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INVESTIGATION OF THE ADDITIVES FOR CHANGING ON PHASES AND 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 prepared by powder technology and the effect of Mg and Zn additives has been studied on the corrosion rate, in artificial saliva. Samples (without additives) were prepared using powder mixture of 55 wt.% Ni and 45 wt.% Ti by blending in a ball mill for two hours, then compacted at 800 Mpa, and then sintered at 950 ^{o}C for 9 hours under controlled atmosphere (argon). The same approach was made for the samples with 0.1, 0.2 and 0.3 wt% of Mg and Zn additions. XRD test shows that the sintered samples are consisting of two phase's martensite and austenite at room temperatures.From the results; it was found Zn additives increase the corrosion rate while Mg additives decrease the corrosion rate.

Keywords: shape memory alloys, corrosion, SMA phases, NiTi SMA

الخلاصة

سبائك ذاكرة الشكل (نيكل- تيتانيوم) تعتبر من المواد الساحرة المستخدمة في التطبيقات الاسنان. في هذا البحث تم انتاج السبائك بطريقة ميتالورجيا المساحيق وتم دراسة تأثير اضافات المغنيسيوم والزنك على معدل التاكل في محلول اللعاب الصناعي.النماذج الاساس (بدون اضافات) تم تحضيرها بخلط المساحيق بنسب وزنية(55 wt% Ni) ، (45 wt% Ti) بواسطة طاحونة الكرات لمدة ساعتين ثم تم كبس الخليط بضغط 800 Mpa 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 بنسب وزنية 0.1 و0.2 و0.3 من الزنك والمغنيسيوم. اختبار حيود الاشعة السينية اوضح بان النماذج الملبدة تحتوي على طورين هما المارتنسايت والاوستنايت في درجة حرارة الغرفة. من خلال النتائج وجد ان اضافة الزنك تزيد من معدل التاكل بينما اضافة المغنيسيوم تقلل معدل التاكل الكيميائي.

INTRODUCTION

Shape memory alloys (SMA) constitute a group of metallic materials with the ability to recover a previously defined length or a shape when subjected to an appropriate thermo mechanical load [Hodgson DE1990]. 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.

Basically, SMA presents two well-defined crystallographic phases, i.e., austenite and martensite [smart.tamu.edu2001]. 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 %) [Hodgson DE1990]. Depending on the type of transformation experienced by these alloys, the crystal structure of martensite can be either monoclinic or orthorhombic [Otsuka K 1999, Wu SK 2000]. When martensite is induced by temperature, it is called twinned martensite. The twinned martensite has 24 variants, i. e., 24 subtypes with different crystallographic orientations [Funakubo H 1987]. 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 alloy [www.sma-inc.com 2001]. 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.

Eventually the aim of this work is to prepare thermal NiTi by powder metallurgy approach and studying the effect additives on the developed phases and corrosion rate.

Experimental

Ni-Ti powder (master mixture; 55 wt% Ni with 45 wt% Ti) was prepared using a ball mill by mixing for two hours. This mixture was used to prepare samples with 0.1, 0.2, and 0.3 wt% of Mg and Zn additions. After mixing, they were compacted at 800MPa, by placing the powder in a die made from D2 tool steel with a diameter of 15mm.

Following the compaction, all of the samples were sintered at 950 °C for 9 hours (the samples were allowed to heat up with the heating rate 7°C /min) under argon atmosphere and were allowed to cool down at the furnace-cooling rate. Following that, the samples were ground and polished.

Corrosion rate was measured for each sample where anodic and cathodic polarization curves were obtained using artificial saliva as the electrolyte at 37^{o}C 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.

Results and Discussions

XRD Pattern

All of the prepared samples were compacted at (800 MPa) and sintered at 950 °C for 9 hours. The sintering temperature used (950 °C) was about 0.8 of the melting temperature of the NiTi intermetallic compound (T_m =1310 °C) [J. T. Al-haidary 2006], and holding that 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. [Bing-Yun 1999].

The phases developed as a result of the sintering process were investigated using the XRD technique. It is seen from fig. (1) 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. On the other hand, there might be some sort of oxides, which are lower than the detectability of the used XRD when they are less than 5%. Figure (1) show that the master sample 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, [Li Bing-Yun 1998].

Mg and Zn were added at a maximum percentage of (0.3 wt %) respectively, this is a very small amount to be detected by the XRD as shown in figures (2-7).

Corrosion Rate Determination

Figure(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 to the Ni which in turn results in a reduction in the corrosion rate of the bulk. The reason for the 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 from a protective oxide film helps in keeping the corrosion rate not to influenced by the 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)

Conclusions

1. The samples sintered at 950oC 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. the corrosion rate decreases with increasing the wt% of Mg, this can be attributed to the higher activity of Mg compared to Ni
3. The corrosion increase with increase Zn.

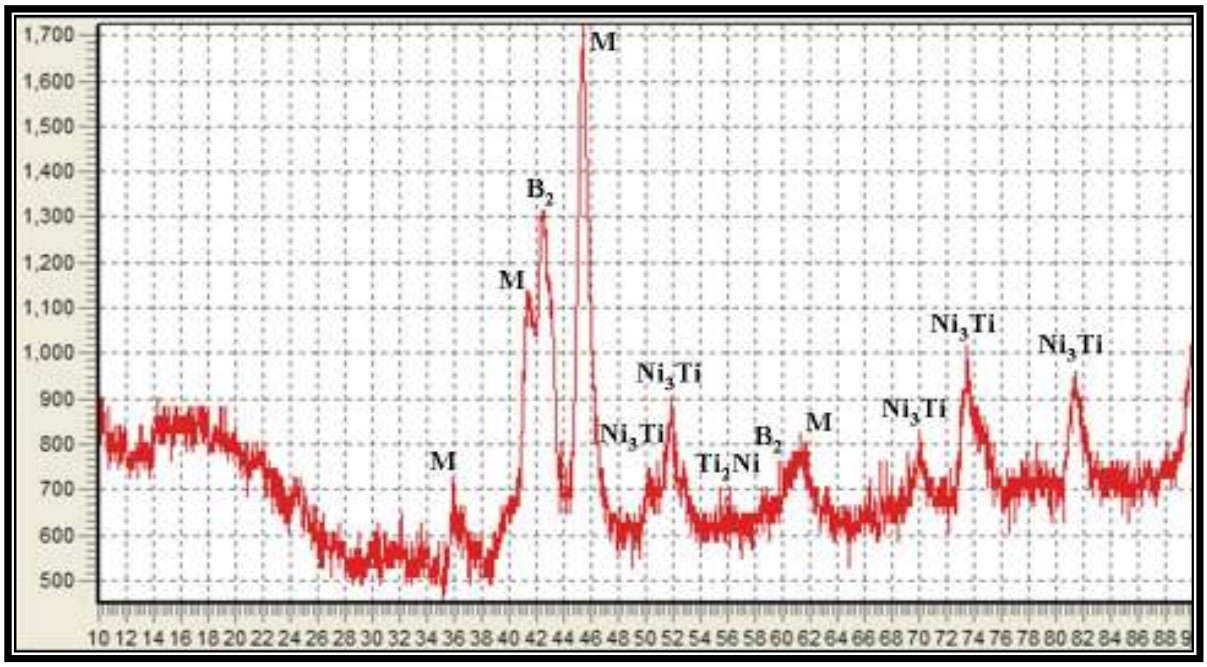

Fig (1): XRD pattern of a master sample pressed at 800MPa and sintered at 950°C for 9 hrs.

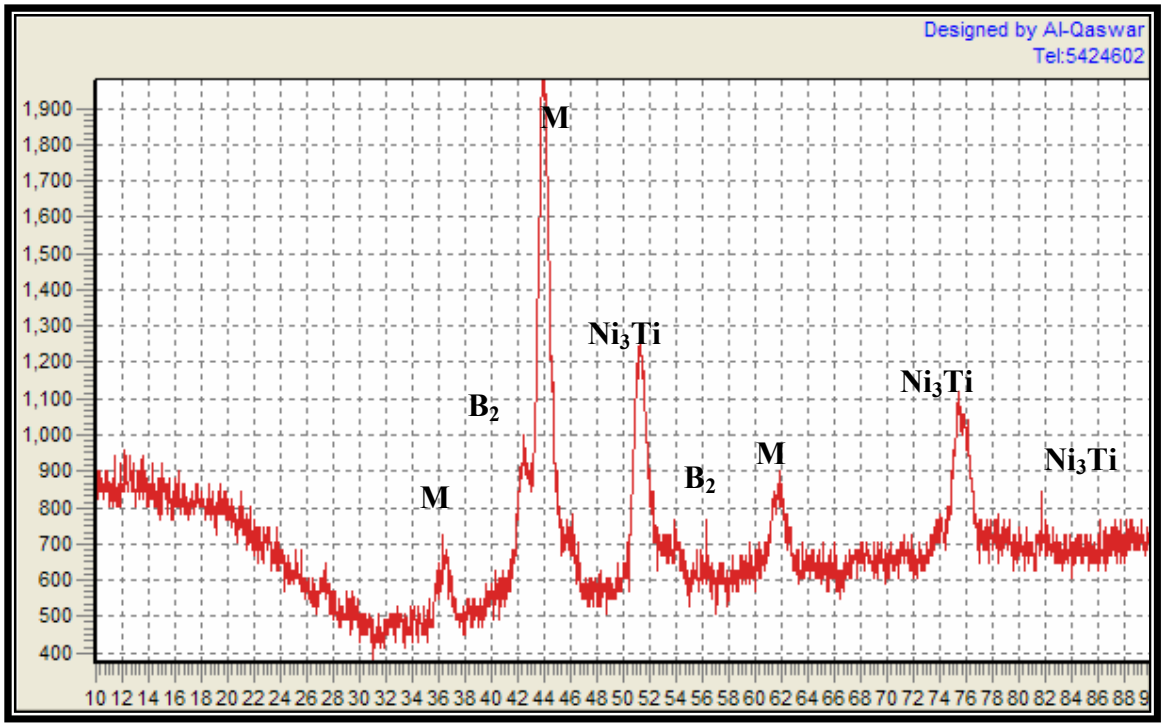

Fig (2): XRD pattern of the master with 0.1% Zn sample pressed at 800MPa and sintered at 950oC for 9 h

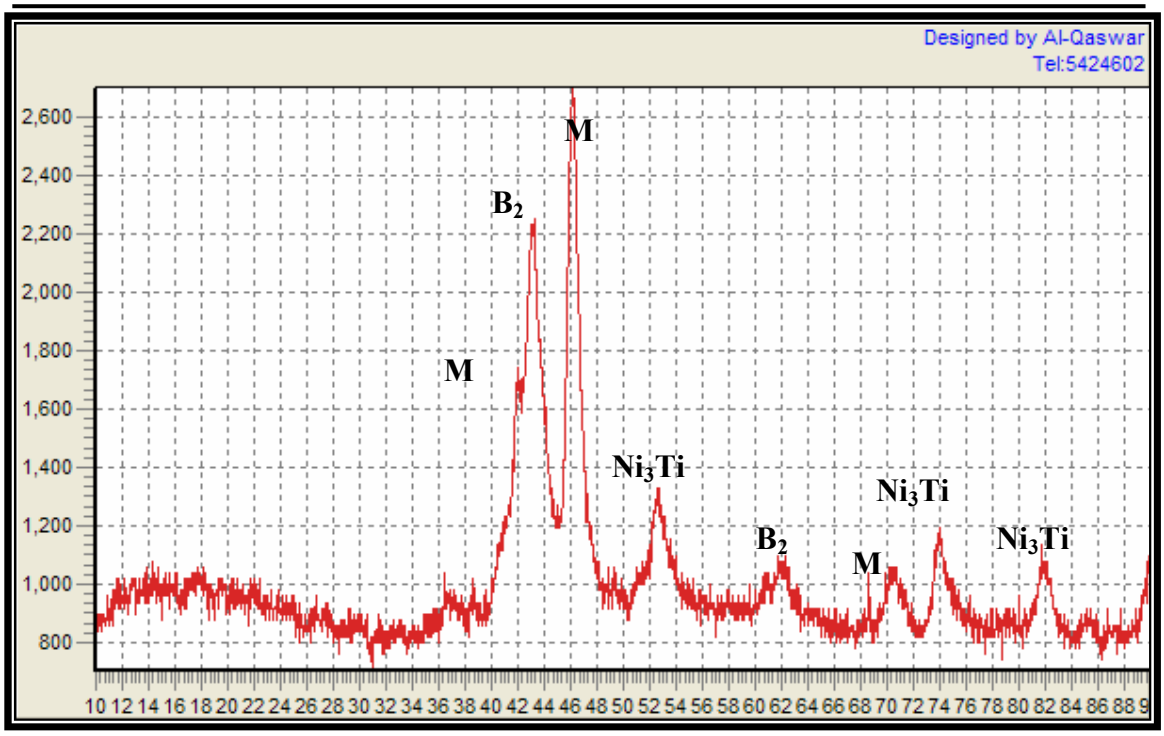

Fig (3): XRD pattern of the master with 0.2% Zn sample pressed at 800MPa and sintered at 950°C for 9 hrs

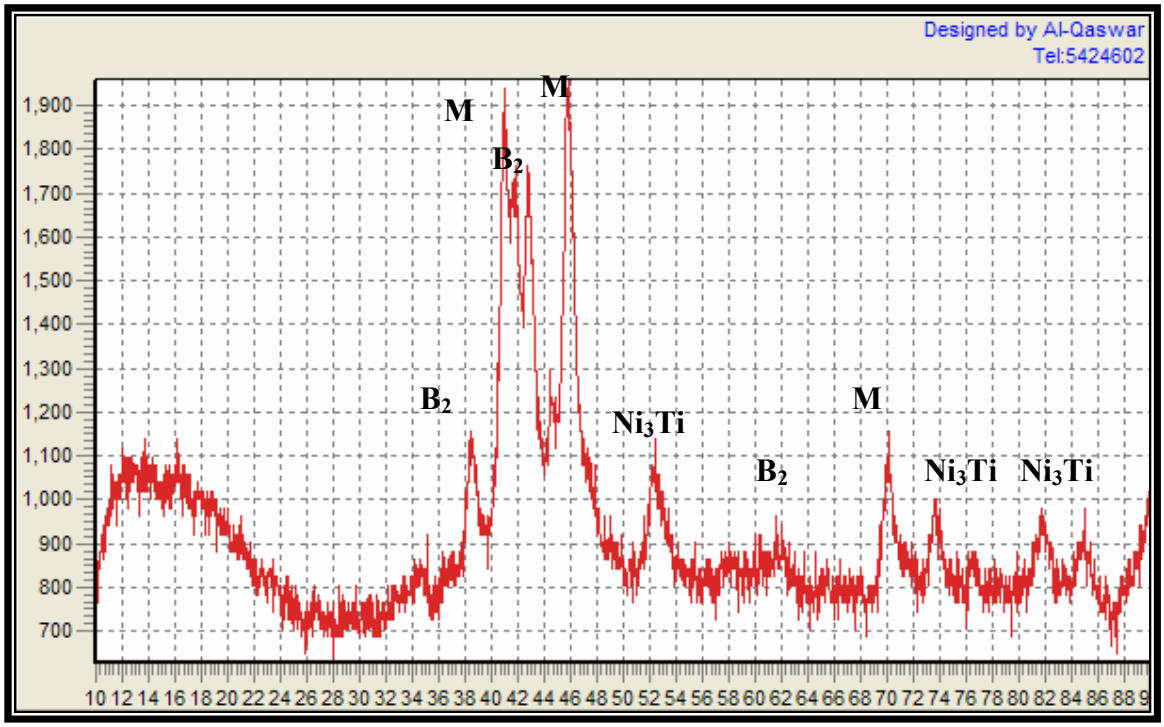

Fig (4): XRD pattern of the master with 0.3% Zn sample pressed at 800MPa and sintered at 950oC for 9 hrs

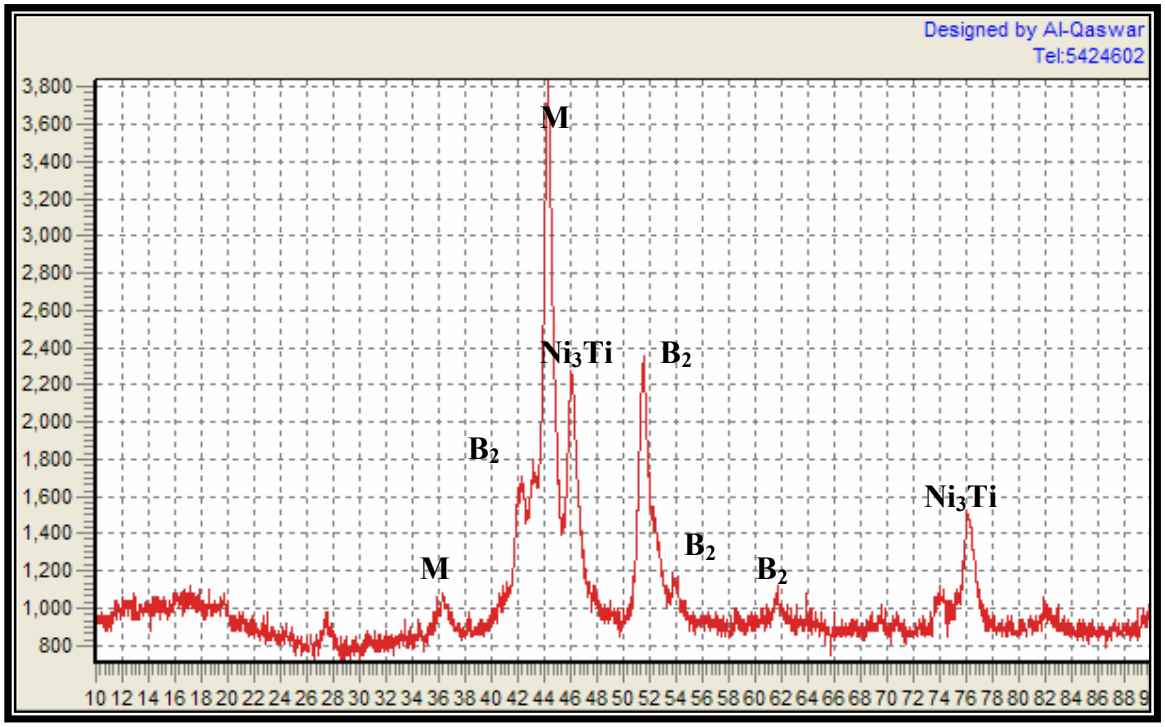

Fig (5): XRD pattern of the master with 0.1% Mg sample pressed at 800MPa and sintered at 950°C for 9 hrs

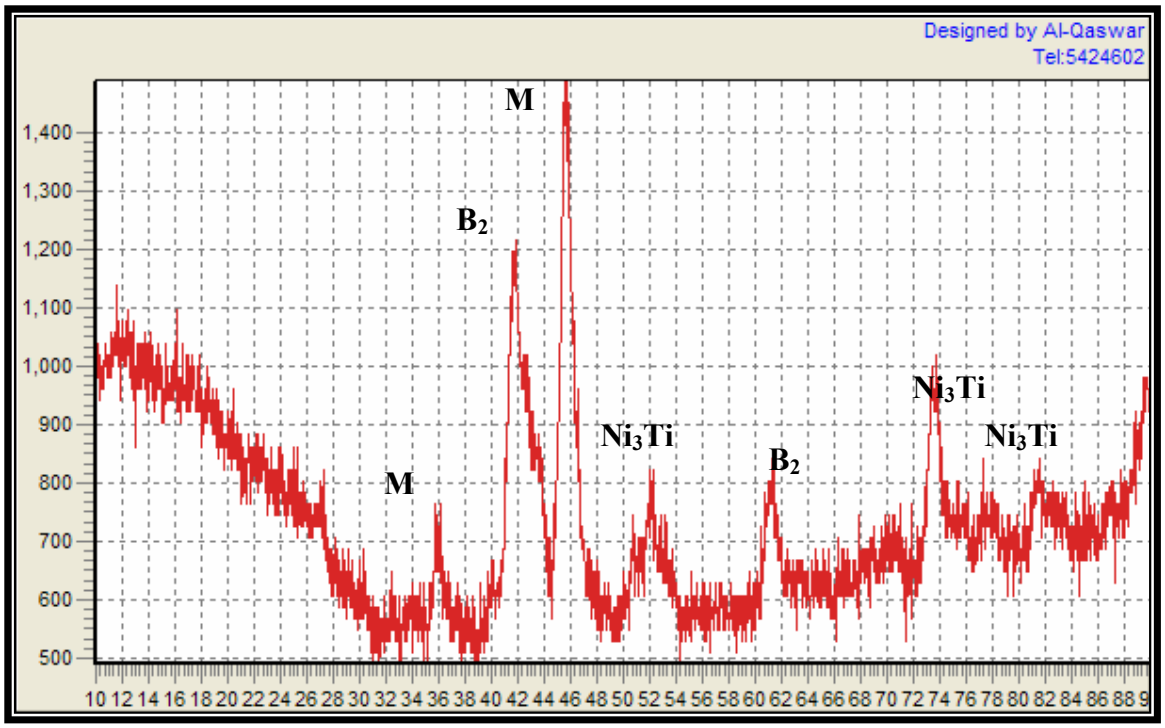

Fig (6): XRD pattern of the master with 0.2% Mg sample pressed at 800MPa and sintered at 950°C for 9 hrs

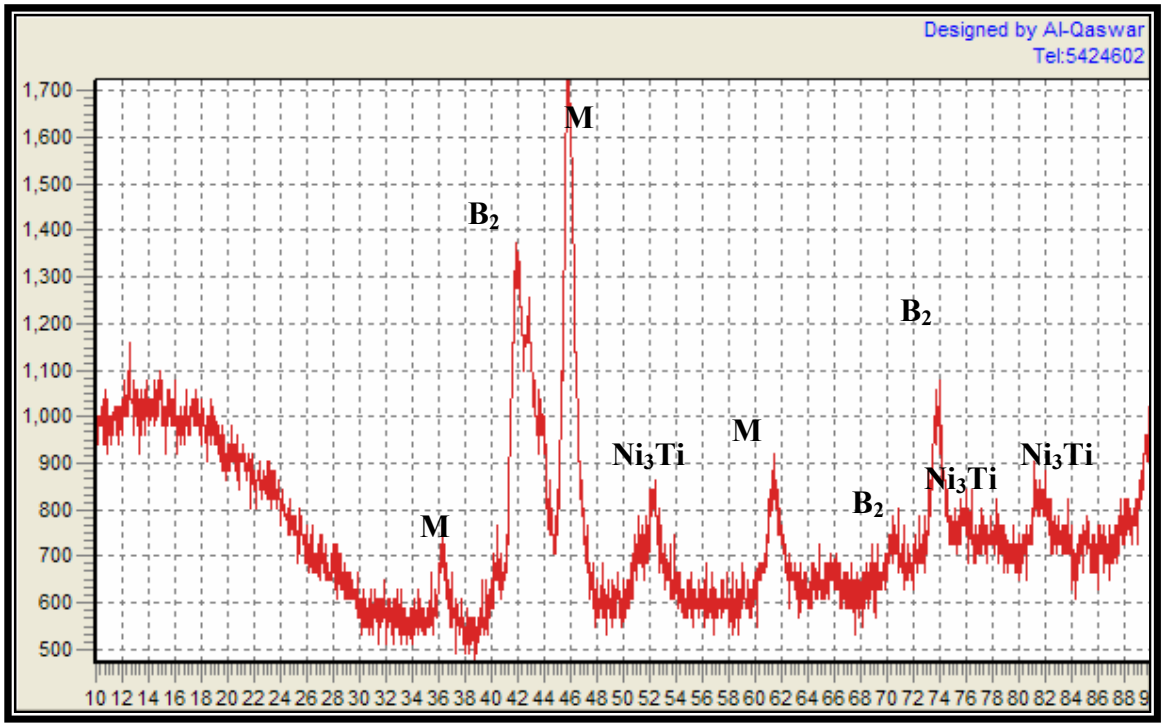

Fig (7): XRD pattern of the master with 0.3% Mg sample pressed at 800MPa and sintered at 950°C for 9 hrs

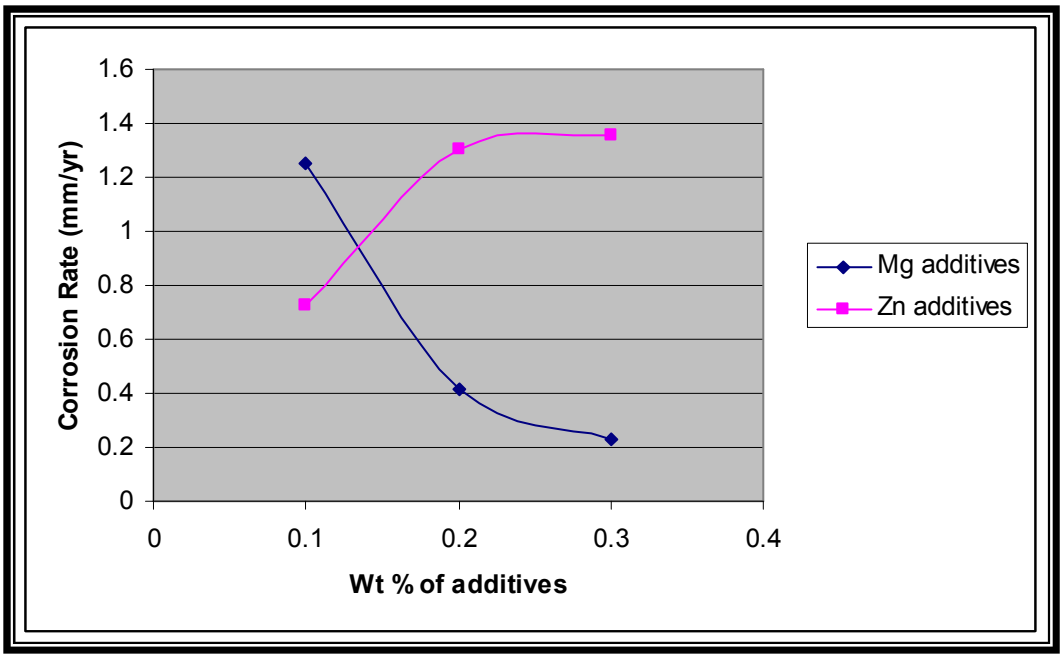

Fig (8): Corrosion rate (mm/yr) for the master with various percentages Of Mg & Zn pressed at 800MPa and sintered at 950°C for 9 hrs.

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