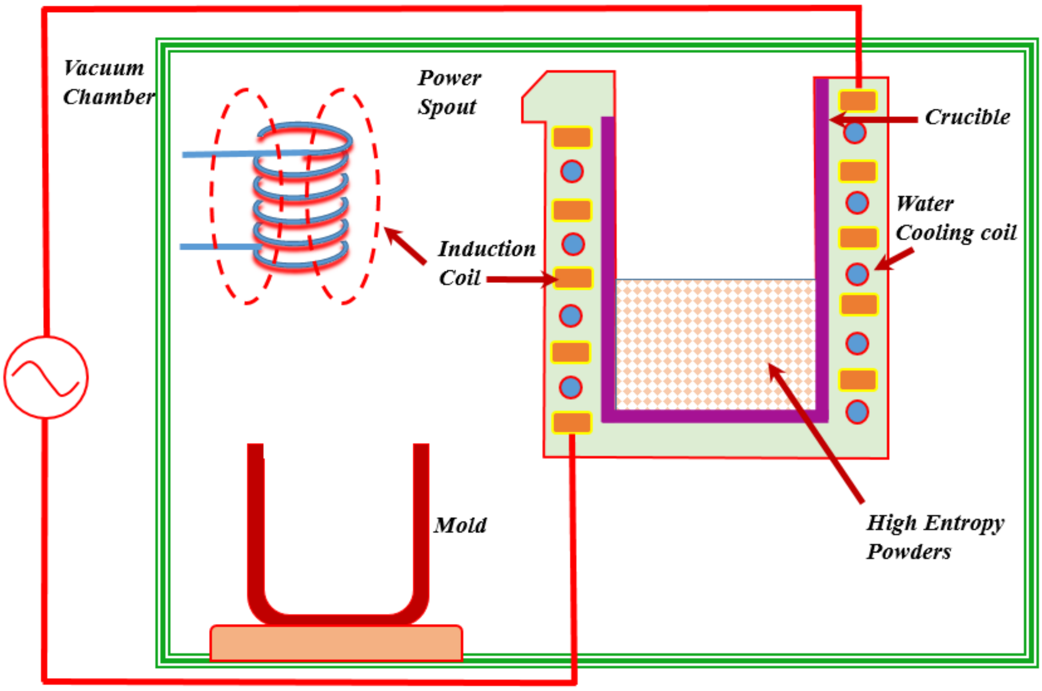

Figure 2 Vacuum induction melting process [36]

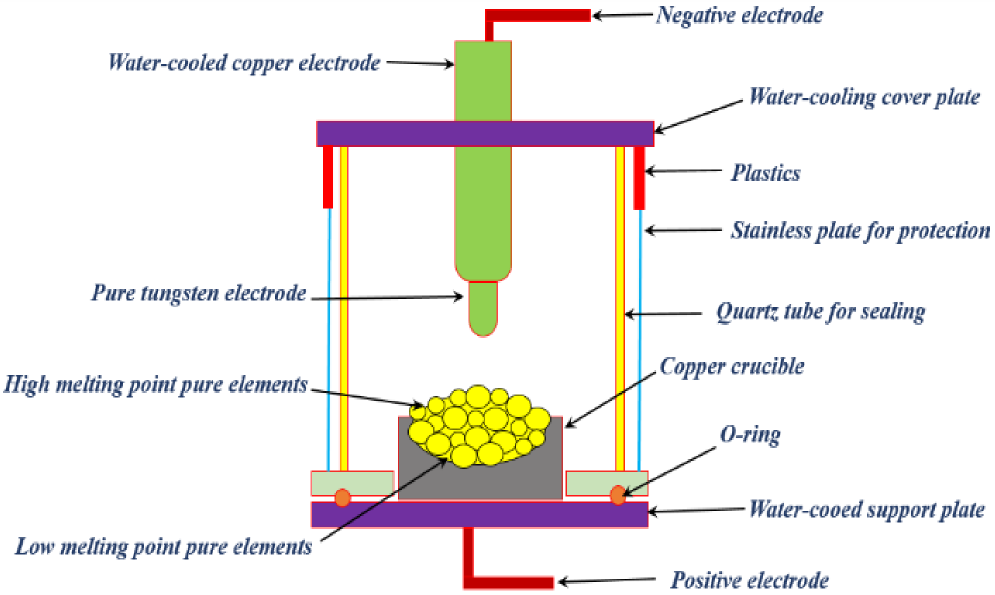

Figure 3 A schematic diagram of an arc melting method [46]

2.4. Electron Beam Melting Process

The Electron Beam Melting (EBM) process (Figure 4) is an additive full melting process that the electron beam is used to melt the metallic powders. The product acquires a particular shape with a high-density, thus the technique has some advantages in technological applications especially SMAs, such as aerospace and medical fields, also it provides high-quality materials that are more expensive and difficult to apply in other technological fields [47, 48]. Arcam AB corporation in Sweden was the first metallurgist that manufactured alloy with the EBM technique [49].

The energy source for melting is an electron beam emitted from a tungsten filament and regulated by two magnetic coils for concentrating and regulating the direction and diameter of the beam. The process is carried out under a vacuumed atmosphere to eliminate impurities and to produce high-strength properties of the final product [49].

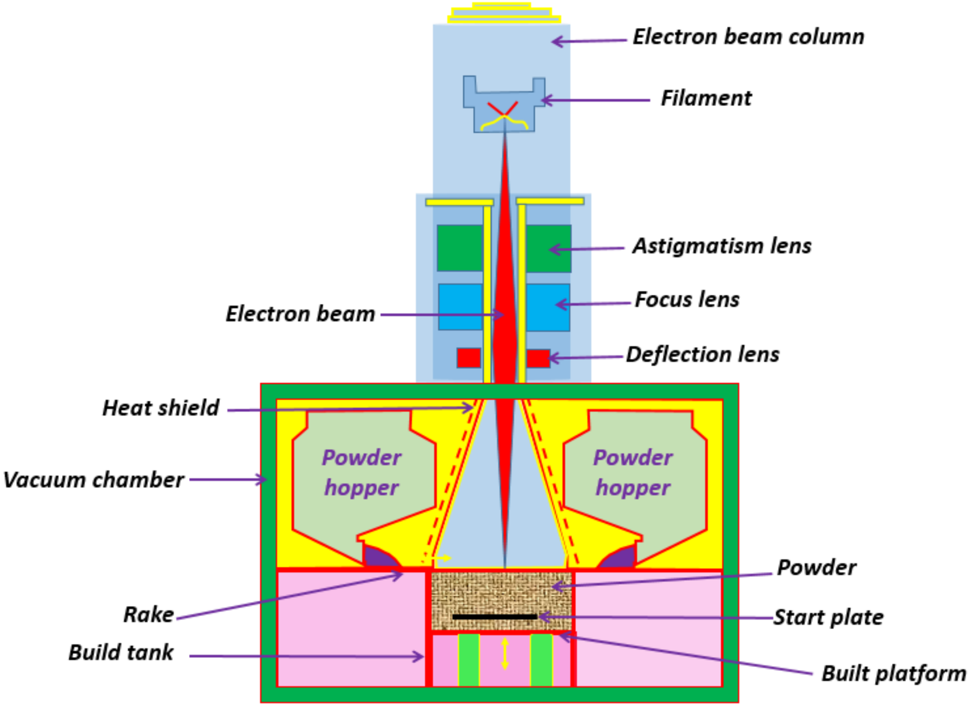

Figure 4 Components of the electron beam melting (EBM) process [50]

3. Characteristics

Shape memory alloys (SMAs) have many important uses in today's world of technology and developing engineering technologies because they can be used in a system to provide actuation, sensing, energy dissipation, monitoring, and healing of structure. SMAs can play important roles because they have several interesting physical and mechanical excellent properties, such as good corrosion resistance, high fatigue life, high damping capacity, and good flexibility to produce possible shape and size. These properties are related to the main two superior behaviors which are superelasticity (SE) and shape memory effect (SME) [6, 51, 52]. Among all types of SMAs, NiTi-based SMA has more technological applications especially in biomedical applications because it has excellent mechanical properties and high biocompatibility [53].

Additionally, adding the chemical element into Ni-Ti alloy has a positive effect to improve their thermomechanical properties [54-56]. Copper (Cu) is one of the elements that improve some properties of Ni-Ti alloys [29, 39, 44], ii.e., Ni-Ti-Cu SMA is one of the best Ni-Ti-based alloys that have some special behaviors that attracted of research attentions.

3.1. Temperature Hysteresis

Thermal hysteresis of an SMA is the temperature difference between the forward phase transformation (austenite(A)→martensite(M)) and reverse phase transformation (martensite(M) → austenite(A)) temperatures [57]. Ni-Ti-Cu is one of the best types of ternary Ni-Ti-based SMAs which has a wide application area because it has the narrowest temperature hysteresis compared to the other types of Ni-Ti SMAs. Also, its hysteresis can be more narrowed from 30 to 10 °C by increasing the Cu amount (about 5-10 at .%) instead of Ni without changing in the phase transformation temperatures [58]. Miyazaki et al. discovered that the temperature hysteresis of Ni-Ti-Cu SMA was decreased by 16K (from 27K to 11 K) when the Cu additive was increased from 0 to 9.5 at .%. Tsuji and Nomura studied some shape memory characteristics of NiTiCu by increasing the amount of Cu composition. They found that by increasing the Cu amount from 6.1 at.% to 9.2 at.% the temperature hysteresis was diminished from 22K to 18 K [45].

3.2. Damping Capacity

Damping capacity is the ability of the materials to absorb mechanical shock and convert it to heat energy [59]. SMAs have comparably high damping capacity, especially the Ni-Ti-based SMAs [60, 61]. Also, the copper (Cu) element has a significant effect to improve the damping capacity of a binary Ni-Ti alloy. It is reported that the Ni-Ti-Cu SMAs recorded the highest damping capacity compared to the other types of Ni-Ti SMAs [62]. Yoshida, et al. studied the damping capacity of Ni-Ti-Cu, and they showed that the value of damping capacity was increased with increasing the amount of Cu content in Ni-Ti-Cu alloy [63]. LO et al. studied B2 ↔ B19 ↔ BI9' phase transformations of a Ni-Ti-Cu SMA. They realized that the value of the damping capacity of the alloy in the B2 ↔ B19 transformation is greater than its value in B19 ↔ BI9' [64]. The same results were reported by Igata and co-authors [65].

3.3. Corrosion Resistance

Corrosion is the degradation that is known as a negative reaction occurred on the surface of a metal with the environment. The corrosion resistance is the superior behavior of smart materials (especially SMAs) [66]. Ni-Ti-Cu is one of the best types of SMAs that can be used in technological applications, especially in the medical field because they have high corrosion resistance [67]. Also, the corrosion resistance of Ni-Ti-Cu SMA can be improved by some techniques such as increasing the Cu content [68], and/or heat treatment [69]. Craciunescu et al. found that increasing the Cu additive into the Ni-Ti-Cu alloy has a significant effect to improve the corrosion resistance because the Cu addition increases the thickness of TiO_2 layer on the surface [68]. Sun et al. showed that the corrosion resistance of Ni-Ti-Cu was increased by increased the time of ageing in the high temperatures [70].

3.4. Biocompatibility

A Biomaterial can adapt itself to the chemical reaction in the human body [71, 72]. Smart Biomaterials especially shape memory alloys can be used inside the human body as implants, which have two main superior behaviors including bio functionality and biocompatibility [73-75]. Biofunctionality is the ability of a biomaterial to carry out the required function when it used in a medical application, while, biocompatibility means that the biomaterial is not harmful inside a body [76]. Ni-Ti-Cu SMAs have wide medical applications and are listed in biomedical material because of their high biocompatibility [77]. Li, et al. discovered that the corrosion behavior and biocompatibility of Ni-Ti–Cu alloys are better than the binary Ni-Ti–alloys, because the Cu content can be enhanced the antibacterial properties of Ni-Ti-Cu [78]. Also, Es-Souni and co-workers investigated that the biocompatibility of Ni-Ti-Cu was increased by increasing the Cu content because Cu can reduce the temperature hysteresis and enhanced the corrosion resistance [9].

4. Conclusion

This study aims to review different manufacturing techniques conducted by researchers to produce NiTiCu SMAs. Also, different characteristics and important results have been highlighted. Based on the results of several researchers, it can conclude that:

Ni-Ti-based SMAs has more technological application compared to the other families because of their interesting behaviors such as high biocompatibility, high strain recovery, flexibility, and antirust.

Alloying Ni-Ti by Cu element could improve some of its behaviors. Copper can reduce the temperature hysteresis, and hence improves the shape memory effect and fatigue life.

Ni-Ti-Cu SMA has a widespread medical application and is listed in biomedical material because of its high biocompatibility and corrosion resistance.

It is reported that the Ni-Ti-Cu SMAs recorded the highest damping capacity and narrowest temperature hysteresis compared to the other types of Ni-Ti SMAs.

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