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NICKEL MANGANESE FERRITE FOR THERMOCHEMICAL WATER-SPLITTING AND HYDROGEN PRODUCTION

by

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ABSTRACT:

Nickel- manganese ferrite ," $NiMnFe_4O_6$ " for thermochemical water splitting and hydrogen production has been prepared. Starting with the stoichiometric ratios of the oxides of Fe, Mn,and Ni," $NiMnFe_4O_6$ " was prepared through solid state reaction at 1200°C to form the spinel structure as detected by XRD. 8mol.% Yttria Stabilized Zirconia (YSZ), and Ceria – 20mol.% Gadolina were used as supporting materials. The effect of the sintering temperature on the properties of the produced ferrite mixed with the supporting materials was studied. It was found that the open porous material cannot be produced with a sintering temperature ≥ 900°C. The weight loss of the different porous materials and their powders were studied using thermogravimetry in air.

Keywords: Hydrogen production; Nuclear hydrogen; Thermochemical; Nickel Manganese Ferrite.

1. Introduction:

Efficient and environmentally friendly methods for producing hydrogen are important as the world explores the use of hydrogen as a clean energy source. The thermochemical cycles at high temperatures from nuclear power plants or concentrated solar energy are very promising methods for hydrogen production.

Water is the ideal source of hydrogen because of its abundance, low cost and the absence of CO_2 emission. Thermochemical water-splitting consists of the conversion of water into hydrogen and oxygen by a series of endothermic and exothermic chemical reactions. The net reaction is equivalent to :

$H_2O \rightarrow H_2 + {}^1/_2\, O_2$, with $\Delta H = 286$ KJ/mol[1,2].

The advantage of using a thermochemical reaction to produce hydrogen over the classical alkaline water electrolysis, is the low efficiency of the later which is around 20% (total of 30% for electricity * 65% for water electrolysis). Theoretically, the efficiency to produce hydrogen through thermochemical reaction, when in high temperature reactors, could be as high as 50%, because it is Carnot cycle-limited, which means that high temperature improves the conversion efficiency.

After the first cycle of water-splitting (Vanadium-Chlorine) was proposed in 1964, more than 2000 potential thermochemical cycles have been tested and checked in terms of appropriate reaction temperature, reaction velocity and economic aspects. Major problems arise from the large material flows, introduction of impurities, and by the potential creation of toxic and environmentally unacceptable species[3-5]. The final preference of these thermochemical cycles gave about 25 cycle. Table 1 gives some of them.

The aim of this work is to study the preparation conditions of the Nickel Manganese Ferrite for the thermochemical water-splitting and hydrogen production applications.

Table (1) : Chemical cycles for Hydrogen production

Cycle name	Temp., (°C)	Reaction
Sulfur –Iodine cycle[6],	850 120 450	$H_2SO_4 \rightarrow SO_2 + H_2O + 1/2\ O_2$ $I_2 + SO_2 + 2H_2O \rightarrow 2HI + H_2SO_4$ $2HI \rightarrow I_2 + H_2$
Julich Center EOS[7]	800 700 200	$2Fe_3O_4 + 6FeSO_4 \rightarrow 6Fe_2O_3 + 6SO_2 + O_2\ (g)$ $3FeO + H_2O \rightarrow Fe_3O_4 + H_2\ (g)$ $Fe_2O_3 + SO_2 \rightarrow FeO + FeSO_4$
AachenUniv. Julich[7],1972	850 170 800	$2Cl_2\ (g) + 2H_2O\ (g) \rightarrow 4HCl\ (g) + O_2\ (g)$ $2CrCl_2 + 2HCl \rightarrow 2CrCl_3 + H_2\ (g)$ $2CrCl_3 \rightarrow 2CrCl_2 + Cl_2\ (g)$
Gas de France[7]	725 825 125	$2K + 2KOH \rightarrow 2K_2O + H_2\ (g)$ $2K_2O \rightarrow 2K + K_2O_2$ $2K_2O_2 + 2H_2O \rightarrow 4KOH + O_2\ (g)$
Tokyo Inst. Tech.Ferrite[8]	1000 600	$2MnFe_2O_4 + 3Na_2CO_3 + H_2O \rightarrow 2Na_3MnFe_2O_6 + 3CO_2(g) + H_2(g)$ $4Na_3MnFe_2O_6 + 6CO_2\ (g) \rightarrow 4MnFe_2O_4 + 6\ Na_2CO_3 + O_2\ (g)$
Nickel Ferrite[9]	800 800	$NiMnFe_4O_6 + 2H_2O \rightarrow NiMnFe_4O_8 + 2H_2\ (g)$ $NiMnFe_4O_8 \rightarrow NiMnFe_4O_6 + O_2\ (g)$

LASL – U[7]	25 250 700	$3CO_2 + U_3O_8 + H_2O \rightarrow 3UO_2CO_3 + H_2$ (g) $3UO_2CO_3 \rightarrow 3CO_2$ (g) $+ 3UO_3$ $6\ UO_3$ (s) $\rightarrow 2\ U_3O_8$ (s) $+ O_2$ (g)
UT – 3 Univ. of Tokyo[10]	600 600 750 300	$2Br_2$ (g) $+ 2CaO \rightarrow 2CaBr_2 + O_2$ (g) $3FeBr_2 + 4H_2O \rightarrow Fe_3O_4 + 6HBr + H_2$ (g) $CaBr_2 + H_2O \rightarrow CaO + 2HBr$ $Fe_3O_4 + 8HBr \rightarrow Br_2 + 3FeBr_2 + 4H_2O$
US – Chlorine[7]	850 200 500	$2Cl_2$ (g) $+ 2H_2O$ (g) $\rightarrow 4HCl$ (g) $+ O_2$ (g) $2CuCl + 2HCl \rightarrow 2CuCl_2 + H_2$ (g) $2CuCl_2 \rightarrow 2CuCl + Cl_2$ (g)
Ispra Mark 9[11]	420 150 650	$2FeCl_3 \rightarrow Cl_2$ (g) $+ 2FeCl_2$ $3Cl_2$ (g) $+ 2Fe_3O_4 + 12HCl \rightarrow 6FeCl_3 + 6H_2O + O_2$ (g) $3FeCl_2 + 4H_2O \rightarrow Fe_3O_4 + 6HCl + H_2$ (g)
Ispra Mark 2[11] (1972)	100 487 800	$Na_2O.MnO_2 + H_2O \rightarrow 2NaOH$ (a) $+ MnO_2$ $4MnO_2$ (s) $\rightarrow 2Mn_2O_3$ (s) $+O_2$ (g) $Mn_2O_3 + 4NaOH \rightarrow 2Na_2O.MnO_2 + H_2O + H_2$ (g)
Ispra Mark 3[21]	850 170 200	$2Cl_2$ (g) $+ 2H_2O$ (g) $\rightarrow 4HCl$ (g) $+ O_2$ (g) $2VOCl_2 + 2HCl \rightarrow 2VOCl_3 + H_2$ (g) $2VOCl_3 \rightarrow Cl_2$ (g) $+ 2VOCl_2$
Ispra Mark 6[11]	850 170 700 420	$2Cl_2$ (g) $+ 2H_2O$ (g) $\rightarrow 4HCl$ (g) $+ O_2$ (g) $2CrCl_2 + 2HCl \rightarrow 2CrCl_3 + H_2$ (g) $2CrCl_3 + 2FeCl_2 \rightarrow 2CrCl_2 + 2FeCl_3$ $2FeCl_3 \rightarrow Cl_2$ (g) $+ 2FeCl_2$
Ispra Mark 8[11]	700 900 100	$3MnCl_2 + 4H_2O \rightarrow Mn_3O_4 + 6HCl + H_2$ (g) $3MnO_2 \rightarrow Mn_3O_4 + O_2$ (g) $4HCl + Mn_3O_4 \rightarrow 2\ MnCl_2$ (a) $+ MnO_2 + 2H_2O$
Ispra Mark 1C[11]	100 900 730 100	$2CuBr_2 + Ca(OH)_2 \rightarrow 2CuO + 2CaBr_2 + H_2O$ $4CuO$ (s) $\rightarrow 2Cu_2O$ (s) $+ O_2$ (g) $CaBr_2 + 2H_2O \rightarrow Ca(OH)_2 + 2HBr$ $Cu_2O + 4HBr \rightarrow 2CuBr_2 + H_2O + H_2$ (g)
Ispra Mark[11], CO/Mn_3O_4	977 700 700	$6Mn_2O_3 \rightarrow 4\ Mn_3O_4 + O_2$ (g) C (s) $+ H_2O$ (g) $\rightarrow CO$ (g) $+ H_2$ (g) CO (g) $+ 2\ Mn_3O_4 \rightarrow C + 3\ Mn_2O_3$

2. Experimental work:

Stoichiometric amounts of pure oxides (99.9purity of commercially available powders) of Fe_2O_3, NiO and MnO were mixed to prepare the spinel $NiMnFe_4O_6$ by the conventional solid state reaction technique.

The mixed oxides were calcined at 1000°C/24h in air. The calcined powders were ground and then pressed using a uniaxial press (Hydraulic press – Perkin Elmer) to form pellets of 1cm diameter. The pressed pellets were then sintered at 1200°C/2h. The phases in the sintered material were analyzed using X-ray diffraction [(XRD) - 3A Shimadzu – Japan].

The sintered material was then ground and divided into two parts. Two different additives were used to act as supporters for the ferrite. The first was 8 mol% Y_2O_3 zirconia and the second was Ceria -20mol.% gadolinia, to explore the effect of supporting porous material. The mole ratios of the Zirconia support were 2 and 4 to 1 mole of the spinel ferrite, and 4 mole Ceria – gadolinia also to 1mole of the spinel ferrite. 8 wt% of starch was added as a binder for all samples. Pellets were prepared from the three mixed materials – spinel / support – powder by pressing and then sintering at different temperatures ranging from 850 ^{o}C to 1200 ^{o}C. Thermogravimetric measurements were performed using a TG analyzer (Shimadzu, TG – 50A). The microstructures of the different samples was examined by the Scanning Electron Microscope (SEM), [JEOL].

3. Results and Discussion:

The solid state reaction between the three oxides Fe_2O_3, NiO and MnO took place during sintering at 1200 ^{o}C / 2h. The product had the spinel structure of $\mathbf{NiMnFe_4O_8}$ as shown in the XRD pattern, Fig 1.

Y.Tamaura et al.[12] investigated the thermal activation of the spinel-type $\mathbf{NiMnFe_4O_8}$ and the subsequent water-splitting reaction which are given by:

$$\mathbf{NiMnFe_4O_8 \rightarrow (activation\ at > 800°C) \rightarrow NiMnFe_4O_{8-x} + x/_2O2\ .}$$

$$\mathbf{NiMnFe_4O_{8-x} + xH_2O \rightarrow (water\text{-}splitting\ at < 800°C) \rightarrow NiMnFe_4O_8 + xH_2}$$

In the first endothermic step, $NiMnFe_4O_8$ is thermally activated above 800°C to form an oxygen deficient ferrite. An important factor is the dissociation of the material to release oxygen. So that, when used in the second stage it will absorb oxygen from steam and release the hydrogen. Thermogravimetric analyses were performed on sintered materials composed of the spinel $\mathbf{NiMnFe_4O_8}$ and the different additive

supporting materials to study their effect as well as the effect of sintering temperature on the weight loss of the material.

The thermo gravimetric analysis of Y. Tamaura and M. Tabata[13] on the ferrite samples showed 0.3% weight loss during the activation step in the temperature range 700°C to 1100°C, with a max. rate for oxygen evolution at temperature 820°C to 827°C.

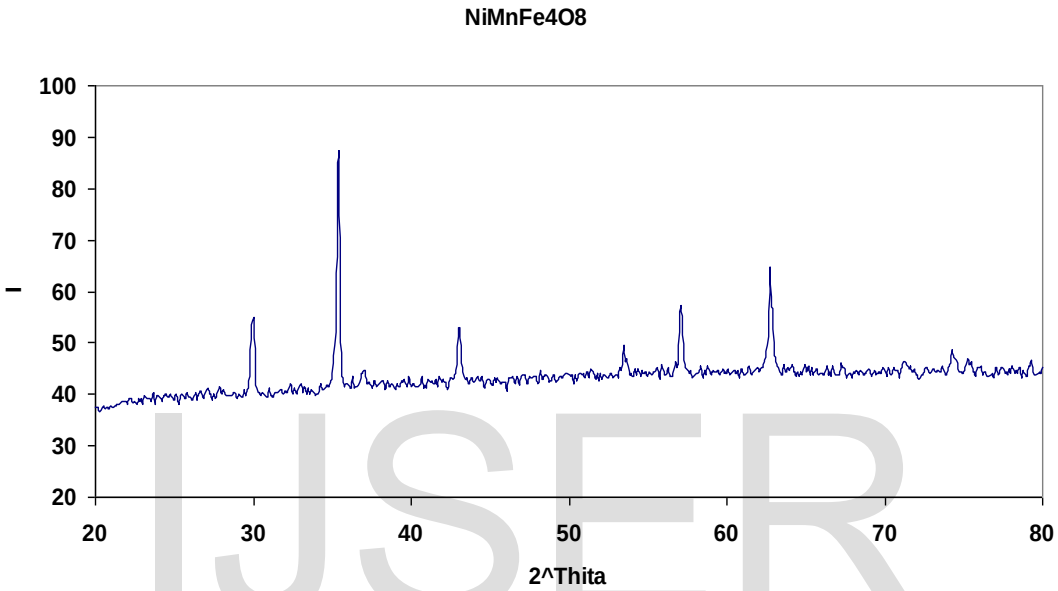


Fig. (1): XRD pattern of the ferrite $NiMnFe_4O_8$ sample.

T.Kodama and N.Gokon[2], in their Nickel Manganese Ferrite system proposed a two step water-splitting reaction at 800°C, and reported that this cycle requires more moderate reaction temperature than those of the normal ferrite processes. However the amount of hydrogen evolved in this system is very limited because water-splitting was caused by the small magnitude of the nonstoichiometry in the spinel type ferrite as compared to that accompanying the Fe_3O_4 / FeO phase transition in the normal ferrite processes.

Fig. (2) shows the Thermogravimetry (T.G.) of the sample $NiMnFe_4O_8$ + 4mole 8-YSZ, sintered at 850°C, while fig. (3)shows the TG of the same sample measured at a lower heating rate. The weight loss started at about 730°C, and continued during the holding time at 820°C. During the cooling of the sample, the weight increased but did not return to its value at the beginning of heating. This may be attributed to the effect of mixing Zirconia with $NiMnFe_4O_8$. Fig. (4)shows the weight loss of $NiMnFe_4O_8$+

4mole Ceria gadolinia sample sintered at 850°C. The weight loss of the sample started at about 650°C, and continued during the holding time at 820°C. During the cooling the sample weight increased, but also did not return to the original weight at the beginning heating.

The samples sintered at 850°C were very brittle most probably because this temperature was not enough to complete the sintering process. However when going to higher temperatures all the sintered samples showed no weight loss. This may be attributed to closing the pores of the sintered material when it is heated at temperatures above 850°C.

Fig. (5) shows the weight loss of $NiMnFe_4O_8$ + 2mole 8YSZ sample sintered at 900°C. The sample was well sintered, but it gave the result of fig.(5) for the first test only. Upon repeating the test for this sample, the result was zero weight loss, which may be attributed also to closing the pores of the treated material when it was heated in temperature 880°C (the holding temperature during the test).

Fig. (6) represents The SEM of samples of $NiMnFe_4O_8$ + 2mole 8YSZ sintered at different temperatures 850°C, 900°C and 1200°C. It can be seen from the figures that the pores volume decreased with the sintering temperature.

Fig. (7) represents the weight loss of pure $NiMnFe_4O_8$ powder, which started at a temperature about 660°C, and returned to its original value upon cooling at a temperature 550°C, with a maximum holding temperature at 820°C.

Fig. (8) represents the weight loss of Zirconia – 8Y powder, which started at a temperature about 700°C, and returned to its value at a temperature 700°C also, with a maximum holding temperature at 820°C.

The first step for water splitting will be heating the material, Zirconia with $NiMnFe_4O_8$, in a vacuum at 800°C. The Zirconia deficient in the vacuum will play a good effect in taking any oxygen from the Nickel manganese ferrite. The addition of steam will produce hydrogen. If we put a Palladium screen to take the hydrogen spontaneously, then this device can developed to work spontaneously.

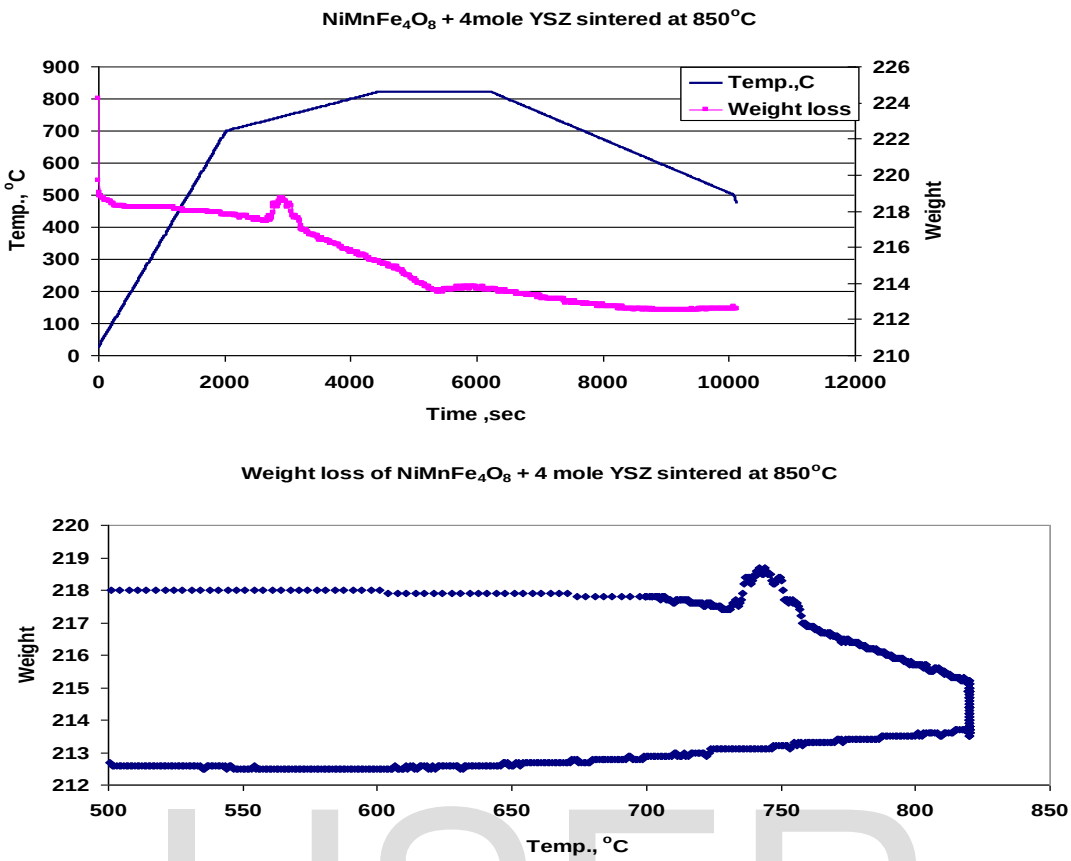


Fig. (2): Thermo-Gravimetery (with heating rate 5°C /min) of $NiMnFe_4O_8$ + 4moleYSZ, sintered at 850°C.

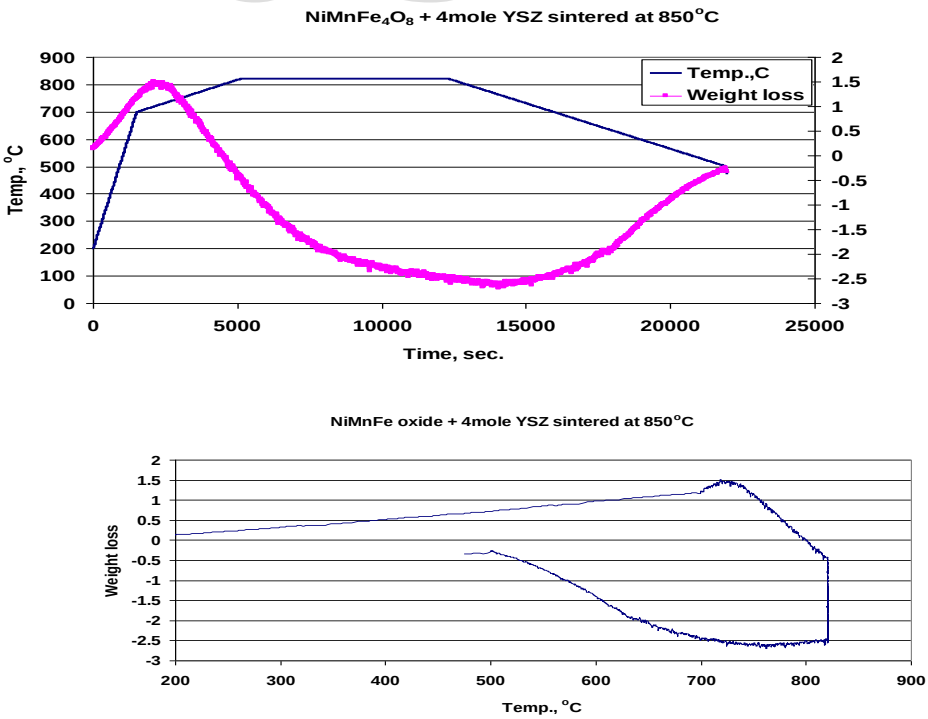
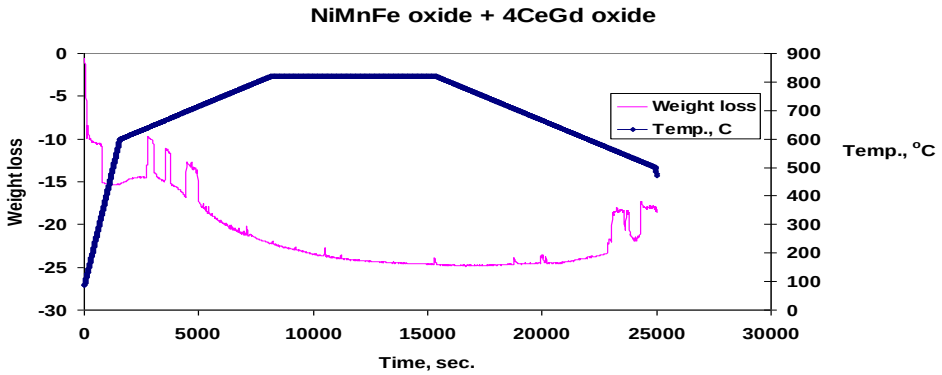


Fig. (3): Thermo-Gravimetry (with heating rate 2°C /min) of $NiMnFe_4O_8$+ 4moleYSZ, sintered at850°C



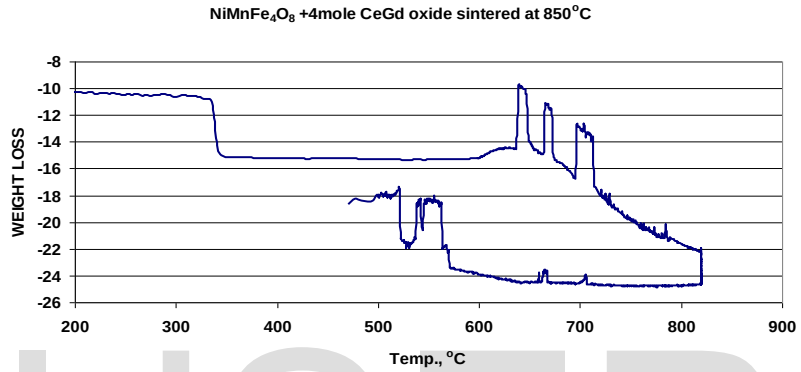
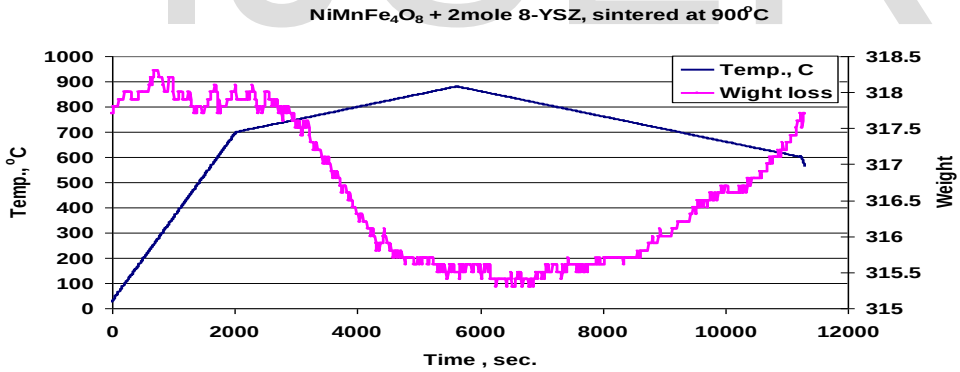


Fig. (4): Thermo-Gravimetry of $NiMnFe_4O_8$+ 4mole Ceria gadolinia, sintered at 850°C.



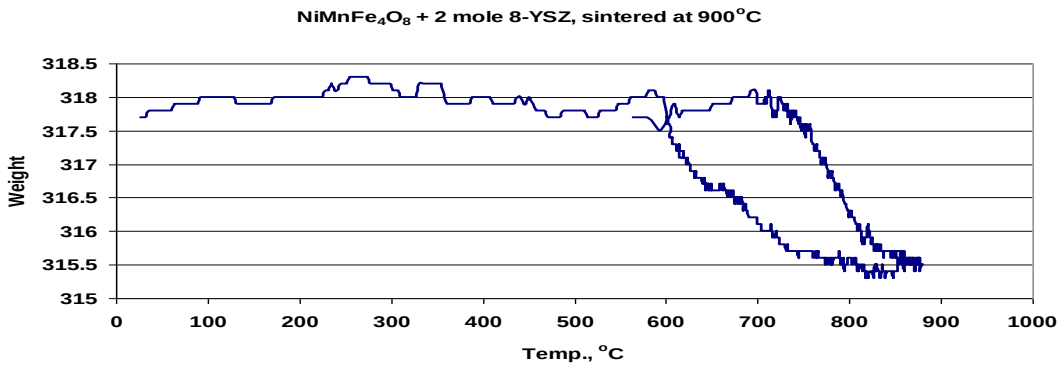
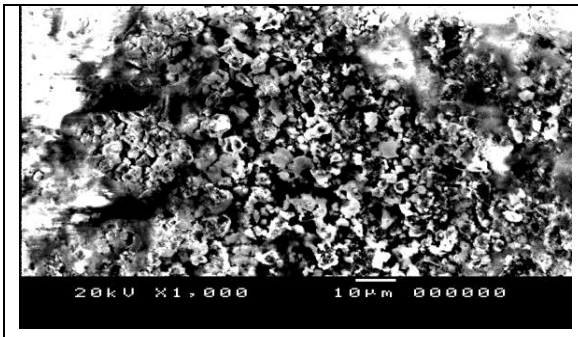
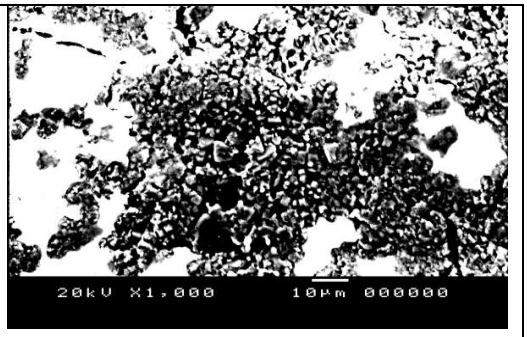


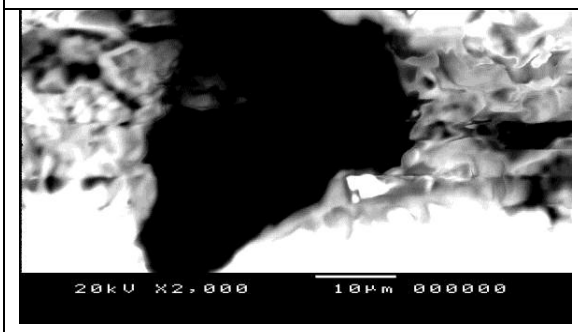
Fig. (5): Thermo-Gravimetry of $NiMnFe_4O_8$+ 2mole YSZ, sintered at 900°C.



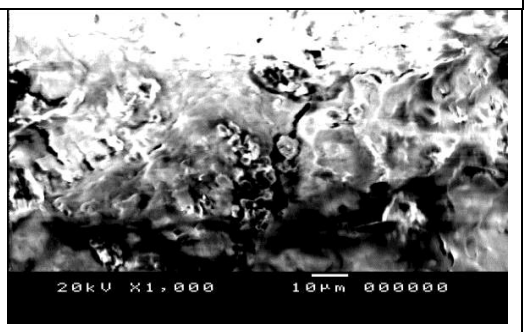
$NiMnFe_4O_8$+ 2mole YSZsintered at 900°C



$NiMnFe_4O_8$+ 2moleYSZsintered at 1200°C

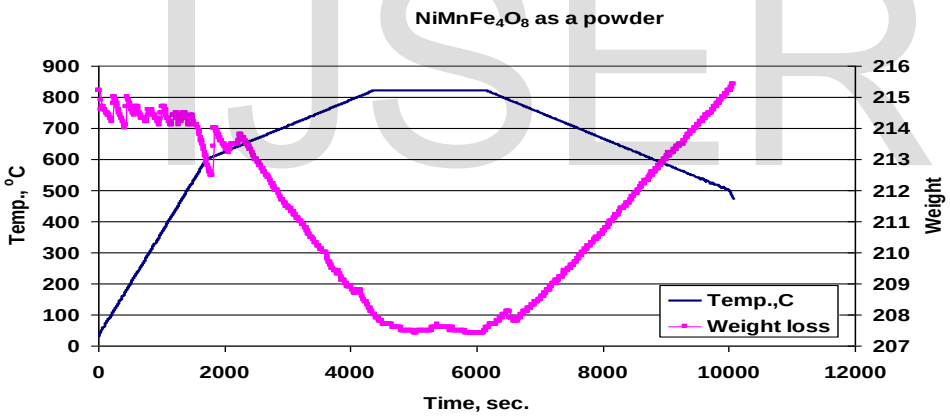


$NiMnFe_4O_8$+ 2moleYSZ sintered at 850°C



$NiMnFe_4O_8$+ 4moleYSZ sintered at 850°C

Fig. (6) : SEM of $NiMnFe_4O_8$ + YSZ samples.



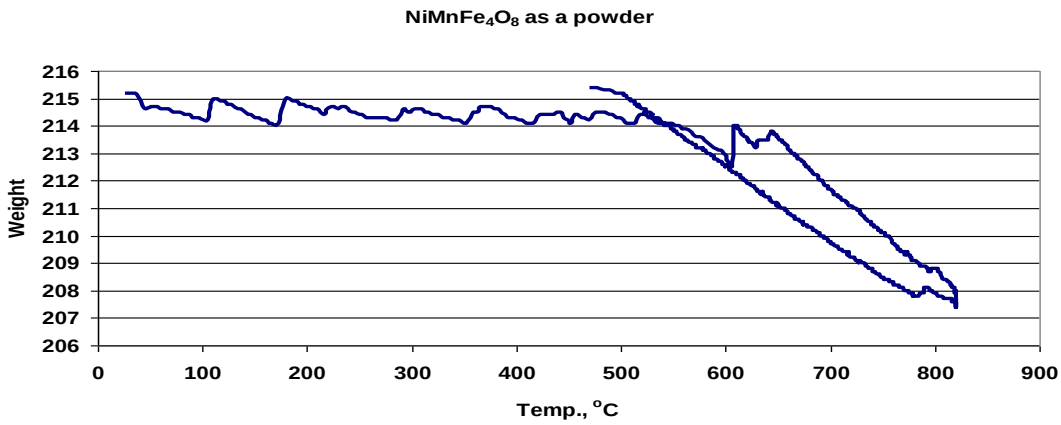


Fig. (7): Thermo-Gravimetry of $NiMnFe_4O_8$ as a powder.

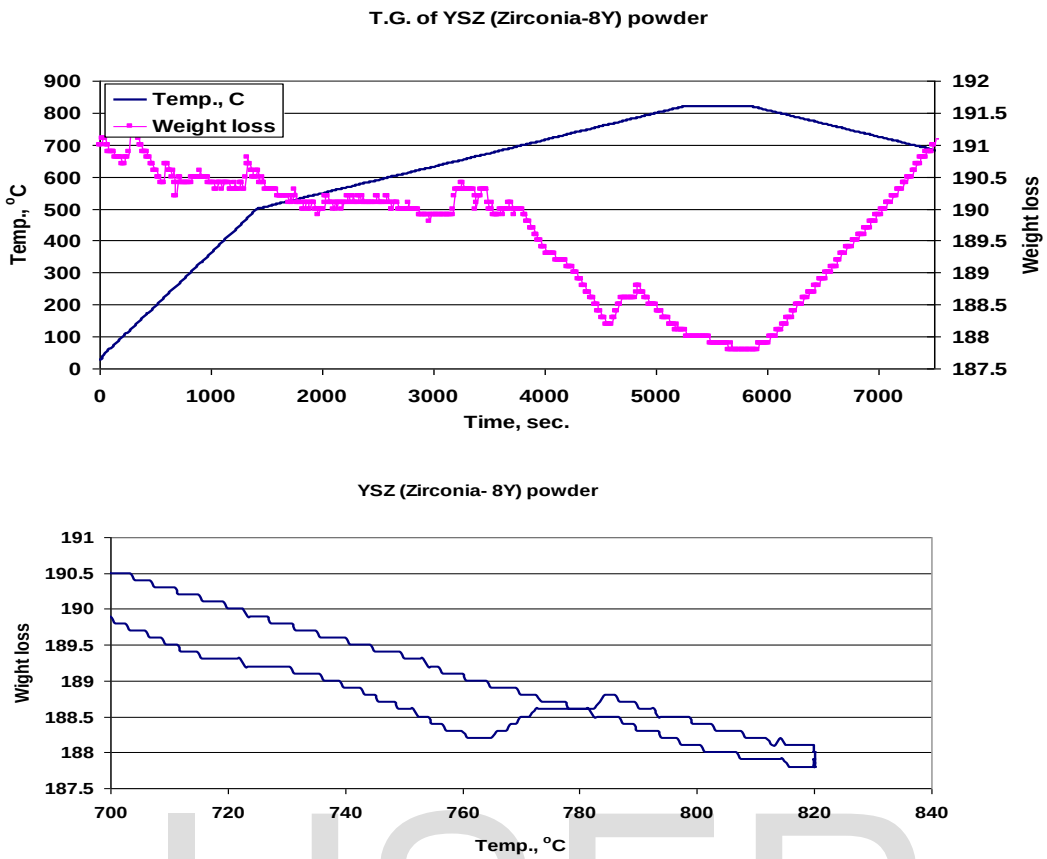


Fig. (8): Thermo-Gravimetry of 8YSZ powder.

4. Conclusions:

The Nickel Manganese Ferrite, "$NiMnFe_4O_8$", is a promising material for hydrogen production as a thermochemical water-splitting. The optimum working temperature of the ferrite lies between 820°C and 830°C as a maximum to avoid closing the pores or the complete sintering of the material. Mixing this material with Yettria Stabilized Zirconia (YSZ) can enhance the removal of oxygen from the Nickel Manganese Ferrite, "$NiMnFe_4O_8$", at high temperature in vacuum.

5. References:

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المقدمة :

النيكل منجانيز الحديدى لفصل الماء وأنتاج الهيدروجين بواسطة الكيمياء الحرارية

درست مادة النيكل منجانيز الحديدى كنظام لفصل الماء فى خطوتين فى درجة حرارة 800 °م. , وقد تم تفاعل الأكاسيد فى حالتها الصلبة بنسبها الكيمائية المتكافئة فى درجة حرارة 1200°م. ليتكون التركيب البلورى الأسبينل الخاص بالنيكل منجانيز الحديدى والتى تم رصدها بأستخدام الأشعة السينية الحيودية, وقد ثبتت هذه المواد مع مادة الزركونيا سيراميك و تم تصنيع عينات مسامية منهم من نوعين من الزركونيا ايتريا والزركونيا سيريا لتجربة تأثير الزركونيا المسامية. وقد تم دراسة الأوزان المفقودة بالتسخين لهذة المواد المسامية ومساحيقها.