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Research Article

Corrosion study of CuAlZn Shape Memory Alloys in 3.5 NaCl Solution

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Abstract

In this study , Cu-based shape memory alloys of Cu-25Zn-4Al alloy as master alloy have been prepared by powder metallurgy technique in different alloying elements. The addition of alloying elements such as manganese and titanium with (0.5%wt,0.7%wt and 1%wt) of each element added to the master alloy. After mixing of powders ,compaction stresses of (450,550,650 and 750 Mpa) have been used to compact the master alloy to choose best compress . disc samples (13mm in diameter) and cylinder samples (10mm in diameter) have been prepared by using 650 Mpa as best compress . then sintering process in vacuum tube furnace has been achieved by three stages ,the first stage is at (350˚C) for 2hr. ,second stage is at (550˚C) for 1hr. and third stage is at (900˚C) for 3hr. all samples are solution treatment by heating up to (850˚C) for (1hr.) then rapid quenched in (ice water +salt) . The results obtained from this study have been presented .it found that at 650Mpa the green density is(6.84g/cm³) and green porosity is 16.88% ,while apparent density and porosity of sintering master sample are (4.731 g/cm³) and (25.95%) respectively . Corrosion results have been shown that corrosion rate decrease with addition Mn% and Ti% addition alloying where the (Cu-25Zn-4Al-1%Mn) alloy has (10.678 mpy) in sintering state while (Cu-25Zn-4Al-1Ti) alloy has (1.732 mpy) in quenching state .

Keywords: *Corrosion, Shape Memory etc.*

1. Introduction

The shape memory effect (SME) was observed in a bent bar of AuCd. In 1938, the transformation was seen in brass (copper-zinc). However, it was not until 1962, when Buehler and co-workers discovered the effect in equiatomic nickel titanium((Ni-Ti), that research into both the metallurgy and potential practical uses began in earnest. Within 10 years, a number of commercial products were on the market, and understanding of the effect was much advanced. Study of shape memory alloys has continued at an increasing pace since then, and more products using these materials are coming to the market each year As the shape memory effect became better understood, a number of other alloy systems that exhibited shape memory were investigated(Hodgson *et al*,1990) In 1975, Andreasen, of Iowa University, made the first implant of a superelastic orthodontic deviceto day, these applications are being developed in different fields of science and engineering(Machado, Savi ,2003) . Shape memory alloys (SMAs) have been introduced to biomedical fields due to its unique functions of shape memory effect and superelasticity. Titanium–nickel SMAs are now widely used for practical biomedical applications (Zheng *et al* ,2006) . The corrosion resistance of the implant alloy is a very important determinant of its biocompatibility. As pointed out above, the nature of the environment and the surface treatments have a marked influence on corrosion.(Puranen ,1999) . From literature it was observed that corrosion rate of austenite was more than martensite (quenched) in Cu-Al-Ni SMAs.This demon-strates that shape memory alloys have more corrosion resistance than tradition alloys due to super elastic behavior of polycrystalline structure, Since SMAs find a wide application in the marine, aerospace applications and it is also used in the medical application like Stents, these are the most effective components for treating heart coronary diseases, so it becomes necessary that the shape memory alloys be biocompatible to the environment in which it is being used, so it is important to evaluate the corrosion behavior of the SMAs and also to improve the corrosion resistance of the alloy(Sathish *et al* ,2013). Amongst the most interesting medical alloys developed in the last few years are the NiTi-alloys with nearly equiatomic nickel and titanium distribution. This provides them with several advantages. The most important are (i) their shape memory effect, (ii) their superelasticity and (iii) a good biocompatibility where

These alloys are successfully applied in orthopaedic surgery (Rocher *et al* ,2004). In practical applications, as the alloys are exposed to different corrosion media for a longer period of time they are prone to corrosion and pitting. Therefore study of corrosion potential and pitting potential of the alloys are necessary before they are put into biomedical and indus-trial applications. From literature it was observed that corrosion rate of austenite was more than martensite (quenched) in Cu-Al-Ni SMAs.This demon-strates that shape memory alloys have

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2. Experimental Procedure

Experimental procedure used to prepare samples from the elemental powders through the blending of powders in the mixing operation, compaction and finally sintering based upon typical steps of powder metallurgy technique. The used in this study to prepare several alloys with average particle size and purity are shown in table .1.

Table 1: Powders used in this study.

Powder	Average particle size (mesh)	Purity %	Origin (country).
Copper	-320	99.90	Sky Spring Nanomaterials ,Inc.USA
Zinc	-320	99.90	Sky Spring Nanomaterials ,Inc.USA
Aluminum	-320	99.90	SkySpring Nanomaterials ,Inc.USA

Blended mixtures from elemental powder given in table (2.1) with different weight percent have been prepared in this stage. Main mixtures include Cu+25Zn+4Al, has been prepared. Furthermore; additives from Ti, Mn to the main mixture have also been prepared. Compositions of prepared alloys from elemental powders used in this study have been shown in table .2.

Table 2: Mixtures and their compositions prepared in this study

Alloy No.	Composition (weight percent of powders)
1	Cu + 25 Zn +4Al
2	Cu + 25 Zn +4Al + 0.5 Mn
3	Cu + 25 Zn +4Al + 0.7 Mn
4	Cu + 25 Zn +4Al + 1 Mn
5	Cu + 25 Zn +4Al + 0.5 Ti
6	Cu + 25 Zn +4Al + 0.7 Ti
7	Cu + 25 Zn +4Al + 1 Ti

Wet mixing for constituents of the mixtures has been done by electric rolling mixers . Alumina balls with different diameters and Alumina gars have been used to mix and refine metal powders for about 6 hours. Medical alcohol (ethyl alcohol 96%) has been used in wet mixing. cold uniaxial pressing in double action dies has been used.compression machines is used to compact green disc samples for physical and micro structural tests and cylinder samples for dry sliding wear test .Various compression stresses from(450,550, 650 and 750 Mpa) using double action alloy steel dies fixed in the compression machines with 1800 KN capacity. Samples with dimension (13 mm in diameter and 5.5mm thickness) are showed in Fig.3.4 have been prepared for microstructure and corrosion test .The loading rate has been used to press green compact 0.3 KN\min .the final stage for preparing the sample is sintering process that include the following stages:

1-Heating green compact from room temperature to 350°C with 10°C/ min rate of heating.
2-Soaking time 2hr in 350°C.
3- Raising the heat to 550°C.
4.Soaking time for 1hr at 550°C.
5. Slow cooling in furnace.
6. Heating the samples from room temperature to 900°C with 10°C/ min rate of heating.
7. Soaking time for 3hr at 900°C.
8. Slow cooling in furnace attempt of sintering have been done using vacuum up 10^{-3} torr , then all the samples are quenched in ice water.

3. Results and discussion

3.1Green density and green Porosity of compacts

Green density of master alloys compacts are shown in Fig.(1.1) with respect to compacting pressure , Green density increases with increasing compaction pressure. Three stages occur during compaction process ,the first stage powder particles are rearranged. In the second stage elastic and plastic deformation of the particles have been took place.

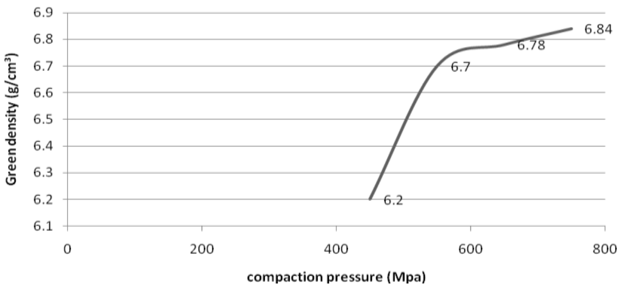

Fig.(1.1) The green density with compact pressure for master alloy

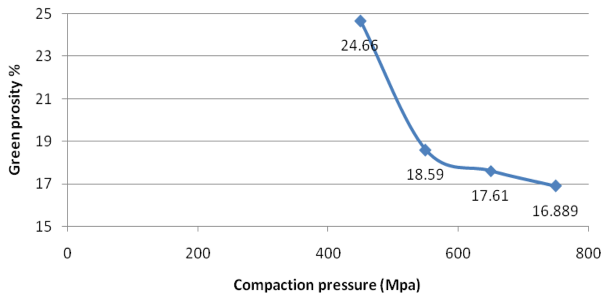

Fig (1.2) The porosity with compact pressure for compaction samples

The third stage of compaction includes fracture of powder particles which have been embrittled through work hardening. Green porosity which the complimentary of green density, has been shown in Fig.(1.2) for green compacts from master alloys. With increasing of compacting pressure, the density of the powder mass increases because the total amount of porosity in the mass decreases . The highest density is found at the top of the outer circumference where wall friction causes maximum relative motion between particles, The density at the circumference decreases rapidly from the top downward with the lowest compact density near the bottom (Abid , 2008).

3.2 Apparent density and porosity of sintering sample

Apparent density has been determined after the samples of master alloy with different compact pressure had been sintered .its increases with compact pressure increases as shown in figure (1.3) because that the space between particles fills with small particles .apparent density depended on factors such as particles size and distribution ,surface area ,particle shape ,etc. Apparent porosity of sintering master alloy is determined after alloy compressed under different pressures as shown in figure (1.4).

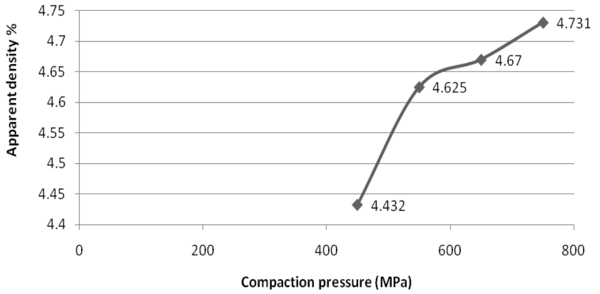

Fig (1.3) Apparent density for master alloys

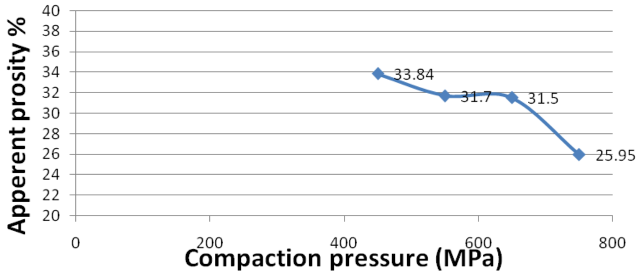

Fig (1.4) Apparent porosity against compact pressure for master alloys

3.3 Corrosion test results

Tafel Corrosion has been used to investigate corrosion behavior for the master alloy with addition in sintering and quenching state .the corrosion solution has been used in the test was NaCl solution (3.5gmNaCl + 96.5ml distillation water) at room temperature . measurements of open circuit potential during 50 second of immersion were performed to obtain some information about the evolution of the corrosion process. Polarization curves were measured potentiostatically at rate of 0.35Mv/s .

The resultants after corrosion test presented in the figures following :

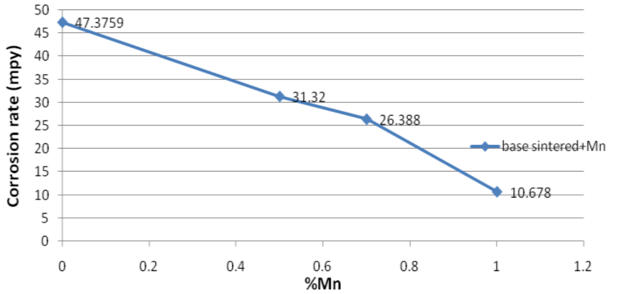

Fig (1.5) Corrosion rate vs. %Mn relation for base alloy sintered in NaCl solution

From the figure (1.5) observed that corrosion rate decreases with Mn alloying element addition because formation of the protective films (chlorine and oxidizes of the elements) on the surface of the specimens which is protect not adhere with the substrate. This protection prevents metals ions from dissolved in solution. also figure (1.6) observed that corrosion rate decreases with Ti alloying element addition because the Ti form a protective oxide film helps in keeping the corrosion rate.

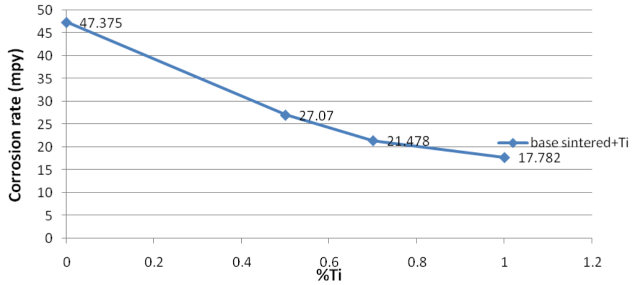

Fig (1.6) Corrosion rate vs. %Ti relation for base alloy sintered in NaCl solution

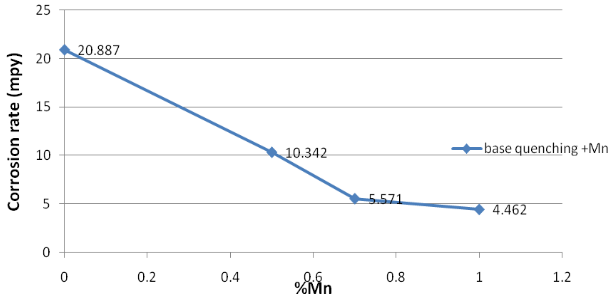

Fig (1.7) Corrosion rate vs. %Mn relation for base alloy quenched in NaCl solution

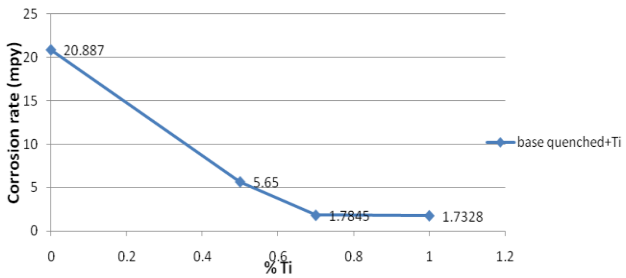

Fig (1.8) corrosion rate vs. %Ti relation for base alloy quenched in NaCl solution

Rate of corrosion for sample in austenitic structure is much greater than for martensitic structure .This demonstrates that shape memory alloys have more corrosion resistance than tradition alloys due to hyper elastic behavior of polycrystalline structure. It is probable that ordering in structure caused by phase transformation is affected on the corrosion behavior of Cu-Zn-Al shape memory alloys.

Hamza,A.S.(Hamza,2013) has been studied the tafel corrosion for Cu-11%Al-4%Ni and Cu-13%Al-4%Ni shape memory alloys with addition Cr and Ag alloying elements in NaCl and 5% NaOH solutions .according to the obtained results it is clear that quenched alloy (Cu-13%Al-4%Ni-0.9%Ag) is more corrosion resistance so that corrosion current is2.7μ Am in 3.5%NaCl solution as well as sintered alloy (Cu-13%Al-4%Ni-0.9%Ag) corrosion current is 29.2 μ Am in 5%NaOH solution .

In this study the results have been shown that quenching alloy (Cu-25Zn-4Al-1%Ti) is more corrosion resistance so that corrosion current is3.54 μ Am in the NaCl solution , while corrosion current of (Cu-25Zn-4Al-1%Mn) is 9.14 μ Am at quenching state. Potentiostatic polarization curve after sintering and quenching processes have been shown in the appendix A

Conclusion

1. Apprenty density is increased with increased compact stress from (4.43) at 450Mpa to (4.73) at 750Mpa while percent of porosity is decreased of (33.84) to (25.95) at same condition .
2.Sintering at 350˚C for 2hr. and at 550˚C for 1hr. then at 900˚C for 3hr. is sufficient to yield phases and microstructure of alloy upon X-ray diffraction.
3. (Cu-Zn-Al) shape memory alloy forms intermetallic compound of (γCu5Zn8) in sintering state ,also it forms (βCu0.61Zn0.39) in quenching state.
4.Corrosion rate for alloys has been decreased with increasing the percent of alloying elements (Mn ,Ti).
5.Among the alloys ,quenched alloy (Cu-25Zn-4Al-1%Ti) has less corrosion rate .

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