# Laser induced self-propagating high-temperature synthesis of TiNi alloy

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TiNi alloy, especially porous TiNi, a good biocompatible material, can be made by laser induced self-propagating high-temperature synthesis (SHS). A 40-W $CO_2$ laser was used to ignite the powders of Ti and Ni, and TiNi intermetallic compound was synthesized by SHS in a reaction kettle of stainless steel. High-speed photography, X-ray diffraction, and scanning electron microscopy were used to investigate and analyze the reaction process, phase composing, and microstructure of the product, respectively. The influence factors on the reaction process and the product were discussed. The results indicate that laser induced SHS is an efficient, energy-saving method; The phase ingredient of the product consists of TiNi, $Ti_2Ni$, and $Ni_3Ti$. With the increase of the preparing pressure of the sample, the reacting rate decreases; With the increase of the laser power and the preheating temperature, the reacting rate increases. Under the condition of 30°C/min, the synthesis reaction had been carried out consistently and completely.

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TiNi alloy, a very good shape memory alloy, has been applied in many fields since 1960. Besides its super elasticity and shape memory, porous TiNi alloy also has other good properties such as lower density, porosity, sound permeance, etc.[1].

Self-propagating high-temperature synthesis (SHS) namely combustion synthesis, is an advanced method for material producing, which mainly utilizes the latent energy emitted by the reactant to synthesize materials and has the advantages of fast reacting, lower energy consuming, controllable ingredients, and purer products[2,3]. Laser induced ignition has drawn attention due to its high energy density, fast heating speed, adjustable power, and no pollution. Nie *et al.*[4] successfully composed intermetallics Ni-Al system by the method of laser inducing and reaction controlling, and produced cladding layers on steel matrix. Using high power $CO_2$ laser, Xu *et al.*[5] fabricated intermetallics of NiAl reinforced by (W,Ti)C particle, and investigated the mechanisms of forming structure, control, and reinforcing and the change of ingredients. Guo *et al.*[3] studied the densification mechanism of Ni-Al-Cu powder materials. Wang *et al.*[6] designed the technique of fabricating Zr-Al-Ni-Cu amorphous alloy, and found that when laser ignition power increases, the proportion of amorphous phase is higher and the hardness of the product is lower. We synthesized porous Mg-Ni hydrogen storage alloy by laser induced SHS with argon as shielding gas[7]. And by laser cladding technology with coaxial powder feeder, cladding layers with TiC, WC were synthesized[8] on Al alloy matrix. In this paper, laser was used as ignition source to induce SHS of TiNi alloy.

Ti and Ni powders were used in the experiment, the parameters are listed in Table 1. The atomic proportion of Ti and Ni adopted in the experiment is 1:1, hence the weight proportion is 47.88 : 58.69. After separably weighted with a scale according to the proportion, powders Ti and Ni were evenly mixed, and then compacted into a cylinder samples at different pressures. The size of the sample is 15 mm in diameter, 4 − 6 mm in height.

The reaction was carried on in the kettle as shown in Fig. 1, with argon as shielding gas. The sample was preheated by an electric heater placed in the kettle, and the preheating temperature was measured by a thermometer ($T_{\max} = 500°C$) which was above the sample 10 mm, thus the measured temperature is a little lower than the actual preheating temperature. The 40-W $CO_2$ laser was used to ignite. High-speed photography (FASTCAM Super 10 K/10 KC, 250 frames/s), whose lens was placed

**Table 1. Parameters of Ti and Ni Powders**

| Powder | Purity (%) | Particle Size (mo) | Particle Size ($\mu$m) | Main Impurities |
|---|---|---|---|---|
| Ti | $- \geq 99$ | 200 − 300 | 76 − 53 | Te, Si, O |
| Ni | $\geq 99.5$ | 200 | 76 | Te, Si, H, O |

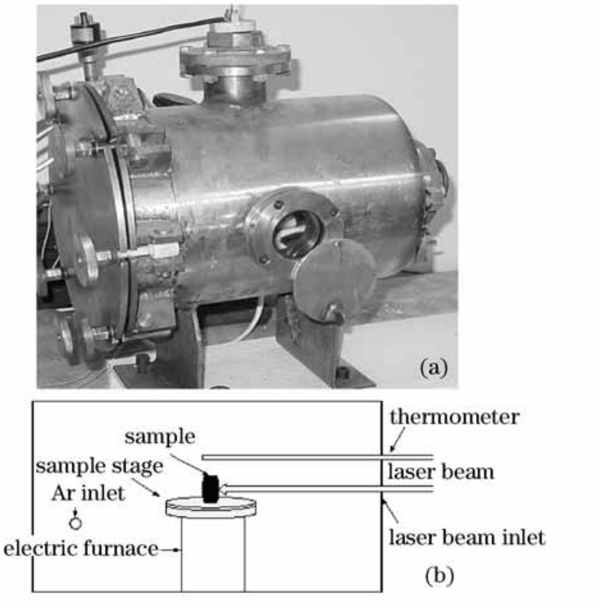

Fig. 1. (a): The reaction kettle photograph; (b): schematic diagram of the kettle.

in the position vertical to the laser beam, was used to take pictures through a look-in window during the reaction. After reaction, an X-ray diffractometer (XRD) was applied for phase identification of the product and a scanning electronic microscope (SEM) for microstructure investigation.

Photographs taken by high-speed photography during the reaction were stored in JPG format and automatically played with ACDSee, the interval between two pictures being 5 ms. The changed pictures which could be observed clearly were written down in order to distinguish the stages of the reaction.

By this method, the whole reaction can be described as the following. It needed 8 minutes to preheat the sample to 240°C, during which no changes could be seen. When the laser beam irradiated the sample, a dark red spot appeared at once on the surface of the sample. The red spot expanded until to 481.62 s, then part of the irradiated area was ignited, red flame appearing. Before this flame, the spot had been in dark, so this stage can be defined as preheating period. Until to 482.10 s, blazing flame appeared in the irradiated area, emitting dazzling light, which indicated that the reaction had fully carried on, and the neighborhood of the light spot became bright, propagating outside constantly. Then turned off the laser, and the reaction was going on. When it was 482.56 s, the whole sample was in burning, emitting dazzling light. After that, the burning phenomenon became weak, and the reaction was over.

The time of the whole reaction underwent 0.46 s (482.56 − 482.10 = 0.46 s), so the velocity of self-propagating reaction was calculated as: $v = 9$ mm/0.46 s=19.6 mm/s, where 0.46 s was the reaction time and 9 mm was the distance between the ignition point and the farthest end.

In Fig. 2, XRD result shows that there are $Ti_2Ni$, TiNi, and $Ni_3Ti$ phases in the product, and there are no diffraction peaks of pure Ti and Ni, which indicates that the reaction between Ti and Ni is complete.

From the SEM photographs, there are pores (see Fig. 3) and holes (see Fig. 4) in the TiNi product, which is the unique phenomenon of SHS. The interconnection among the pores is very good and forms the closed holes.

Three factors contribute to the formation of the holes. 1) Amount of heat emitted by self-propagating reaction can instantly evaporate the impurities in the raw powders and make the gas absorbed in the powders out. 2) The mutual diffuse speed of Ti atom and Ni atom are very different under high temperature. The diffuse speed of Ni atom in Ti is 4000 times higher than that of Ti atom in Ni when they are in the temperature of 900°C[9].

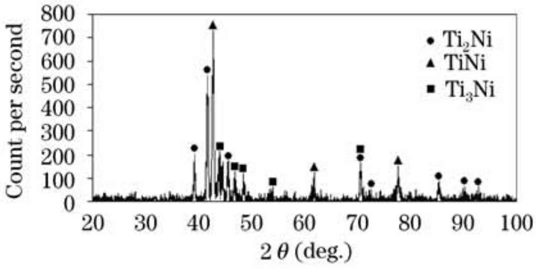

Fig. 2. X-ray diffraction pattern of the product.

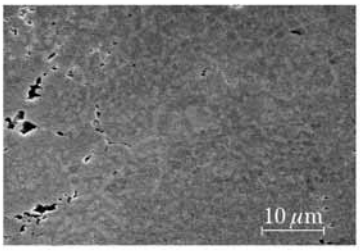

Fig. 3. SEM photograph near holes of the product.

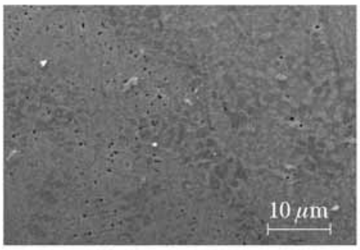

Fig. 4. SEM photograph near holes of the product.

In addition, under such high temperature, atoms move nearly along only one direction, making the place previously occupied by Ni atom become pores quickly. Meanwhile the compound of Ti and Ni was formed, causing the volume expanding and the holes increasing. 3) Original pores in compact sample are also the source of the holes in the product. Parts of pores are air holes, which come from a) gas elements such as hydrogen and oxygen in the Ti and Ni powders, which would escape from the molten sample, however some gases could not escape in time because of the rapid solidification of the molten body in the lower environment temperature, thus forming the holes; b) pores in the sample itself. The sample was made by pressure and it was not very compact, so there existed micro-holes with air, then formed gas holes later in the reaction; c) impurities with low melting point. A high temperature area could be formed during the reaction due to the high reaction heat, where these impurities would change into gas holes.

Different preparing pressures lead to different roughness of the sample surface. When the other conditions are consistent, the lower the pressure, the smaller the surface roughness of the sample. Then it can absorb more laser energy to make the ignition time shorten; Meanwhile the pressure directly affects the density of the sample, the higher the pressure, the higher the density, as shown in Fig. 5, and the preheating temperature is 200°C. When irradiated by the laser, the sample with higher density easily conduct the heat to the neighborhood, shorting the ignition time. For the sample with lower density, a pit would occurred in the irradiated area and spark spray would be observed during the reaction, which indicated there was melting in the reaction. The lower the pressure, the worse the contact between Ni and Ti powders until induced reaction could not be finished.

Under the same conditions, increasing pressure would bring more $Ti_2Ni$ in the product, which is related to the cooling process of the alloy after the reaction. The higher pressure led to the longer ignition time, and the heat conduction made the temperature distribution in the sample become uniform. With increasing the

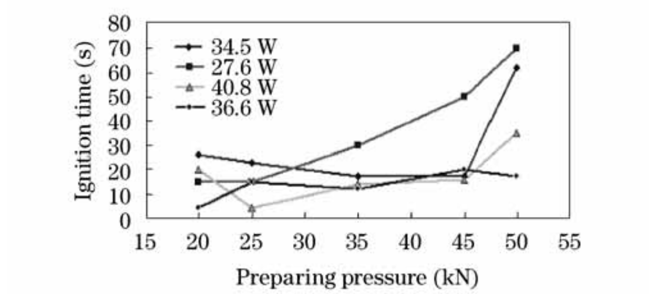

Fig. 5. The profiles of ignition time versus preparing pressure at different laser powers. The preheating temperature is 200° C.

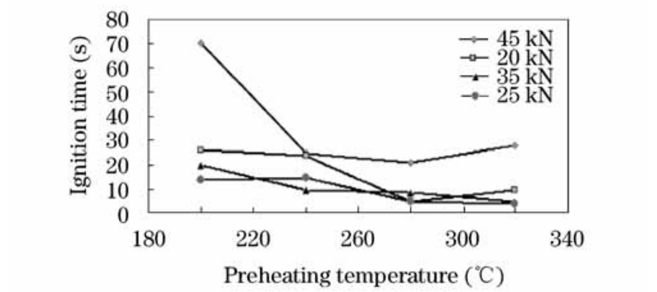

Fig. 6. The relationship between ignition time, and preheating temperature at different preparing pressure. The laser power is 40 W.

environment temperature of the sample, the temperature gradient decreased, which made the cooling speed of the product slowen, therefore it is easier for the formation of segregation and more $Ti_2Ni$ phase.

Part of heat was lost during the reaction because the kettle could not meet the absolutely adiabatic condition. According to the experimental criteria of SHS, external heat energy is needed to complete the TiNi alloy reaction, for the TiNi alloy belongs to weak heat discharged system. When the preheating temperature went up to 200 − 300°C, the laser ignition time became shorter, where the laser power was 27.6 W, as shown in Fig. 6. The melting phenomenon appeared when the preheating temperature was above 300 °C; while the preheating temperature was under 150 °C, although the advancing of the burning wave could be seen, no apparent reaction occurred in the sample.

The preheating temperature is a very important parameter of SHS of TiNi alloy. Mutual diffusing happened between Ti and Ni when their powders were preheated or heated, which led to the formation of $Ti_2Ni$. The higher preheating temperature contributed to more $Ti_2Ni$ phase, and this is because as the preheating temperature rose, and the environment temperature also went up, the temperature gradient decreased, and the cooling speed slowed making easier for the occurrence of element segregation.

When the sample was preheated slowly, namely preheating speed of under 10 °C/min, the heat produced by reaction during the diffusing process would lose into the environment, moreover, the firstly produced TiNi alloy would work as thinner[10], and all of which would go against the SHS, making it impossible to induce the reaction happened, even the laser irradiation time was prolonged.

When the whole sample was preheated rapidly, namely preheating speed of above 100 °C/min, the amount of the lost heat and the TiNi phase were small, thus the heat emitted by the reaction focused on the sample and made the temperature far above the melting point, the whole sample being melted. The SHS could go smoothly when the preheating speed was 30 °C/min or so.

As the increase of the laser power, the ignition time of the sample became shorter. For the samples with the same pressure, the higher the laser power, the shorter the ignition time. When the laser power was very high, the sample could fastly reach the adiabatic temperature, in the same time, the spark could be observed during the reaction, which indicated that melting and gasification occurred in the sample. After finishing the reaction, a pit was formed in the irradiated area and the trace of melting was obvious.

In conclusion, 1) laser induced SHS can synthesize TiNi intermetallic compound at very fast speed, which has been proved by photographs taken by high-speed photography. The reaction process can be shown repeatedly by ACDSee software, combining the dynamic analysis method with static analysis method. The result shows that the theorical analysis agrees with the experimental results. 2) TiNi alloy can be made by laser induced SHS, and the product consists of $Ti_2Ni$, TiNi, and $Ni_3Ti$ phases without pure Ti and Ni elements. A lot of interconnection holes exist in the product. 3) The factors that affect the process of laser induced SHS are pressure, laser ignition power, preheating temperature, and preheating speed. When the pressure is high, the reaction will become slow; when the ignition power and the preheating temperature are high, the reaction will go quickly; the optimum preheating speed is 30°C/min, at which the reaction can go smoothly.

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