Influence of laser parameters in generating the NiTi nanoparticles with a rotating target using underwater solid state Nd: YAG laser ablation

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Abstract. The great effort that the scientific community has put in the last decade in the study of nanoscience and nanotechnology has been leading the research toward the development of new methodologies of nanostructures synthesis. Among them, Pulsed Laser Ablation in Liquid, PLAL, is gaining an increasing interest thanks to several promising advantages, which include: environmental sustainability, easy experimental set-up (which does not require extreme conditions of the ambient of synthesis), long-lasting stability of the nanoparticles, which are produced completely free of undesired contaminants or dangerous synthesis reactants. In this work, a drop wise flow of deionized water on the periphery of NiTi rotating target was tested as a procedure for the significant production of NiTi nanoparticles. This is a novel technique to improve the ablation efficiency of nanoparticles than the existing techniques of laser ablation. The influence of varying external parameters like laser wavelengths and laser fluences on the size distribution of nanoparticle was investigated. Second harmonic and third harmonics of Nd: YAG nanosecond laser with three different laser fluences of 30 J/cm², 40 J/cm² and 50 J/cm² was used to ablate the nitinol (Ni-55%, Ti-45%) target. The average particle size and redistribution was characterized by dynamic light scattering (DLS) and the crystalline formation of NiTi nanoparticles were analyzed by X-ray diffraction, where it confirms the alloy formation of NiTi nanoparticles.

1. Introduction
Nanoparticles, due to their novel and often enhanced properties, are now more and more used in manufacturing. Nanoparticles are 100 times smaller in diameter than human hair and have attracted great attention due to the number of application possibilities based on the wide range of available physical, chemical, mechanical, electrical and even biological properties [1-7]. The properties of metal nanoparticles strongly depend on their shape and size distribution. So number of researches have been done to control these parameters through various synthesis methods such as milling, grinding, thermal gas-phase decomposition process, electrochemical etching and chemical methods like sol-gel process. But all of these processes have drawbacks related to the purity and variety of accessible materials [1, 2, 7]. Under water pulsed laser ablation is an alternative method to address the deficits of the conventional methods as the nanoparticles can be generated from almost any solid material [7, 8]. But this method is lacking with high productivity and [9, 10]. The proposed approach to synthesis the NiTi nanoparticle was a novel technique where the laser ablation was carried on the circumference of the rotating cylindrical target rotating at constant rpm. The drop wise flow of deionized water was applied on the periphery of the target which quenched the nanoparticles just after the ablation through laser. Thus it synthesized
significant amount of nanoparticles where the formation efficiency was much more than the existing liquid assisted laser ablation techniques. The influence of different laser wavelengths and fluences was investigated for the particle size, morphology and ablation efficiency. It was observed that minimum particle size of 130 nm was investigated for the laser wavelength of 355 nm with fluence of 50 J/cm².

2. Experimental Procedure
The experimental setup for liquid assisted NiTi nanoparticle ablation was shown in figure 1. The pulsed Nd: YAG nanosecond laser with a frequency of 10 Hz and pulse duration of 5-8 ns was used for ablation. Laser wavelengths of 355 nm and 532 nm were generated by using KDP crystals to synthesis the nanoparticle from the cylindrical NiTi target (dia: 30 mm and height: 6 mm). The target (Nitinol 55 : 55% Ni and 45% Ti) was mounted on the shaft of DC motor operated in a constant voltage supply where the laser irradiation was perpendicular to the circumference of the target. Laser beam generated by the Nd: YAG laser was focused on the target using a converging lens (focal=30cm). The beam diameter around 0.5 mm was measured by using a laser burn paper and observing the point under a microscope. On the periphery of the target, a drop-wise flow of deionized water was applied at the focusing point to ensure that the ablation was happened in liquid environment. This also help in quenching of the nanoparticle just after the plume burst due to laser irradiation on the target. The quenched particle collected in the acrylic bucket. The energy of the laser pulse was measured using a power meter. The experiments were performed by ablating the target material with different laser fluences of 50 J/cm², 40 J/cm² and 30 J/cm². The nano-particles generated by laser ablation were collected on a glass slide (10×10×1 mm) by drop wise evaporation on a hotplate kept at 90° C and were characterized afterwards. The particle size distribution and phase transformation was analyzed by DLS and XRD.

3. Results and Discussion
3.1. 532 nm Laser Wavelength
The effect of laser wavelengths and fluences on the morphology and size of the nanoparticles were examined where NiTi nanoparticles were synthesized with different fluences of 30 J/cm², 40 J/cm² and 50 J/cm² shown in figure 2 (a, b, c, d). According to the table 1, it was observed that the particle size was in higher range with decrease in laser fluence to 30 J/cm². The formation efficiency of nanoparticles increases at higher fluence which was observed in the fig. 4. This will increase the concentration of colloidal solutions where nanoparticles appear as diffused particles at higher fluences [10]. The nanoparticles are excited due to the absorbance of photons and the temperature of nanoparticles increases which help to fragment them. It was observed that the some of the particles were in bigger size which might be due to the nucleation process takes place during ablation. From the XRD analysis the only peak of NiTi was observed which might be due the energy required to observe this stable phase [11].

3.2. 355nm Laser Wavelength
The same investigations were done by reducing the laser wavelength to 355 nm. It was again observed that the particle size was increasing with decrease in laser fluence in figure 3 (a, b, c, d). The XRD analysis at that wavelength shows the peaks of NiTi and TiO₂ at the fluences of 40 J/cm² and 50 J/cm², but at 30 J/cm² fluence the only peak of Ni₄Ti₃ was investigated. The possible reason for the stable phase of NiTi at higher fluences was due to the energy barrier to observe those phases [11]. The reason for getting the peak of Ni₄Ti₃ is might be due to the higher photons energy at lower wavelength leads to rapid transformations of crystal phases [10]. The oxide peaks was observed might be due the possible chance to ablate the nanoparticle in air contact as the flow rate of the liquid was not in continuous stream. The interaction of the alloy with the oxygen content results in the formation of titanium oxide [2].
Formation Efficiency: It was observed that the ablation rate of the NiTi target was increased with increasing the laser fluence and laser wavelength [12]. The figure 4 shows the amount of ablated target material for the samples prepared with 532 nm and 355 nm wavelength, with respect to the three different laser fluences. Thus the ablation depth is the function of beam energy, pulse duration and wavelength.

Table 1. Intensity of nanoparticles at different wavelengths and fluences

| Sample | Wavelength (nm) | Fluence (J/cm²) | Particle Size (nm) with Max. intensity |
|--------|-----------------|-----------------|---------------------------------------|
| A1     | 532             | 50              | 140                                   |
| A2     | 532             | 40              | 170                                   |
| A3     | 532             | 30              | 380                                   |
| B1     | 355             | 50              | 130                                   |
| B2     | 355             | 40              | 250                                   |
| B3     | 355             | 30              | 300                                   |

Figure 3. DLS images at 355 nm laser wavelength with fluences of (a) 30 J/cm², (b) 40 J/cm², (c) 50 J/cm² and XRD image (d) of NiTi nanoparticle

Figure 4. Formation efficiency of nanoparticles at different wavelengths and fluences
Conclusion:
Nanosecond Nd: YAG under water laser ablation on a rotating target is a convenient way and free from other pre-requisite processes to generate pure and stable nanoparticles with high formation rate as compared to other methods. This is a new approach to increase the ablation rate (formation of more nanoparticles in lesser time) of pure nanoparticles where laser wavelength and fluence has an important role in controlling the size and morphology of the nanoparticles. Increase in laser fluence leads to decrease in particle size and increase in formation efficiency. Minimum particle size of 130 nm was observed for the laser wavelength of 355 nm with fluence of 50J/cm². Finally it can be concluded that the alloy form of NiTi nanoparticle was observed based on the XRD plots at different wavelengths and fluences. In future, this method can be used to obtain ultrapure bio-conjugated metal nanoparticles for drug targeting, drug delivery and bio-response studies.

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