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high-temperature synthesis (SHS) at the different preheating temperatures (i.e. 350, 400, 500 and 600 ◦C) andmilling time (0.5, 1 and 2h). The crystal structure of all samples was characterized by X-ray diffraction pattern. The results show that the product sample is NiTi phase along with other secondary intermetallic compounds. The results prove that the dominant phase is NiTi if the powders milled 1 hour milling and preheated 400◦C.

Key word: milling; preheating; NiTi; combustion synthesis,

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PO-250

Effects of Platinum Doping on the Structure and Photoelectrochemical Properties of Sol-gel Spin Coated Fe_2O_3 Thin Films

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In this work, we report the effects of platinum (Pt) doping on structure and photoelectrochemical properties of Fe_2O_3thin films. The platinum doped-Fe_2O_3 thin films were prepared by sol-gel and spin coated on fluorine-tin-oxide coated glass substrate. Influences of dopant concentration on the material properties were examined by X-ray diffraction (XRD), X-ray photoelectron spectra (XPS), field emission scanning electron microscopy (FESEM), and optical spectroscopy. The photoelectrochemical characteristics were investigated at room temperature. It was demonstrated that heat treatment in air atmosphere greatly enhanced the XRD peak intensity and photocurrent density efficiencies.

Results of XRD and XPS showed that α-Fe_2O_3 can be obtained using 500 ^oC annealing in air. The direct band gaps of the samples obtained from reflectance and transmittance spectra measurement were found to vary from 1.98 to 2.03 eV. The flat band potentials of samples were obtained from the Mott-Schottky analysis and found to be in the range of -0.135 V to -0.6 V. The maximum photocurrent density of undoped and 0.1 at.% Pt-doped Fe_2O_3 thin films was 0.5 mA/cm^2 and 0.7 mA/cm^2 (at 0.5 V vs. Ag/AgCl) under a 300 W Xe lamp system, respectively. These good photoelectrochemical results and stability of the Ptdoped Fe_2O_3 thin film warrants further investigation for broader applications in the future.

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PO-251

On the milling and preheating on fabrication of combustion synthesized NiTi

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The main goal of the current research has been concentrated on the fabrication of NiTi alloy using combustion synthesis. The effect of preheating temperature and milling time on the fabrication of porous NiTi has been considered. For this purpose Ni and Ti with 50 at.% Ni powders were milled and cold pressed under 150MPa pressures. The porous NiTi alloy samples were synthesized by self-propagating high-temperature synthesis (SHS) at the different preheating temperatures (i.e. 350, 400, 500 and 600 ◦C) andmilling time (0.5, 1 and 2h). The crystal structure of all samples was characterized by X-ray diffraction pattern. The results show that the product sample is NiTi phase along with other secondary intermetallic compounds. The results prove that the dominant phase is NiTi if the powders milled 1 hour milling and preheated 400◦C.

Key word: milling; preheating; NiTi; combustion synthesis,

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A study on the milling and preheating on fabrication of NiTi produced by combustion synthesis

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Abstract

The main goal of the current research has been concentrated on the fabrication of NiTi alloy using combustion synthesis. The effect of preheating temperature and milling time on the fabrication of porous NiTi has been considered. For this purpose Ni and Ti with 50 at.% Ni powders were milled and cold pressed under 150MPa pressures. The porous NiTi alloy samples were synthesized by self-propagating high-temperature synthesis (SHS) at the different preheating temperatures (i.e. 350, 400, 500 and 600 ˚C) and milling time (0.5, 1 and 2h). The crystal structure of all samples was characterized by X-ray diffraction pattern. The results show that the product sample is NiTi phase along with other secondary

intermetallic compounds. The results prove that the dominant phase is NiTi if the powders milled 1 hour milling and preheated 400°C.

Key word: milling; preheating; NiTi; combustion synthesis

Introduction

NiTi has some unique properties like shape memory effect, superelasticity, excellent corrosion resistance, wear resistance and good biocompatibility. Besides those, porous NiTi alloy has similar mechanical characteristics with natural bone, which makes it like an ideal biological engineering material, especially in the orthopedic surgery and orthodontics. Moreover, the porous structure of the alloys would help tissue cell in growth, nutrition exchange and medicament transportation [1].

Recently combustion synthesis of intermetallics has attracted research interest because of its highenergy efficiency, high productivity, possibility of near net shape forming, keeping the composition very close to the stoichiometry and purity of the alloy high[2].

Two variants of combustion synthesis (CS) are recognized, namely the Self-propagating High temperature Synthesis (SHS) mode and the Thermal Explosion (TE) mode. The SHS mode involves triggering the reaction by rapid heating of one

end of the specimen. The reaction zone propagates as a wave front through the sample, driven by the exothermicity of the reaction. In the TE mode, the compacted reactant powders are heated up to a rapid rate in a furnace until the reaction is initiated uniformly throughout the sample [3].

Porous NiTi have fabricated with combustion synthesis. This process can avoid the problems associated with casting, like segregation or extensive grain growth and have the added advantages of precise control of composition and easy realization of complex part shapes[4]. Unlike the mentioned benefit, the presence of second phases, such as Ti_2Ni and Ni_3Ti or in some cases even elemental Ni is the common feature for porous NiTi produced by SHS. The main reason of being undesirable phases can be attributed to the fact the composition fluctuated in the specimen because of insufficient mixing of powders. Indeed the heat of formation is low because of un-adequate particle size of the reactants and leads to form 0brittle phases like Ti_2Ni and Ni_3Ti instead of NiTi. Moreover, they can lead to the cavitation corrosion and deteriorate the biocompatibility of porous NiTi in the physiological environments [ ]. In the TE mode because of lack of up propagated wave undesirable phases are not appeared due to composition fluctuation. Since the TE mode reaction is usually initiated by heating the reactants in a furnace, its heating rate to the ignition temperature is orders of magnitude lower than that of SHS mode reaction. For a typical TE mode reaction, the rate is in a range of 10 to

500°C/min in comparison with 10^4 to 10^6°C /min for SHS mode reaction. Thus, in the TE mode reaction, the reactions occurring during the heating to the ignition temperature, i.e. precombustion reaction should be more pronounced than in the SHS mode reaction [ ]. Unfortunately, like the thermodynamic stable phases undesired Ti_2Ni and Ni_3Ti phases can be formed during the CS process and it is not possible to remove them by the subsequent heat treatment. Therefore, it is very necessary to decrease the amount of undesired Ti_2Ni and Ni_3Ti phases in porous NiTi by improving the CS technique [ ].

Mechanical alloying cause reactants better mix and create high-energy surface reaction inter-diffusion process; therefore MA can solve the problem of the presence of second phases. Goh *et al.* fabricated the porous NiTi by the addition of nano crystalline Ni-Ti reaction agent in SHS. They could resolve their need to preheating by using 50%nanoparticles. Undesired Ti_2Ni and Ni_3Ti phases were present in final product [ ]. Zhou *et al.* investigated the effect of milling times of Ni/Ti powders on coating by SHS [8].

In spite of importance of role of mechanical milling on combustion synthesis, this subject has not been attention by investigators. Thus the main goal of the current research is to elucidate the influence of mechanical milling on fabrication of porous NiTi by CS (TE mode). Also it will be tried to find out the role of preheating on undesirable phases.

Experimental Procedure:

Ni powders with purity of 99.8% and average particle size of about 5μm and Ti powders with purity of 95%and average particle size of about 150 μm (Merck Company) were used. The powders were mixed mechanically to achieve Ni-50Ti (at %). The mixed powders were cold pressed with a pressure of 150MPa. The green powder discs were placed in the furnace at different 350, 400, 500 and 600°C temperatures.

In order to find out the role of milling time on specification of NiTi produced with CS, some powders were milled at different times (0.5, 1 and 2h) by high-energy planetary ball mill with two different sizes of hardened steel balls (8 mm and 12 mm). The milling process was carried out at room temperature and under argon atmosphere. The ball-to-powder weight ratio and the milling speed were kept 40:1 and 250 rpm respectively. The milled powders were compacted and were placed in the furnace at 400°C temperature. The temperature of powder compact was measured by a thermocouple, placed in the sample during the compaction of the reactant powders, during combustion presses.The phase constituent of the product was characterized by X-ray diffraction (XRD) analysis. The microstructure of the products was evaluated using both SEM and optical microscopes.

Results and discussion

I. Influence of preheating temperature

Fig. 1 shows temperature profiles measured for the samples synthesized at 350, 400, 500 and 600°C temperatures without milling. Sample placed in the furnace at 350°C temperature only reached the furnace temperature (with insufficient 2.4°C/s heating rate) and did not show any reaction and it seems the preheating was not enough for the combustion synthesis of porous NiTi, because of being the relatively low exothermic character of the reaction between titanium and nickel.

In Sample with preheating 400°C temperature, the precombustion reaction temperature, combustion temperature and heating rate are150 ,258°C and 3.2°C/s respectively. Combustion synthesis performed at 400°C preheating temperature implies that both heating rate and combustion temperature are sufficient. Also in other samples combustion synthesis occurred and in all samples as preheating temperature increased, the reaction rate increased. The fast reaction is the favorable outcome because of lack of enough time for fabrication undesired Ti_2Ni and Ni_3Ti phases. More difference between sample temperature and furnace temperature causes the sample heated faster to reach the reaction start temperature. Since the reaction is time dependent and a diffuse process, therefore with an increase the heating rate, the reaction will start at a higher temperature. In fact the reaction start temperature depends on both factors. The characteristics of the temperature profiles

(Fig. 1) are summarized in Table 1. Ignition temperatures of samples 2 to 3 with increasing preheating temperature, has increased. While in sample 4 with increasing preheating temperature, the combustion temperature is reduced. Furthermore, Precombustion temperature for all samples with increasing preheating temperature has increased.

If suppose both Ni and Ti powders are so fine that every particle contains one atom only. When they are ideally mixed, each Ni atom contacts with a Ti atom and vice versa. Hence, every atom will react with its dissimilar atom in its neighboring environment at ignition temperature (at this temperature the atoms have gained sufficient energy to react). The consequence is that the reaction will suddenly take off and no precombustion stage would exist. However, such fine powders are impossible and, besides; powders cannot be mixed so ideally. Actually, a particle of powder has many thousands of atoms. However, if it is supposed that the powders are mixed ideally, i.e. every Ni(Ti) particle contacts with a Ti (Ni) particle and, since every particle contains thousands of atoms, only those which are in the outside layer of those particles contacting dissimilar atoms have the chance to react. At the ignition temperature, these mutually contacting Ni and Ti atoms start to react, forming a thin product (Ni-Ti compound) layer. The atoms in the inner particle then have to diffuse through this layer to continue the reaction. Hence, the reaction rate is controlled by the diffusion rate of Ni(Ti) atoms in the Ni-Ti

compound. On the other hand, the reaction between Ni and Ti releases heat which enhances the diffusivity of Ni(Ti) atoms. This, in turn, results in more reaction releasing more heat which then increases the diffusivity of atoms again. This process starts at precombustion temperature and continues until ignition temperature at which the reaction rate increases dramatically, resulting inthe explosive combustion stage. [9].

In the system of nickel and titanium according to the higher diffusion rate of nickel rather than titanium, initial reaction usually leads to the formation Ni_3Ti and it means that the diffusion barrier layer is Ni_3Ti in Ni-Ti system [10,11]. Beside, the probability of creation of oxide layer on Ti particle is so high because of the presence of oxygen in reaction atmosphere. If the diffusion barrier layer is Ni_3Ti when heating rate is lesser than the critical content, precombustion reaction consumes (one or both) elemental particles before ignition [9]; and if diffusion barrier layer is TiO_2 at low heating rate, thickness of oxide layer increase too fast and impede the diffusion presses.

Fig. 2 shows XRD patterns of the products with different preheating temperature. The spectrum of XRD for sample 1 indicates the peaks Ni_3Ti and TiO_2 along with un-reacted Ni. Perhaps the sequence of phase formation is, at the beginning of the process, the oxide layer formed and the released heat provide the diffusion condition for formation Ni_3Ti. In samples 2, 3 and 4 the height of peaks

belongs to Ni_3Ti phase reduce as preheating temperature increases. Considering the a decrease in precombustion duration with increasing preheating temperature can explain the reduction in the amount of Ni_3Ti in the final product; because its formation depends on diffusion processes and is time dependent. Therefore, an increase in preheating temperature improves the final product properties. However, an excessive increase of the preheating temperature can increase combustion temperature and causes to oxidize the sample. In sample 4 the height peak of TiO_2 is more than sample 3 and also formation of Ti_2O_3 can be observed. When the sample temperature is so high, there is a competition between NiTi formation and oxidation reactions for consumption of titanium. In addition, due to the high tendency of titanium to oxidation, possibility of the formation NiTi is low.

Combustion synthesis of nickel and titanium in low preheating temperatures not fully occurred and Ni_3Ti unwanted phase in the final product is present with large quantities. Indeed, during the ignition, the amount of Ni_3Ti unwanted phase and unreacted materials decreased as preheating temperature increased. However, high temperature activates the titanium oxidation reaction and leads to formation NiTi although still unreacted nickel will be present in the product. Titanium dioxide is brittle as well as Ni_3Ti and the properties of the final product are undesirable. Therefore, only preheating temperature cannot control the phase formation in the combustion synthesis method.

II. Influence of Ball milling

In s series of the samples and efore combustion synthesis the raw powder mixture ball milled. Fig. 3, 4 show the results of profile temperature and XRD patterns of samples. In fact the samples milling at different times (i.e. 0.5, 1 and were placed in furnace with temperatures 400°C. The characteristics of the temperature profiles (Fig. 3) are summarized in Table 2. Reaction rate in milled samples is faster than unmilled samples. In samples without ball milling, reaction time is of about 50s, while for milled sample is about 10s.

Fig. 5 shows structure of powder particles before and after ball milling. As seen the powder particles convert to a laminar structure because of milling and make the path of diffusion shorten. It causes to decreases the needed heat for precombustion as diffusion rate increases.

Combustion temperature of the ball milled samples is higher than that of unmilled samples because of higher elements for main reaction and with increasing milling time, the temperature increases in samples. XRD patterns of samples 5 and 6 show the amounts of unreacted materials are less than that of the unmilled samples. It implies that an increase in combustion temperature because unreacted materials play like diluents.

Sample 5 with precombustion duration shorter than the sample 3 has roughly the same amount of Ni_3Ti because amount of unreacted nickel in the two samples is

not equal. In sample 5 due to higher temperature and diffusion rate in less time than sample 3 larger amounts Ni_3Ti was produced.

In sample 6 the reach temperatures are 1350°C. In comparison with combustion temperature of sample 4 (1366°C) and even sample 3 with the 1010°C combustion temperature amount of titanium oxide is much less because the very short reaction time. Titanium in the raw materials consumed fast, and oxidation has not the opportunity. Ignition duration decreases with increasing milling time due to temperature increase and the liquid phase appearing in the sample.

In sample 7 due to precombustion, the diffusion process and the diffusion rate increase with the ball milling process and a decrease in temperature is reasonable. XRD diagrams for sample 7 show that the oxidation of titanium occurred and nickel as an element in the material remains. Short precombustion duration, ignition duration, and combustion temperature can be attributed to the formation of titanium oxides instead of NiTi. The reason of variation appeared in sample 7 is due to changes in the nature of the initial reaction. In fact ball milling can increase the activate surface of reaction, and ignition temperature for oxidation titanium or even for NiTi can be reduced.

Conclusions

1. Samples without milling process contented undesirable phase. The main reason can be attributed to the low diffusion rate.

2. Comparison between ignition duration sample 2 and 6 implied the effective role of 1h ball milling on it.

3. In sample 6 (1h milling time and 400°C preheating) NiTi phase observed. This is because high diffusion rate leaded to rapid production NiTi before titanium oxidation.

References

[1] Mehmet Kayaa, Nuri Orhana, and Bulent Kurta, "The effect of solution treatment under loading on the microstructure and phase transformation behavior of porous NiTi shape memory alloy fabricated by SHS," *Journal of Alloys and Compounds*, 2008.

[2] S.H. Lee, J.H. Lee, Y.H. Lee, and D.H. shin, "Effect of heating rate on the combustion synthesis of intermetallics," *Materials Science and Engineering A*, vol. 281, pp. 275–285, 2000.

[3] A. Biswas, S.K. Roy, K.R. Gurumurthy, and N. Prabhu, "A study of self-propagating high-temperature synthesis of NiAl in thermal explosion mode," *Acta Materialia*, vol. 50, pp. 757–773, 2002.

[4] Gul Tosun, "A study on microstructure and porosity of NiTi alloy implants produced by SHS," *Journal of Alloys and Compounds*, vol. 487, pp. 605–611, 2009.

[5] B.Y. Taya, C.W. Goh, Y.W.Gu, C.S. Lim, and M.S. Yong, "Porous NiTi fabricated by self-propagating high-temperature synthesis of elemental powders," *journal of materials processing technology*, vol. 202, pp. 359–364, 2008.

[6] C.L. Chu, "Fabrication and properties of porous NiTi shape memory alloys for heavy load-bearing medical applications," *Journal of Materials Processing Technology*, vol. 169, pp. 103–107, 2005.

[7] Y.W.Gu, C.S. Lim,B.Y. Tay C.W. Goh, "Influence of nanocrystalline Ni-Ti reaction agent on self-propagating high-temperature synthesized porous NiTi," *Intermetallics*, vol. 15, pp. 461-467, 2007.

[8] Chang-Jiu Li, Guan-Jun Yang, Guan-Jun Yang, Geng Li Yong Zhou, "Effect of self-propagating high-temperature combustion synthesis on the deposition of NiTi coating by cold spraying using mechanical alloying Ni/Ti powder," *Intermetallics*, vol. 18, pp. 2154-2158, 2010.

[9] J.J. MOORE H.C. YI, "Combustion synthesis of TiNi intermetallic Part III Microstructural characterization," *JOURNAL OF MATERIALS SCIENCE*, vol. 27, pp. 5067-5072, 1992.

[10] z.Xiu, x.Xu j.Laeng, "Phase formation of Ni–Ti via solid state reaction," *PHYSICA SCRIPTA*, vol. T129, pp. 250–254, 2007.

[11] M. Ishio, T. Takasugi H. Inoue, "Texture of TiNi shape memory alloy sheets produced by roll-bonding and solid phase reaction from elementary

metals," *Acta Materialia*, vol. 51, pp. 6373–6383, 2003.