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Effect of (Zn & Mg) on Corrosion Behavior of Shape Memory Alloys

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Abstract

Nickel-Titanium shape memory alloy (Nitinol or NiTi) is a fascinating material for dental applications. In this work the alloy has been produced by powder metallurgy approach. The effect of Mg and Zn additives studied on the; hardness, porosity percentage, and corrosion rate has been studied. Master Samples (without additives) were prepared using powder mixture of 55 wt% Ni and 45 wt% Ti by mixing them in a ball mill for two hours, then compacted at 300, 400, 500, 600, 700, and 800 Mpa, then sintered at 950 ^{o}C for 9 hours under controlled atmosphere (argon). The same approach was used for the prepared samples with Mg and Zn additions compacted at 800 Mpa. XRD examination shows that the sintered samples are consisting of two phases martensite and austenite at room temperatures, this mean thermal NiTi shape memory alloy. From the results, it was found that Mg additives increase hardness and decrease the corrosion rate while Zn additives increase the corrosion rate.

تأثير الزنك والمغنيسيوم على سلوك التأكل لسبائك ذاكرة الشكل

الخلاصة

تعتبر سبائك ذاكرة الشكل (نيكل- تيتانيوم) من المواد الساحرة المستخدمة في التطبيقات الاسنان. تم انتاج السبائك في هذا البحث بطريقة ميتالورجيا المساحيق وتم دراسة تأثير اضافات المغنيسيوم والزنك علىالصلادة ونسبة المسامية و معدل التاكل.

تم تحضير النماذج الاساس (بدون اضافات) بخلط المساحيق بنسب وزنية (55 wt% Ni , 45 wt% Ti) بواسطة طاحونة الكرات لمدة ساعتين ثم تم كبس الخليط بضغط (300، 400، 500، 600، 700و 800) ميكابسكال وبعدها اجراء عملية التلبيد لمدة 9 ساعات وبدرجة حرارة 950 م^{o} وبجو مسيطر عليه بواسطة غاز الاركون. نفس الطريقة استخدمت لتحضير النماذج مع الاضافات وتم كبسها عند ضغط 800 ميكابسكال.

اوضح اختبار حيود الاشعة السينية بان النماذج الملبدة تحتوي على طورين هما المارتنسايت والاوستنايت عند درجة حرارة الغرفة وهذا يعني سبيكة ذاكرة الشكل الحرارية .و وجد من خلال النتائج ان أضافة المغنسيوم يقلل معدل التاكل بينما اضافة الزنك يزيد معدل التاكل.

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1. Introduction

Shape memory alloys (SMA) constitute a group of metallic materials with the ability to recover a previously defined length or shape when subjected to an appropriate thermomechanical load [1]. When there is a limitation of shape recovery, these alloys promote high restitution forces. Because of these properties, there is a great technological interest in the use of SMA for different applications. Although a relatively wide variety of alloys present the shape memory effect, only those that can recover from a large amount of strain or generate an expressive restitution force are of commercial interest. Particularly important among them are alloys based on Ni-Ti and on Cu, such as Cu-Zn-Al and Cu-Al-Ni. SMA based on Ni-Ti are the alloys most frequently used in commercial applications because they combine good mechanical properties with shape memory. [2]

Basically, SMA presents two well-defined crystallographic phases, i.e., austenite and martensite [3]. Martensite is a phase that, in the absence of stress, is stable only at low temperature; in addition, it can be induced by either stress or temperature. Martensite is easily deformed, reaching large strains (~8 %) [1]. Depending on the type of transformation experienced by these alloys, the crystal structure of martensite can be either monoclinic or orthorhombic [4, 5]. When martensite is induced by temperature, it is called twinned martensite. The twinned martensite has 24 variants, i. e., 24 sub types with different crystallographic orientations [6]. On the other hand, when martensite is induced by stress these 24 variants of twinned martensite become only one variant. As a consequence, there is a crystallographic orientation, aligned with the stress direction, which is called detwinned martensite. The austenite phase is stable only at high temperatures, having a single variant with a body-centered cubic crystal structure.

Martensitic transformation explains the shape recovery in SMA. This transformation occurs within a range of temperatures which varies according to the chemical content of each specific alloy [7]. In general, four characteristic transformation temperatures can be defined: M_s and M_f, which are the temperatures at which the formation of martensite starts and ends, respectively, and A_s and A_f, which are the temperatures at which the formation of austenite starts and ends, respectively.

The aim of this work is to Produce thermal NiTi (a sample consisting of martenictic and austenitic phases at room temperature), by powder metallurgy approach and Studying the effect of Zn and Mg addition on the hardness, porosity percentage and corrosion rate.

2. Experimental

Ni-Ti powder (master mixture; 55 wt% Ni with 45 wt% Ti) was prepared using a ball mill for mixing the powder for two hours. This mixture was used to prepare samples with 0.1, 0.2, and 0.3 wt% of Mg and then for Zn additions. After mixing, six master samples each weighting 5 grams, they were compacted at 300, 400, 500, 600, 700 and 800MPa respectively, by placing the powder in a die made from D2 tool steel with a diameter of 15mm. Samples with additions of 0.1, 0.2 and 0.3 wt% Mg and similar percentage of Zn were also prepared and compacted at 800MPa.

Following the compaction, all samples were sintered at 950 °C for 9 hours (the samples were allowed to heat up with same the heating rate) under argon atmosphere and then cooling down, at the furnace-cooling rate, to room temperature. The sintering process for all specimens has been done under controlled atmosphere (argon gas) to avoid the samples oxidation. Following that, the samples were ground and polished.

Corrosion rate was measured for each sample were obtained from anodic and cathodic polarization curves using artificial saliva as an electrolyte at 37^oC with a scan rate of 5mV/sec and potential range of (-0.25-0.25 V), the exposed surface area (of the sample) to artificial saliva was 0.78 cm^2.

Vickers hardness was also measured. The average of 10 readings was taken. The phases formed by sintering were detected using the XRD for all of the samples. The porosity percentage was also measured on the basis of density [8],

Porosity % = [1-(actual density/ theoretical density)] x100 ….. (1)

3. Result and Discussion

3.1 XRD Pattern

All of the prepared master samples were compacted at various pressures and prepared samples (master with additives) were compacted at (800 MPa) and all of the samples were sintered at 950 °C for 9 hours. The low compaction rate used is essential to give enough time for the particles to be bonded to each other and therefore increase the density. The sintering temperature used (950 °C) was about 0.8 of the melting temperature of the NiTi intermetallic compound (T_m =1310 °C), and holding at this temperature for 9 hours under controlled argon atmosphere will result in complete sintering reaction due to the enhancement of the interdiffusion between Ti and Ni which in turn leads to an increase in the amount of NiTi phase produced and to a better shape memory effect [9].

The phases produced as a result of the sintering process were investigated using the XRD technique. It is seen from Fig. (2, 3 and 4) that there are probably no pure metals present, which proves that the sintering time and temperature used in this work result in complete sintering reaction. The absence of any oxides is attributed to the controlled argon atmosphere used during the sintering process. Fig (2, 3 and 4) Shows that the master sample and master samples with 0.3 Wt % of Mg and Zn respectively compacted at 800 MPa consisted mainly of two phases (the martensitic phase M and the austenitic phase B_2 at which the volume fraction of the martensitic phase was more than the austenitic one) in addition to Ti_2Ni and Ni_3Ti. The formation of Ti_2Ni and Ni_3Ti might be attributed to the slow cooling of the samples with the furnace cooling rate whereas, in the sintering conditions used throughout this work, the Gibbs free energies for Ni_3Ti and Ti_2Ni were less than that for NiTi and it seems difficult to obtain a final equilibrium structure of NiTi alone just by solid - state diffusion, [10].

3.2 Vickers Hardness

Hardness measurements were made for all of the samples, the hardness values were taken as the average of 10 random readings

Fig. (5) Shows that as the additives percentage is increased, (for Mg additives) the measured hardness value will increase. This agrees with the fact that as, the bonding between the particles is better (i.e. better interdifusion) it is in turn leads to more pores elimination. While the percentages of Zn added (0.1, 0.2, and 0.3wt %) have no significant influence on the hardness because of evaporate of Zn at 950 °C and this increased in hardness may be from high compacting pressure at 800 Mpa.

3.3 Porosity Percentages

Porosity measurements have been made on the basis of density according to Eq. (1). For the master sample, the theoretical density is 6.5 g/cm^3 [11]. And the measured density of the sample is its weight divided by the volume (the samples are of a disc shape with a diameter of 15mm). For the samples with additives, the theoretical density is:

$$r_o = (r_{Ni} \times at\,\%\,Ni) + (r_{Ti} \times at\,\%\,Ti) + (r_{additive} \times at\,\%\,additive) \quad ….. (2)$$

The porosity percentage is maximum for the samples compacted at 300 MPa and minimum for those compacted at 800 MPa which is in good agreement with the expectation; since as the compacting pressure is increased, the adhesion and interdiffusion between the particles is better which results in more elimination of pores. Fig. (6) shows that the porosity percentage decreases with increasing the additives (for each wt% of additives) and it is clear that the percentages of Zn added (0.1, 0.2, and 0.3wt%) have no significant influence on the porosity percentage but this a small decrease in porosity still higher than the porosity of master sample could be observed with increasing Mg &Zn addition from 0.1 to 0.2 to 0.3 wt% respectively (at 800 MPa) which could be increasing pores.

3.4 Corrosion Rate Determination

Corrosion rate for the samples pressed at different pressure shown in Fig. (7). that Indicates the corrosion rate decreases with increasing the compacting pressure from 300 to 800 MPa, respectively, and this is attributed to the decrease in the porosity percentage which in turn reduces the surface area in contact with solution (artificial saliva) and this leads to a decrease in the measured corrosion rate.

Fig.(8) indicate that the corrosion rate decreases with increasing the wt% of Mg, this can be attributed to the higher activity of Mg compared to Ni, therefore, the Mg acts as an anode relative to the Ni which in turn results in a reduction in the corrosion rate of the bulk. The reason for this decrease in the corrosion rate with increasing the wt% of Mg added is due to the increase in the anodic area (Mg), therefore, the Mg is corroded more and the bulk is protected. But though the activity of Zn is less than that of Ti, the Ti form a protective oxide film which helps in keeping the corrosion rate not to influence by Zn addition. The reason for the increase in the corrosion rate with increasing the wt% of Zn added is due to the increase in the cathodic area (Zn)

4. Conclusions

1. The samples sintered at 950°C for 9 hours with 45 wt% Ti result in a two-phase structure (austenite and martensite) at room temperature.The samples with Mg and Zn additions also resulted in the same two phase structure at room temperature.
2. For the master samples; the higher the compaction pressure results in higher hardness, the lower the porosity percentage and the lower the corrosion rate.
3. The corrosion rate decreases with increasing the wt% of Mg.

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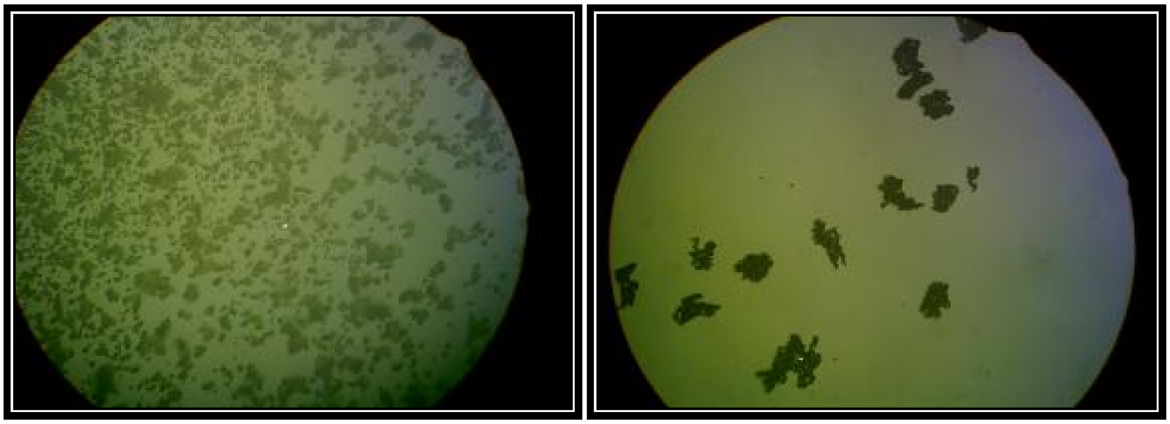
Table (1) purity and particle size of Ni, Ti, Zn and Mg

Metal (Powder)	Purity (%)	Particle Size (µm)
Ni	99.9	16
Ti	99.5	150
Zn	99.5	80
Mg	99.9	45



Ni-powder Ti-powder

Figure (1) particle shape of Ni and Ti powders.

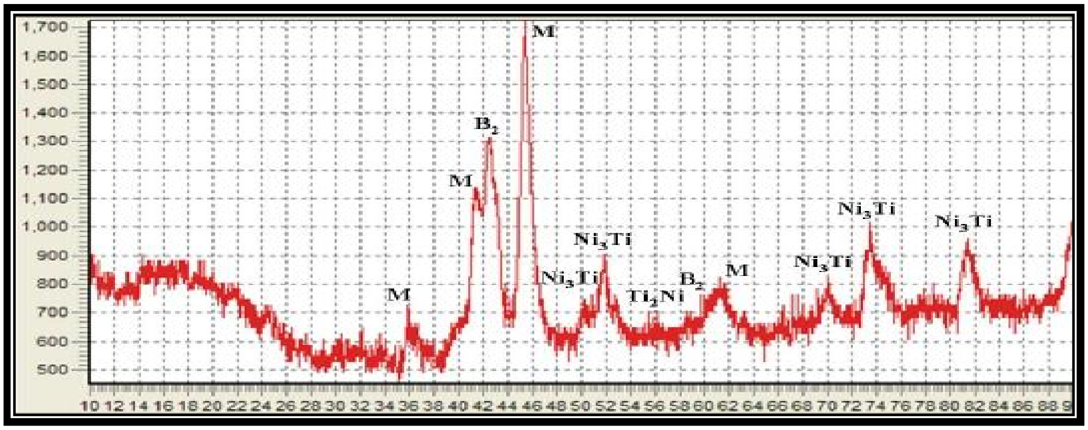


Figure (2) XRD pattern of a master sample pressed at 800MPa and sintered at 950°C for 9 hrs.

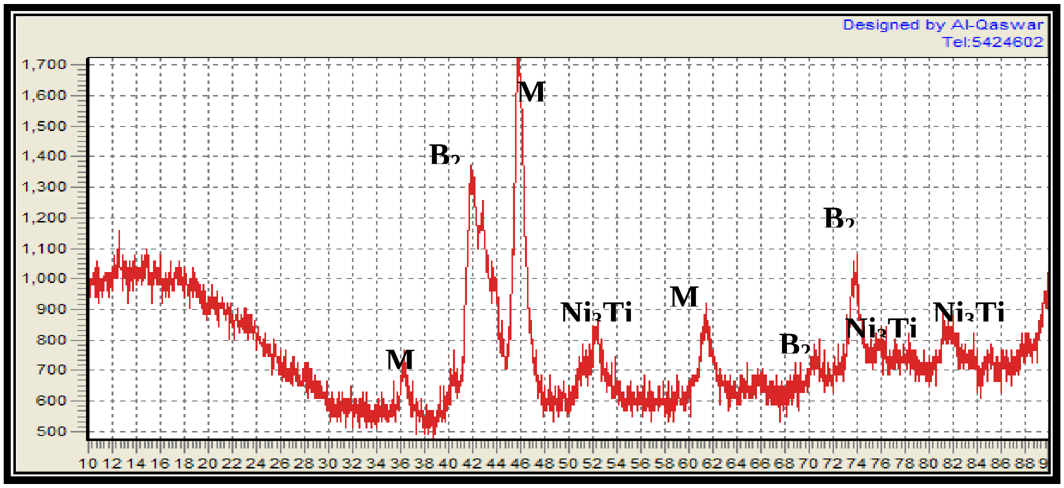


Figure (3) XRD pattern of the master with 0.3% Mg sample pressed at 800MPa and sintered at 950°C for 9 hrs

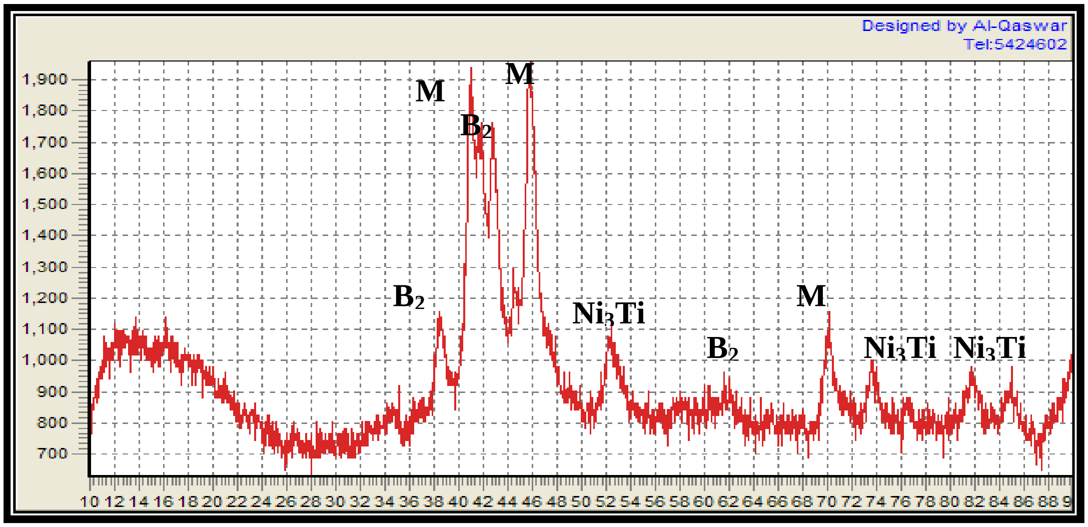


Figure (4) XRD pattern of the master with 0.3% Zn sample pressed at 800MPa and sintered at 950°C for 9 hrs.

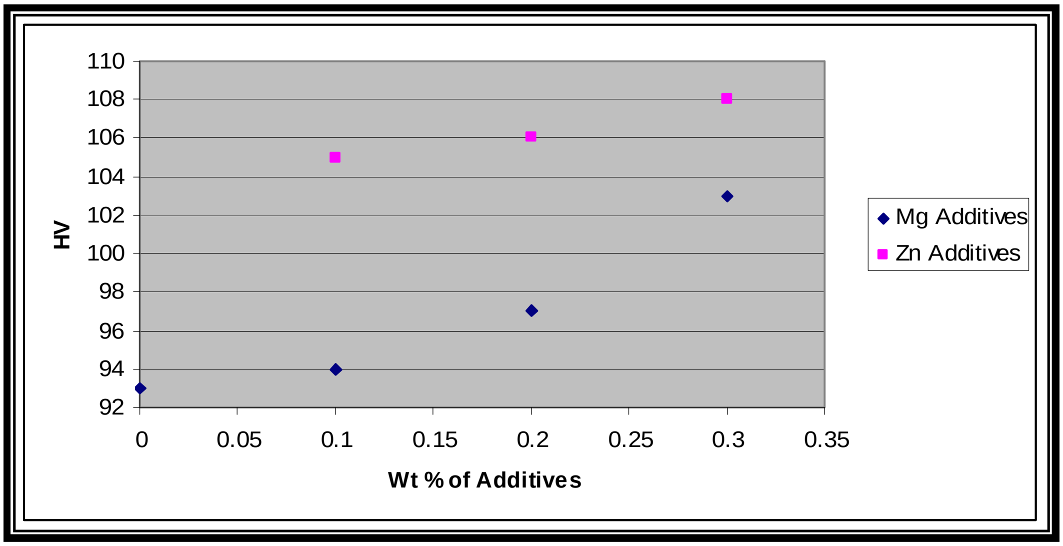


Figure (5) Hardness values for the master with various additives of Mg& Zn pressed at 800MPa and sintered at 950°C for 9 hrs.

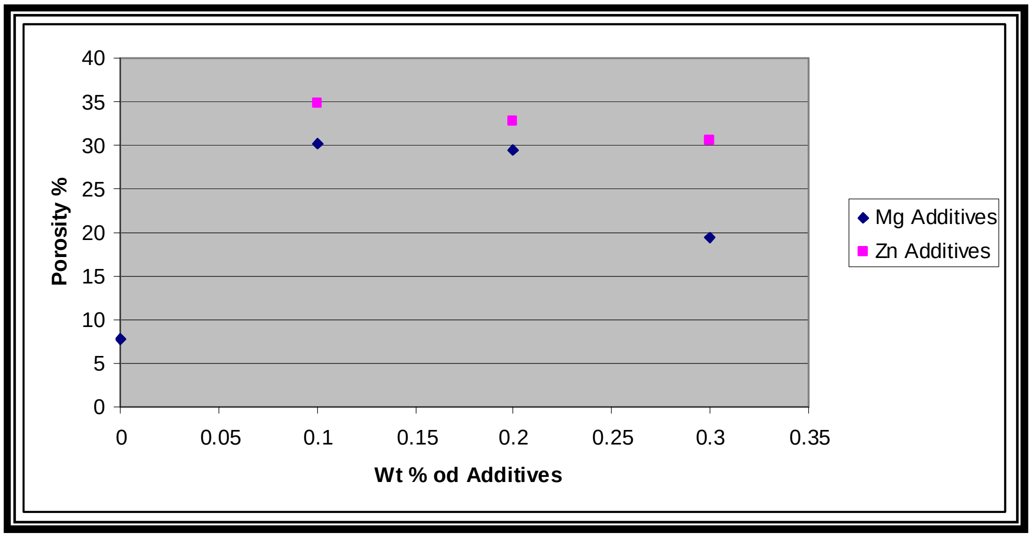


Figure (6) Porosity percentages for the master with various additives of Mg& Zn pressed at 800MPa and sintered at 950°C for 9 hrs.

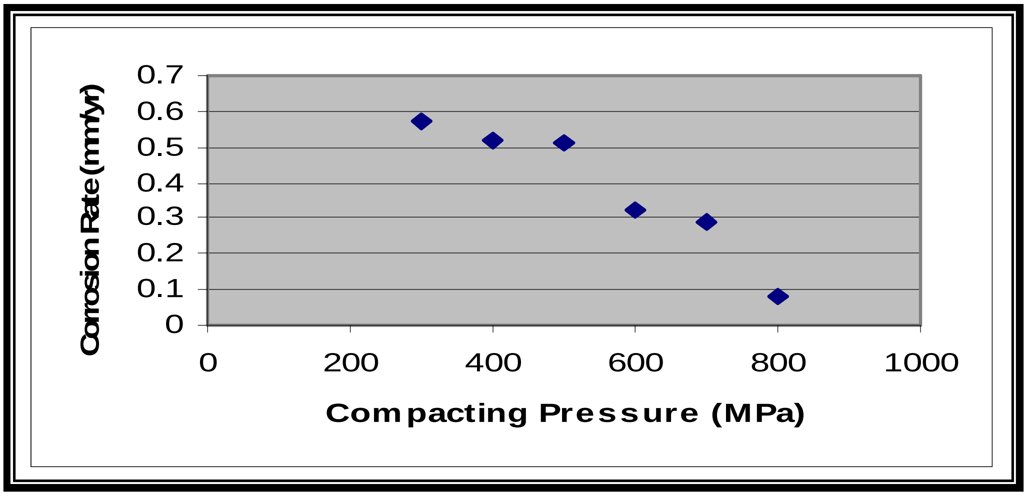


Figure (7) Corrosion rate (mm/yr) for the master sample pressed at different pressure and sintered at 950°C for 9 hrs.

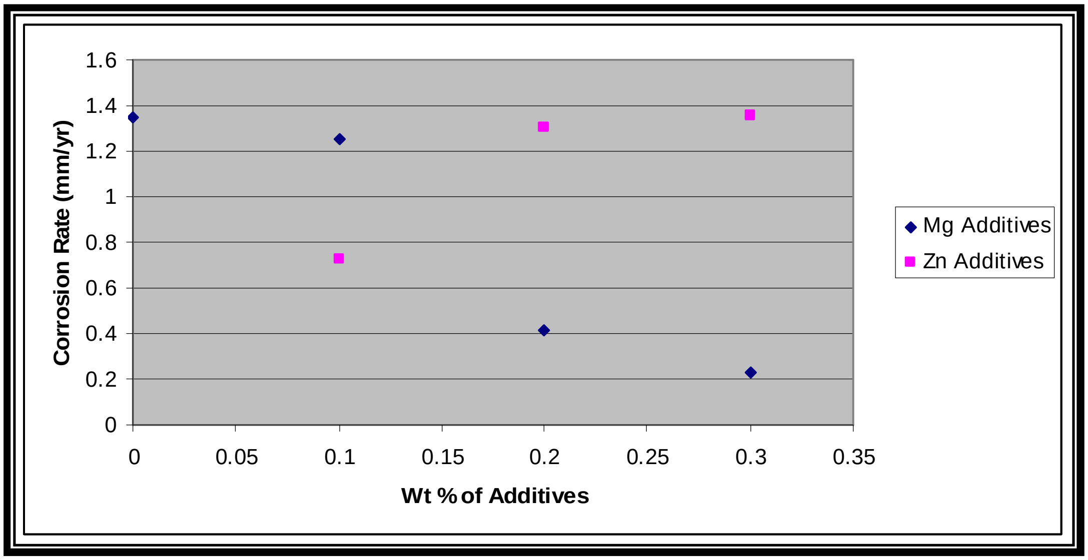


Figure (8) Corrosion rate (mm/yr) for the master with various percentages of Mg & Zn pressed at 800MPa and sintered at 950°C for 9 hrs.