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Scalable patterning on shape memory alloy by laser shock assisted direct imprinting

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ABSTRACT

In this study, patterned microindents are generated on the surface of NiTi shape memory alloy by laser shock assisted direct imprinting (LSADI). During LSADI, the plasma pressure generated by the laser pulse punches the mask into the target material and thus generates patterned indents. It has been demonstrated that thermally controllable surface pattern can be generated on NiTi surface through LSADI. Compared to traditional imprinting techniques, LSADI does not require a sharp mold, nor does it involve any heating or etching process. More importantly, it can be used to pattern metals. It is scalable and can be potentially used in treating functional metallic components for advanced applications.

1. Introduction

Thermally-controllable surface patterns of shape memory alloys (SMAs) are of great technological significance for advanced applications in microelectromechanical systems (MEMS) [1–3], nanoscale sensors and actuators [4], etc. Thermally-controllable surface patterns in NiTi shape memory alloys have been investigated in a few studies [5–7]. However, the feature length of the patterns in most of these studies is in the mm range, and the method to generate the patterns is not scalable.

Patterning of metallic components with micro/nanoscale features is very important and has drawn significant attention in the community. Patterning of metals by etching-related technologies suffers from the disadvantages of low reproducibility and high environmental impact. Imprinting technologies, including nanoimprint lithography (NIL)[8–10], step and flash imprint lithography (SFIL) [11,12] and laser assisted nanoimprint lithography (LAN) [13,14] have been widely used to generate micro/nanoscale patterns on polymeric substrates. It has the advantages of good throughput, high resolution and low cost. However, most imprinting methods are only applicable to polymeric materials, not metals. Applying the imprinting methods on metallic components remains a challenge to the community due to the high hardness of the metals.

Patterning of aluminum [15] and gold [16] by direct imprinting was reported. However, the high pressure (500–1000 MPa) involved could damage the underlying substrates or devices. In addition, most of the direct imprinting methods require the fabrication of a sharp mold, which is time-consuming and will increase the cost. There is an urgent need to develop an advanced direct imprinting method that can be used to generate micro/nanoscale patterns on metallic components with low cost, low environmental impact and easy for mass production. In this study, we report an innovative laser shock assisted direct imprinting (LSADI) process to induce microscale surface patterns on NiTi SMAs. It is expected that this technique can potentially be used for mass production of surface patterns in metallic components for various applications.

2. Experimental methods

The 0.3 mm thick 50.26 at.% Ni wrought NiTi strip used in this study was acquired from Special Metals Corporation (WV, USA). The samples were annealed at 500 °C for 10 min to ensure uniform material properties. According to the differential scanning calorimetry (DSC) study (Fig. 1), the transformation temperatures were $M_f = 36\,°C$, $R_s = 54\,°C$, $A_s = 65\,°C$, $A_f = 89\,°C$. Before LSADI, the samples were grounded with 2000 grid sand paper followed by final polishing with 50 nm colloidal silica solution to get a surface roughness of less than 20 nm, as measured by a Ze-Scope optical profiler from Zygo Corporation (Tucson, AZ, USA).

Fig. 2 shows the schematic of the LSADI process. A thin layer of graphite was sprayed on the NiTi surface to prevent the sample from surface melting by the laser pulse. On top of the graphite lays the copper grid used as both ablative material and the punch. A piece of BK7 glass was used to confine the plasma generated by the laser pulse.

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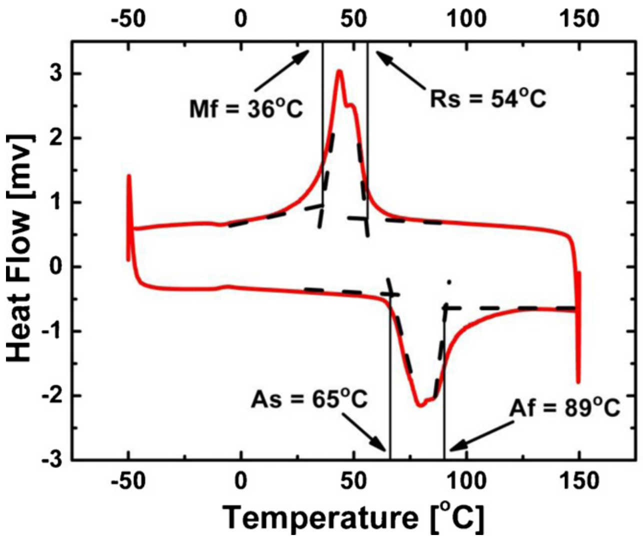

Fig. 1. Transformation temperatures acquired from a DSC scan of the non-processed sample.

The laser beam (pulse duration 5 nanoseconds, wavelength 1064 nm) was delivered by a Q-switched Nd-YAG laser (Surelite III, from Continuum Inc.). The focused laser beam size is 3 mm and the laser energy is 106 mj, corresponding to a laser intensity of 0.3 GW/cm^2. During the LSADI process, a high energy pulsed laser beam penetrates through the BK7 glass and shots onto the copper grid. In a very short instant, the top surface of the copper grid was ionized and plasma was generated. The expansion of the plasma propelled the copper grid into the NiTi samples. Only one laser pulse was used. After peeling of the copper grid and washing away the graphite by acetone, the as-indented structure on the NiTi samples were observed by an FEI Hitachi S-4800 scanning electron microscopy (SEM). To investigate the microstructure evolution, a transmission electron microscopy (TEM) sample was prepared by the lift-out method in the indented region by a Nova-200 focus ion beam (FIB) and examined in an FEI Titan TEM operating at 300 kV.

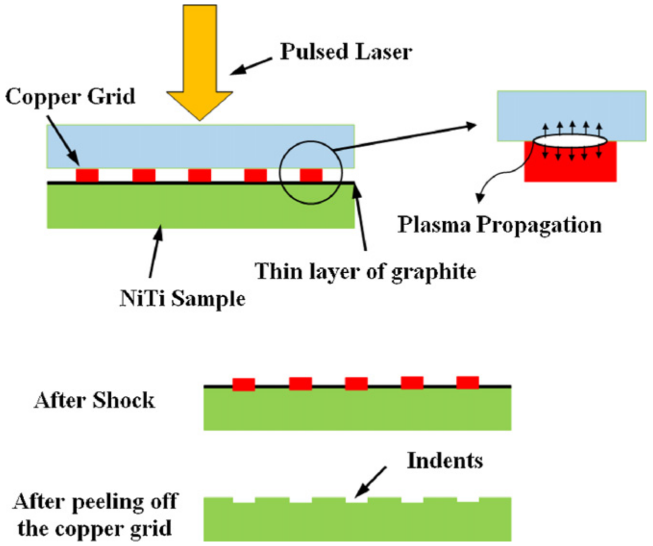

Fig. 2. Schematic representation of the laser shock induced indentation process.

To check the shape memory effect of the indents, the "warm" and "cool" profile of the patterns were recorded by a Ze-Scope optical profiler from Zygo Corporation (Tucson, AZ, USA). The "warm profile" was measured by heating the sample to 110 °C (21 °C higher than the austenite finish temperature to ensure a fully austenite state) by a hot plate placed underneath. After the measurement of the "warm" profile, the sample was chilled by ice water to 0 °C (36 °C below the martensite finish temperature) to ensure a fully martensite state before the measuring of the "cool" profile at room temperature.

3. Results and discussion

Fig. 3a shows an SEM image of the copper grid used as the template for the imprinting processing. Fig. 3b shows the SEM image of the patterned indents created by LSADI. By comparing Fig. 3a and b, it is very clear that the patterns of the grids are inversely copied

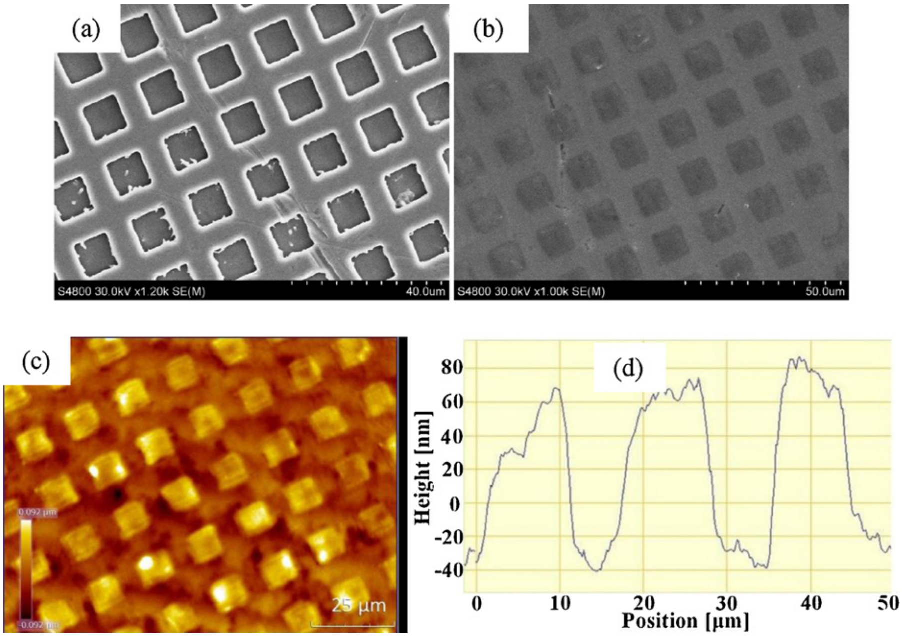

Fig. 3. (a) SEM image of the copper grid used as template (b) SEM images of the indents generated by LSE; (c) optical image of the indents; (d) one-dimensional profile of the indents in c.

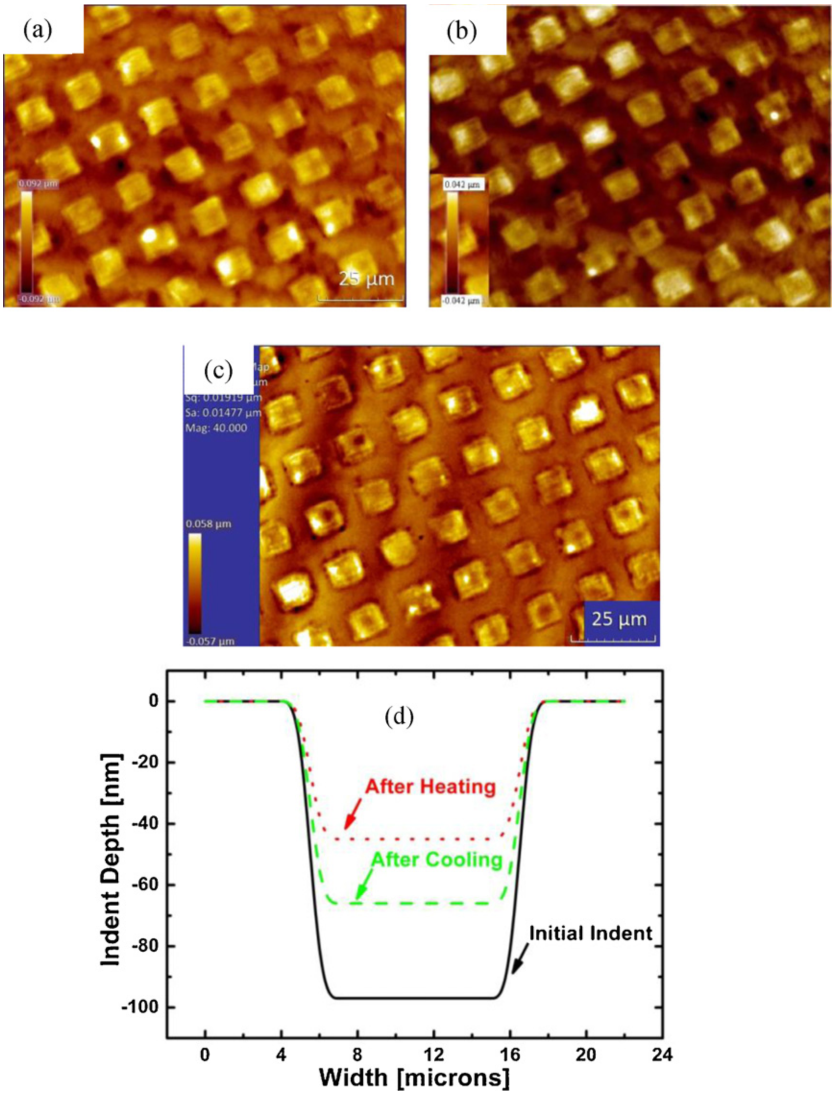

Fig. 4. Optical image of the patterns at different conditions: (a) as-indented, (b) after heating to above Af temperature, (c) after cooling back to room temperature (d) average indent profiles at different condition: black line, the initial indent profile; red line, the indent profile after heating to austenite; green line, the indent profile after heating and cooling to martensite. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

to the surface of the NiTi substrate with high fidelity. Fig. 3c is an optical profile image of the patterned indents. Fig. 3d shows the one-dimensional profile of the indents.

During the LSADI process, a high energy pulsed laser beam penetrates through the transparent confinement media and shots onto the surface of the copper grid. Instantly, high temperature plasma is generated. The expansion of the plasma creates a shock pressure [17], which pushes the copper grid into the samples. The highly dynamic punching force of the copper grid generates plastic deformation in the NiTi substrate and thus generates patterns on the substrate.

Compared to traditional nanoimprint lithography processes, the LSADI process does not involve any heating or etching process. Any patterns of the template can be inversely copied onto the metallic substrate surface with high fidelity if appropriate processing conditions are used. In the LSADI method reported in this study, the patterning process is highly scalable and the feature size can be precisely controlled by manipulating the geometry of the template, in this study the copper grid. Unlike most forming processes, the target substrate does not need to be thin. Bulk samples can also be treated. This characteristic makes LSADI very appealing for patterning functional devices for advanced applications.

For most traditional direct imprinting technologies, a high pressure is typically required to generate plastic deformation in metals for effective imprinting [16]. This can damage the underlying substrates and devices. In the LSADI method reported in this study, the shock pressure generated by the laser pulse is high enough to generate plastic deformation in the target components. At the same time, the shock wave magnitude decreases quickly as it propagates into the materials and the shock pressure duration is very short (around 100 nanoseconds), so that it does not damage the underlying devices.

In the literature, patterned surface indentation on SMAs has been generated by nano-indentation [18,19] laser shock peening [7], and static loading [20]. Shape memory effect is an important characteristic of NiTi alloys. Two-way shape memory effect (TWSME) refers to the ability of SMAs to remember two reversible shapes during heating and cooling [21]. Traditionally, TWSME has been obtained after thermomechanical "training". Recently, it has been reported that TWSME can also be obtained through a single isothermal indentation process without thermal training cycles [5,22].

It is thus of interest to study shape memory characteristics the patterns generated by LSADI. Thus, the "warm" and "cold" profiles

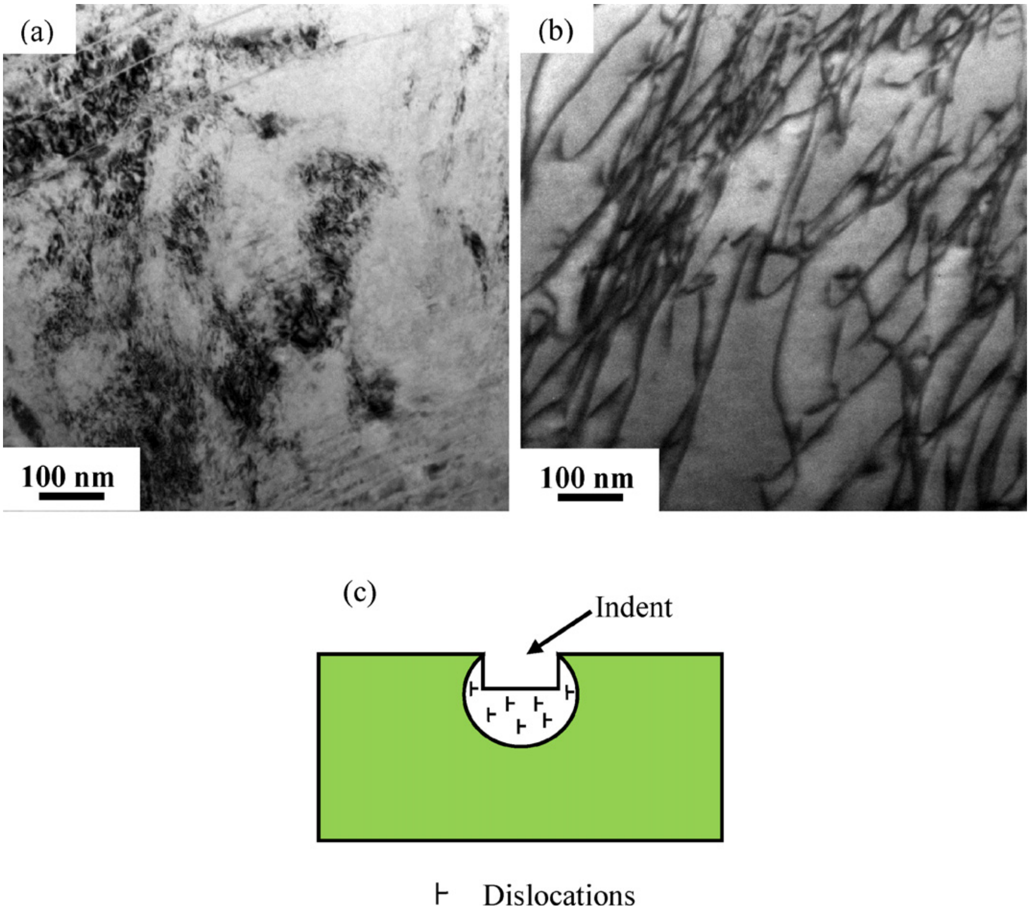

Fig. 5. TEM images showing the microstructure in NiTi before (a) and after (b) LSADI; (c) schematic representation of the dislocations structure in NiTi after LSADI.

of the patterns (Fig. 4a–c) after LSADI were recorded and compared. As shown in Fig. 4, the average depth of the indents in the as-indented sample is 97 (±8) nm. The average depth of the warm profile of the sample is 45 (±12). The average depth of the low temperature martensite profile (cold profile) is 66 (±11) nm. This corresponds to a recovery ratio (ratio of the depth of cold indent to the depth of the initial indent) of 68 pct. This recovery ratio is close to the indents generated by nano-indentation in the study by Frick et al. [18]. Further thermal tests showed that the TWSME is stable even after 10 thermal cycles. By manipulating the temperature, the depth of the pattern can be controlled. This can potentially be used in thermally activated actuators in advanced MEMS devices. Based on these experiments, it can be concluded that thermally controllable surface pattern can be generated in NiTi shape memory alloys through LSADI. It should be noted that due to the low affected depth (100 nm) of the indents generated by LSADI. The surface plastic strain introduced by previous grinding and polishing does affect the process to some extent. Thus, electropolishing or thermal annealing is recommended before LSADI for more precise study in the future.

The fundamental mechanism for TWSME has been discussed by Zhang et al. [5]. It has been proposed that the dislocations generated during indentation are responsible for TWSME. During plastic deformation, the martensitic NiTi alloys first deform elastically until it reaches a critical stress for martensite detwinning. After that, deformation is accommodated through martensite detwinnning, which can be reversed through heating. When martensite detwinning has been exhausted, plastic deformation is accommodated by dislocation slip, and this part of the deformation is non-reversible. After indentation, the plastic deformation creates anisotropic stress field around the dislocations within the martensite phase. This leads to the preferred orientation of the martensite variants when cooled from the austenite phase and thus enabling the material to remember its low temperature shape. By heating the indented patterns to above the austenite finish temperature, martensite transforms to austenite and thus the “warm” profile is assumed. Thus, the depth of the indents can be manipulated by changing the temperature.

Fig. 5a shows the microstructure in NiTi before LSADI. Fig. 5b shows the dislocation structure in the indented region of the NiTi sample after LSADI. It can be observed that networks of dislocations (black lines) are present in NiTi after LSADI, which is an indication of plastic deformation. During the LSADI process, the high pressure plasma propels the copper grid into the NiTi substrate in a very short instant, leading to the high-strain-rate plastic deformation of the NiTi substrate. During this high-strain-rate plastic deformation, the NiTi substrate undergoes drastic change in material microstructure including martensite detwinning and dislocation slip. Fig. 5c shows a schematic representation of the dislocations underneath the indents after LSADI. Compared to the indents generated by static loading [20], the dynamic loading can generate deeper region of plastic deformation (as schematically shown by the region with dislocations under the indented region) and higher dislocation density, which makes more significant two-way shape memory effect.

4. Conclusion

In summary, this study reports a surface imprinting technique called laser LSADI, which can generate patterned indents in metallic surface without heating or etching. Though the indents created by LSADI in this study is in the micrometer range, the feature size can be tuned to sub-micron or even nanoscale by introducing mask material with appropriate sizes. This method can be applied to any metallic surface and the patterns generated can be adjusted by the mask. In this study, it has been used to generate microscale TWSME NiTi SMAs. There is a great potential to apply this method to create complex structure on functional materials and devices. Furthermore, it can be easily scaled up for mass production, and it brings beneficial environmental impact since no chemicals are involved.

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