Simultaneous Optimization of Laser Energy and Coating Thickness in Surface Alloying of Al with Fe

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Abstract. In the two-step deposition technique of the laser surface alloying process, the alloying elements are introduced onto the bulk material's surface. In such process, two main parameters determine the alloying quality: the thickness of the coating and the laser energy supplied onto the specimen. In this work, the laser surface alloying of aluminium (Al) with iron (Fe) is carried out by optimizing both parameters. This is accomplished by assessing the improvement in the hardness after laser treatment. In general, the thicker coating desires higher laser energy to cause surface melting and sequentially diffusion of Fe into molten Al to occur. This is indicated by the linear relationship between the thicknesses for the peak hardness value with the laser energy where by the optimum energy shifted to higher energy for a thicker coating. The increase in laser energy increases Fe particle's chance to migrate via diffusion into the bulk Al substrate. However, at 140µm the optimized energy reaches a peak value at 455mJ which is the maximum energy to be supplied in this process before the coating is lost due to excessive ablation. For thicker coatings, the laser's action does not penetrate enough onto the substrate to cause sufficient melting of the Al surface for alloy formation. The maximum hardness obtained was 40.8 HV at the optimum condition for 140µm thickness treated with 455 mJ. The formation of an alloyed compound is further confirmed by x-ray diffraction technique whereby compounds such as AlFe, Al₁₃Fe₄, and AlFe₆Si are present in the treated specimens.

1. Introduction
Laser surface alloying is one of the surface modification techniques in which high power density laser was exploited to melt metal surface and the alloyed element together to form a thin layer of surface alloy [1]. In such process, the alloying species are typically introduced into the bulk material's surface either by simultaneous injection of the alloying species (in the form of powder or wire) into a laser melted surface layer during the precoating the alloying element on the surface before the laser treatment. The later have more advantages as it provides total control on the alloyed layer's composition [2]. The alloying species' composition can be controlled by varying the mixing ratio of the different alloying elements. Aluminium (Al) has a wide application in industries due to its lightweight and formability [3, 4-5]. However, it has weakness in term of corrosion, wear resistance and less hardness. These attract more research in this area to increases its mechanical properties. Many research types tend towards the application of higher power and continuous laser operation [6-10]. However, less attention has been paid to deploy Q-switched laser for laser surface alloying. The Q-switched Nd:YAG laser has a pulse
duration of nanoseconds. Thus it can efficiently deliver more than 10 MW within a single pulse. With this high peak power hot and dense plasma can easily form during the interaction with the target. At high plasma temperature (~11,000 K), which is much higher than the melting points of coating material, the substrate induces the metal grain. It dissolves the metal into the Al substrate, forming the surface alloy. Once the laser pulse ceases, it cools off with a high quenching rate in the range of 20 to 40 x 10^6 K/s, non-equilibrium occurs in the Al substrate [14]. This results in several new metastable phases which modifies the microstructure of the solidified surface layer. The fast quenching rate also controls alloy elements' penetration depth at the surface, which is typically limited within a micro-depth region [15-17].

In precoated laser surface alloying two main parameters directly dictate the quality of the alloying: 1) the thickness of the coating and 2) the supplied laser energy onto the specimen. It is vital to optimizing both parameters simultaneously. In the coating layer, there is a possibility that the thickness might be too thick. Thus the laser energy might not reach the substrate, or to thins, whereby the material might blow off and fly away immediately after laser interaction due to the transient and megawatt impact of laser radiation thus alloying process not possible. Majority of previous works only focusing on optimizing the laser surface alloying treatment based on energy verification, less attention in modifying the coating thickness itself. Related work has been reported by Vaziri et al. [3] who assumed that Ni's distribution as the alloying element is reasonably uniform at the thickness of approximately 400 µm while using a longer pulse duration of Nd:YAG laser in milliseconds. Zheng et. al., fixed the Cu mixed coating at 200 µm by using flame-spray technique [9] while in other text Bidin et al. setting the precoating at a thickness of 80 µm prior to the laser treatment [7]. In present works, the coating thickness and the laser energy are both optimized and assessing the alloyed formation through microhardness measurement in laser surface alloying of Al with iron (Fe). This information is crucial in a feedback loop control system whereby the optimized parameters are fed into a closed-loop quality computer-control system to yield good quality specimen.

2. Experimental setup

![Figure 1. Experimental setup](image)

Al plate (Goodfellow; 2 mm; 99.0 %) was sliced into a square plate with dimension 1cm x 1cm to be used as substrate. Fe powder (Merck, 98.0%) having a mean particle size of 150 µm is used as the alloying element. Two-step deposition technique was employed to spread Fe powder into the surface of bulk Al. In this process, a thin, less dense Fe coating is produced by spraying Fe powder on the Al surface, preparted with 20 w.t % of polyvinyl alcohol (PVA) as a universal binding agent. By utilizing this technique, a homogenous Fe coating can be achieved; with the thickness of the coating can be tailored by varying the volume of the PVA used to be spread on the Al surface. A set of samples with coating thickness from 120 – 170 µm are prepared and labelled. Digital micrometer screw gauge was
employed to measure the specimen thickness. The pre-coated samples are then sintered at 90°C in 1 hour to dry and evaporate the PVA as the binding agent.

The experimental setup was shown in Figure 1. A commercial Q-switched Nd:YAG laser with maximum peak power 40 MW was used as the laser source. The detailed specification of the laser is described in Table 1. The laser was focused using a lens of 80 mm focal length to achieve enough energy density for alloying process. The sample was mounted on the translation stage set at a defocused distance, 5 mm away from the focal point. The laser alloying process was conducted in open air. Each of the samples is treated with various laser energies in the range of 10 to 520 mJ. The exposure is accomplished by using a single pulse treatment. Vickers microhardness tester (CV instrument) was used to quantify the hardness of the laser treated samples with different Fe coating thicknesses. X-ray diffraction technique (XRD) is used to analyze the specimens for alloyed compounds identification formed during the laser treatment while several cross sectional optical microscope images are taken to visualize the effect of laser penetration.

Table 1. Laser parameters used for alloying

| Laser type    | Q-switched Nd:YAG |
|---------------|-------------------|
| Wavelength    | 1064 nm           |
| Pulse duration| 10 ns             |
| Energy        | 10-455 mJ         |
| Peak power    | 10-45 MW          |
| Beam spot     | 1 mm              |
| Focal length  | 80 mm             |
3. Results and discussions

Figure 2. The microhardness measured for specimens with coating thickness from 120 µm to 170 µm (Note that the thickness of untreated Al specimen is 25 HV)

An increment of hardness after laser surface treatment is an indicator for alloying formation that involves the diffusion of alloy element (inward process) and the migration bulk of substrate material (outward process) that will promote new composite or intermetallic elements. Thus it is crucial to meet an equilibrium point to balance the two parameters (i.e laser energy and coating thickness). Figure 2 shows microhardness of alloyed surface versus energy at different Fe coating thicknesses. Generally, at each thickness, there is optimum energy whereby the hardness is maxima. Such energy is referred as super-lateral energy [14], beyond the critical energy the hardness is dropping.
The surface alloying process concerning the variation of laser energy is illustrated schematically in Figure 3. The hardness is considered non-improvement since the delivered lower energy not even reach the substrate to modify the surface (Figure 3a). As the laser energy gets higher, more area will be melted and reached at the Fe-Al interface (Figure 3b). Optimum hardness is achieved at corresponding critical energy or also known as super lateral energy. This particular point also represents the optimum condition in alloying process. The supplied laser energy is sufficient to causes maximum melting and inter-diffusion between Fe and Al to occur at a given coating thickness. The equilibrium condition between the alloyed element and substrate is achieved, allowing the formation of new inter-metallic phase in the resolidification process (Figure 3c). However, further increases in energy involve excessive ablation, thus damaging the surface through vaporization and particles removals. The surface deformation is illustrated in Figure 3d. As a result, the hardness dropped immediately when the delivering laser energy is getting higher.

![Figure 3](image_url)

Figure 3. Optical microscope cross sectional image across the melt pool at a. 130mJ, b. 395mJ, c. 455mJ, and d. 520mJ for coating thickness at 140 µm
The cross sectional image of the melt pool from the optical microscope is presented in Figure 3 after all the treated specimens are cleaned in the ultrasonic bath. No laser affected zone region is apparent at low energy treatment as in Figure 3a. However, the layers of laser affected zone are observed only for treatment energy at 395 mJ, 455 mJ, and 520 mJ. This region takes up less than 10 µm depth across the substrate. At 520 mJ a crater is formed due to high energy laser impact which leads to surface deformation. At 66.2 J/cm² the laser penetrates through the coating and substrate. The vaporization temperatures cause explosion due to very high-pressure gradient. This effect can be visualized as splashes and droplets as in Figure 3d.

The summarization of the optimized alloying condition is presented in Figure 4. Each coating thicknesses has its critical energy to achieve optimum microhardness. A thicker coating requires higher laser energy for alloying. The thicker coating is used; more Fe will mix with Al at this point, more alloying is expected. This is realized up to the thickness of 140 µm at corresponding energy of 455 mJ. However, more significant than this thickness, the hardness immediately dropping. This can be explained as follows. The thicker Fe coating requires more PVA as the binding agent to be applied before the coating process. This will affect the penetration depth of the laser action into the shallower region. The optimized point lies in the middle level for this special case, between 275 to 330 mJ.

![Figure 4. The optimized alloying process along the coating thickness and the laser energy parameter](image)

The most drastic improvement in the alloyed surface's hardness properties is obtained from 140 µm thickness of Fe coating at corresponding super lateral energy of 455 mJ. This indicates that the melting and subsequent mixing transformation between Fe and Al occur at this particular optimum thickness. The mechanism of Fe-Al based alloy can be explained as follows. The laser has penetrated into the denser coating layer and develops a melt pool of aluminium. The given heat is not enough to melt the Fe, hence leave them still in the form of particle. Marangoni effect occurs when the surface tensions play the role of transferring the mass of Fe through the convection process into the melt pool of Al.
However, latent heat resists and retard the process of melting as well as resolidification. Hence, the delay gives a chance to form a new composite due to the recalcence effect [14]. The heat from the laser's action melts the substrate deep enough to induce diffusion of Fe from the interface into molten Al. When the laser ceases rapid cooling, resolidification is initiated by high quenching rates that begin from the solid part of the substrate and overspread into the melt pool region. The solidified mixture of Al and Fe forms alloy on the substrate surface indicated by the improvement in hardness value.

The alloying is further confirmed by the XRD diffractograph shown in Figure 5. The clear peaks identified dominant phases as; Al and Fe as individual elements, whereas alloy compounds such as common AlFe phase, a metastable Al$_{13}$Fe$_{4}$ phase, and a ternary alloy AlFe$_{6}$Si. These alloyed compounds formed after Fe and Al are mixed while in the liquid and solid phase. While the element silicon that appears and forms a ternary alloy, AlFe$_{6}$Si, may come from the PVA as a bonding agent. These different alloy compounds that form on the Al surface are responsible in improving its hardness properties.

![XRD spectrum on the treated surface](image)

**Figure 5. XRD diffraction on the treated specimen**

4. Conclusion

Al was alloyed with Fe using laser surface alloying technique. The alloying process was optimized by varying the coating thickness of Fe and the energy of laser. Both parameters play an essential role in this alloying process. Considering the thickness parameter, required specific value, not too thin, it will blow-off during the laser mater interaction or too thick either because it requires more adhesive material like PVA and needs a more energetic laser to cause ablation. Thus, the optimised thickness of Fe coating is as 140 $\mu$m at corresponding critical energy of 455 mJ. This optimization alloying is accessible by measuring the hardness as well as the XRD analysis. The new composite are comprised of AlFe, Al$_{13}$Fe$_{4}$, and AlFe$_{6}$Si.
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