SURFACE MODIFICATION BY MEANS OF LASER MELTING COMBINED WITH SHOT PEENING: A NOVEL APPROACH

J. NOORDHUIS and J. TH. M. DE HOSSON
Department of Applied Physics, Materials Science Centre, University of Groningen, Nijenborgh 18, 9747 AG Groningen, The Netherlands

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Abstract—Among the available laser applications laser surface melting has turned out to be a powerful technique for the production of wear-resistant layers. Despite the advantages of this process, laser surface melting results in tensile stresses which may assist crack propagation. In this paper it will be shown that shot peening can overcome this drawback effectively. It turned out that a preceding laser treatment of an eutectic aluminium–silicon alloy is able to amplify considerably the effectiveness of the shot peening treatment. In particular the maximum attainable hardness and compressive stress increase upon increasing the quench rate, i.e. upon increasing the laser scan velocity. The high concentration of silicon in solid solution turned out to be the main reason for the enhanced mechanical performance, not only directly through solid solution hardening, but also by precipitation hardening and by a higher dislocation density. The latter contribution is affected indirectly by a changed cross slip behaviour.

Résumé—Parmi les applications disponibles du laser, la fusion superficielle est devenue une technique puissante pour la production de couches résistant à l’usure. Malgré les avantages de ce procédé, la fusion superficielle par laser donne des contraintes de traction qui peuvent aider à la propagation des fissures. Dans cet article, on montrera que le grenaillage peut surmonter efficacement cet inconvénient. Il s’avère qu’un traitement antérieur au laser d’un alliage eutectique aluminium–silicium est capable d’amplifier considérablement l’efficacité du traitement de grenaillage. En particulier, la dureté maximale accessible et la contrainte maximale en compression augmentent si l’on augmente la vitesse de trempe, c’est-à-dire la vitesse de balayage du laser. La forte concentration de silicium dans la solution solide est la principale raison de l’amélioration des performances mécaniques, non seulement directement par le durcissement de la solution solide, mais aussi grâce au durcissement par précipitation et par une densité de dislocations plus élevée. Cette dernière contribution est affectée indirectement par le changement des conditions de glissement dévié.


INTRODUCTION

Eutectic aluminium–silicon alloys are commonly used for automotive parts like cylinder heads and pistons. These types of alloys combine good castability, low density, good corrosion resistance and a low thermal expansion. The mechanical properties can be further improved by small additions of sodium or strontium [1]. These impurities cause a change in the morphology of the silicon phase, and a decreased spacing between them. The amount of modifier however is quite critical since over-modification results in reduced mechanical properties. Furthermore, losses from the melt and the formation of undesired intermetallic compounds cause additional problems.

Rapid solidification by means of laser surface melting is another way of achieving a fine distribution of the silicon phase [2]. The cellular solidification results in cell sizes in the order of 1 μm, depending on the scan velocity. The depth of the laser tracks is 50–500 μm, which is enough to allow further machining, and depends on the process parameters. In addition laser surface treatment is a process that
offers greater precision and less distortion than most other surface techniques.

In this paper we will examine the combination of laser surface melting technique and shotpeening. The latter technique has been known for much longer time and is commonly applied when the fatigue life time of metals has to be improved. An aluminium–silicon alloy is chosen because it is widely used as a casting alloy and because of its simple phase diagram.

**EXPERIMENTAL**

Homogeneous samples of an eutectic aluminium–silicon alloy, of which the composition is listed in Table 1, have been sandblasted to obtain a rough, well absorbing surface. After ultrasonically cleaning the samples were irradiated using a transverse flow Spectra Physics 820 CO₂ laser. At the surface the power of the beam was 1300 W. The focus point of the ZnSe lens with focal length of 127 mm lays 5 mm above the surface, resulting in a spot diameter of 0.75 mm. X-ray diffraction samples were prepared by making an overlap of laser tracks resulting in a large surface area. In all other cases single laser tracks were used. The laser scan velocity was varied between 1/8 and 8 cm/s. At higher velocities the interaction time was too short to dissolve all of the primary silicon particles.

After laser treatment shotpeening was carried out taking glass beads of an average diameter of 720 μm. The air pressure was 2.6 bar, low enough to prevent ploughing of the sample surface and breaking of the glass beads.

X-ray measurements were carried out using a Philips PW 1830 X-ray diffractometer equipped with a fine focus copper tube and a graphite monochromator in the diffracted beam.

TEM specimens were prepared using a mechanical dimpler, followed by ion milling in the cooled stage of a Gatan 600 dual ion mill. A Jeol 200 CX electron microscope was used for examination of these specimens. Optical microscopy and hardness measurement were carried out on samples embedded in epoxy using the taper sectioning technique, because this leads to accurate hardness values just below the surface.

**RESULTS**

**Hardness measurements**

The surface hardness was measured on various samples treated with different laser scan velocities and peening times. The results are compiled in Table 2. Each value represents an average of four measurements. An exponential fit [3] through the data points is depicted in Fig. 1. It is easy to see that the laser treatment results in hardness values approximately twice as high as the bulk material. Subsequent shotpeening further increases the hardness to a value three times that of the bulk material. A closer examination reveals that the increment of the hardness is the highest for the samples with the highest laser velocity. The saturation values are reached after approx. 100 s for the low and 200 s for the high laser scan velocity samples.

For a sample with laser scan velocity of 8 cm/s a depth profile is measured using a Knoop indenter, Fig. 2. From this figure we may conclude that the maximum peening effects extends to a depth of approx. 150 μm, which is almost as deep as the laser track, namely 200 μm.

**X-ray measurements**

X-ray measurements were carried out to determine the surface stress state after the laser treatment and the shotpeening treatment using [4]:

\[ \frac{d_0 - d}{d_0} = \epsilon = \frac{1 + \nu}{E} \sigma \sin^2\psi - \frac{\nu}{E} (\sigma_1 + \sigma_2) \]  

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**Table 1. Chemical composition of the used alloy**

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Fe</th>
<th>Mn</th>
<th>Cu</th>
<th>Zn</th>
<th>Ti</th>
<th>Si</th>
<th>Al</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al-Si</td>
<td>0.168</td>
<td>0.03</td>
<td>0.01</td>
<td>0.025</td>
<td>0.025</td>
<td>12.0</td>
<td>Bal</td>
</tr>
</tbody>
</table>

**Table 2. Measured surface hardness as a function of laser scan velocity and shotpeen time**

<table>
<thead>
<tr>
<th>Laser scan velocity (cm/s)</th>
<th>Shotpeen time</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1/8</td>
</tr>
<tr>
<td>---------------------------</td>
<td>---------------</td>
</tr>
<tr>
<td>0</td>
<td>88</td>
</tr>
<tr>
<td>6</td>
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<td>10</td>
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<td>110</td>
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<td>115</td>
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<td>40</td>
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<td>360</td>
<td>129</td>
</tr>
<tr>
<td>540</td>
<td>135</td>
</tr>
</tbody>
</table>
Fig. 1. Surface hardness of Al-12Si as a function of laser scan velocity and shotpeen time.

Fig. 2. Knoop hardness in a 8 cm/s track as a function of depth, before △ and after shotpeening +.

Fig. 3. Histogram showing the amount of silicon in solid solution as a function of laser scan velocity and shotpeen time.
where \( \sigma_1 \) and \( \sigma_2 \) represent the stresses longitudinal and transverse to the scan direction. The Young's modulus \( E \) and Poisson's constant \( \nu \) were taken to be 70 GPa and 0.3 respectively. We measured an average value over 10 overlapping laser tracks, and found no large differences of the stresses in the longitudinal and transverse directions. As a consequence: \( \sigma_1 = \sigma_2 \). Therefore the measurements are done for longitudinal stresses only.

These measurements, carried out on the Al \( \langle 422 \rangle \) reflection can also be used to acquire the stress free lattice parameter \( a_0 \) using (1) and equating the strain to zero. The results are plotted in Fig. 3. The values of \( a_0 \) can be converted to the concentration silicon in solid solution [5]. Due to the higher quench rate an increased amount of silicon in solid solution is found in samples with a higher laser scan velocity. After shotpeening the lattice parameter starts to increase, and approaches the bulk value again after 360 s peening time. This may indicate that silicon precipitates are formed during the shotpeening process. The measured stress values are depicted in Fig. 4. It is easy to see that the residual stress state appears to saturate much faster than the hardness. As expected the absolute stress values are higher when the laser scan velocity is higher.

Line profile analyses were performed to acquire information about the dislocation density, in addition to the information obtained by TEM. In order to get accurate results, the reflections used should be carefully chosen. In case of a Warren Averbach multiple line method most sets of reflections fail because of interfering silicon reflections. The best choice is the \( \langle 111 \rangle \) and \( \langle 222 \rangle \) combination although interference from the \( \langle 311 \rangle \) reflection may occur when the peak-widths get large. When a single line analysis is applied, similar arguments lead to the use of the \( \langle 111 \rangle \) reflection. X-ray line profiles may advantageously be analyzed by their Fourier-series decomposition. The Fourier coefficients yield the effective particle size \( D \) and r.m.s. strain \( \langle \epsilon^2 \rangle^{1/2} \). The latter is rather the width of the strain distribution. The results of a Fourier single line method are depicted in Fig. 5. In this figure the obtained values for the microstrain \( \epsilon \) and particle size \( D \) are converted to a density of dislocations with magnitude of the Burgers vector \( b \), using [6, 7]:

\[
\rho = \sqrt{\rho_D b s} = 2\sqrt{3} \frac{\langle \epsilon^2 \rangle^{1/2}}{D b}
\]

When applying equation (2) one should keep in mind that precipitation of silicon may result in local lattice strains [8] which also gives a contribution to the peak broadening. Comparison of our values for the microstrain with the ones obtained by [8] leads us to the conclusion that this contribution is small compared to the microstrain arising from the dislocations.

In Fig. 5 the results for the not lasered samples have been left out because of the large relative error (small peak-width increase when compared with the reference sample). In some cases where the Warren Averbach method is feasible (medium peak-widths), a recalculation yields a similar result.

The sample with laser scan velocity 1/8 cm/s shows a maximum dislocation density of \( 3.4 \times 10^{15}/\text{m}^2 \), which is reached already after 10 s of shotpeening. The dislocation density for the sample with laser scan velocity 1 cm/s is lower, reaching a maximum of \( 1.8 \times 10^{15}/\text{m}^2 \) after 30 s of shotpeening. The sample with laser scan velocity 8 cm/s shows the lowest dislocation density among the lasered samples, with a maximum of \( 1.2 \times 10^{15}/\text{m}^2 \) after 10 s of shotpeening.
velocity of 8 cm/s is still increasing after 360 s of peening. The absolute value is as expected also higher, namely in the order of $10^{10}$/m$^2$.

**Microscopic observations**

Optical micrographs clearly reveal the refined structure caused by the rapid solidification after laser treatment. TEM micrographs are used to estimate the dislocation density of the samples before and after shotpeening. Because the observed densities are without exceptions very high [2], see Fig. 6, only rough estimates can be given here: $10^{13}$/m$^2$ for low laser scan velocity without shotpeening and $10^{14}$/m$^2$ for high laser scan velocity after 360 s of shotpeening. Dislocation cell structures are not observed to be formed during the shotpeening. Apparently the sizes of the cells as started with are too small to allow further division. Minimum energy configurations by the formation of checkerboard-like structure of the original cells is sometimes observed, Fig. 6.

An important observation is the difference in mobility of the dislocations in the low and the high laser scan velocity samples. In the 1/8 cm/s samples the heat input from the electron beam was sufficient to cause thermal activated dislocation movement. In the 8 cm/s sample this was not observed.

The low laser scan velocity samples reveal a breaking up of the solidification structure after shotpeening. This change of structure is not accompanied by an increased dislocation density, which implies dynamical recovery during deformation. The result is a fine granular structure, typical grain size 0.5 to 1 $\mu$m, Fig. 7. Silicon particles originally forming the eutectic cell walls are then more randomly distributed.

Another observed phenomenon in high laser scan velocity samples after shotpeening is the formation of silicon precipitates. The sizes of these precipitates vary from approx. 5 to 50 nm, see Fig. 8.

Most important about the peened bulk samples is the breaking of the original silicon particles, Fig. 9. This indicates that this alloy in the as cast condition is not suitable for a shotpeening treatment.

**DISCUSSION**

Theoretical descriptions on the hardening of crystalline solids involve the movement of dislocations against the resistance provided by various types of obstacles. In our samples we have the following relevant obstacles: substituional silicon atoms, forest dislocations and silicon precipitates. The strength of these various types of obstacles can be calculated using the random obstacle theory for localized obstacles:

$$\tau = \tau_{\text{sub}} + \tau_{\text{dis}} + \tau_{\text{prec}}$$

Fig. 6. Dark field TEM micrograph showing the dislocation structure in peened Al-12Si, laser scan velocity 8 cm/s.

Fig. 7. Dark field TEM micrograph of the fine granular structure in a sample with laser scan velocity 1/8 cm/s, after shotpeening.

Fig. 8. Precipitates in shotpeened Al-12Si, laser scan velocity 8 cm/s.

Fig. 9. Shotpeened induced breaking of primary silicon particles in the as cast Al-12Si alloy.
where the first two contributions can be described using Friedel's relation [9]:

$$\tau_{\text{substitution}} = \mu b L \cos^3(\phi_s/2)$$  \hspace{1cm} (4)

where $\mu$, $b$, $L$ and $\phi_s$ are the shear modulus, magnitude of the Burgers vector, obstacle spacing and critical break away angle, respectively.

In the material we have studied, the relatively high amount (up to 2%) of silicon in solid solution is likely to play an important role. The maximum solubility of Si in Al is only 1.5% at the eutectic temperature, and it decreases to 0.05% at 300°C [5]. This low solubility is caused by the large misfit between Al and Si, while Si still occupies substitutional sites. This large misfit (18%), however, gives the Si atoms a large interaction strength, and thus an already large contribution to the flow stress at relatively low concentrations. To calculate the numeric value of this contribution an estimate of the interaction strength $\xi$ is made by comparison with misfits in other systems [10]. $\xi$ depends on the critical break away angle being $\xi = \cos(\phi_s/2) = 0.04$. This value, together with $L$ rewritten as $b/\sqrt{c}$ results in a contribution to the flow stress of $10^{-1} \mu$, at a solid solution concentration of 1.5%. This value of the flow stress has to be considered rather as an upper limit since a justification of Friedel's relation can be given only for not too weak obstacles and for a low concentration of impurities, i.e. when the mean distance between obstacles is larger than the minimum curvature radius of the dislocation at the obstacle. In fact the critical condition of Friedel's approximation [11], $cW^2/\xi b^3 < 1$ indicates that the present situation is a borderline case ($W$ represents the width of the dislocation). A different approach as presented in Mott-Nabarro's model [12], taking into account the internal stress around each solute [13], predicts a contribution of the flow stress of $4 \times 10^{-4} \mu$.

Regarding the misfit between aluminium and silicon, one should note that silicon is a non-metal and that the tabulated atomic radius might change significantly when embedded in a metal. The rate of lattice contraction as solute is added indicates that the misfit is smaller than the one based on the atomic radii.

In addition, Fleischer [13] pointed out that the modulus mismatch is just as important as size mismatch when considering solid solution hardening. To take modulus hardening into account one should have knowledge about the relative change of the shear modulus $1/G \frac{dG}{dc}$ as solute is added. Since silicon is virtually insoluble in aluminium this is very difficult to measure and to our knowledge no values have been reported in the literature. Nevertheless the modulus mismatch will have its effect on the interaction strength. Therefore we have made an approximation of this mismatch by applying the following equations [14]:

$$G_u - G_{al} \frac{G_u + G_{al} f}{G_u - G_{al} f} \leq G_{al} - G_u \leq G_{al} + G_u + (G_u - G_{al}) (1 - f)$$ \hspace{1cm} (5a)

where $G_{al} - G_u (K_u - K_{al}) \geq 0$:

$$G_l = \frac{1}{2} \left( \frac{1}{G_{al}} + \frac{10}{9K_{al} + 8G_{al}} \right)^{-1}, \quad G_u = \frac{1}{2} \left( \frac{1}{G_{al}} + \frac{10}{9K_u + 8G_u} \right)^{-1}$$ \hspace{1cm} (5b)

In these equations $G_{al,al}, K_{al,al}$ represent the shear and bulk modulus of the aluminium and silicon phase respectively, and $f$ denotes the volume fraction of silicon inclusions. It must be emphasized that this method neglects all electronic effects, and should only be used as a first order approximation.

The resulting value of the relative modulus change together with the value of the change in lattice parameter can be combined using the method as was developed by [13] in order to obtain a numeric value for the interaction strength. This method results in $\xi = 0.042$, which is very similar to the estimate based upon the non embedded atomic radius.

The second contribution to the flow stress, arising from the dislocation-dislocation interaction, also needs to be considered. The numeric value of the dislocation density can be obtained by TEM or by the X-ray peak width experiments. The estimates based on the TEM micrographs are in the order of $10^{13}/m^2$ after laser melting, and are raised by one or two orders of magnitude after subsequent shotpeening. The results obtained by the X-ray peak width measurements exceed these estimates by more than one order of magnitude. To explain the difference between these results one should keep in mind that during the preparation of the TEM samples dislocations can be lost at the sample surface. Furthermore densities obtained by X-ray methods often exceed those obtained by TEM. This tendency of over-estimating is stronger with increasing degree of deformation [7]. To calculate the numeric value of the contribution to the flow stress Friedel's equation is rewritten as:

$$\tau_{\text{dial}} = \alpha \mu b \sqrt{\rho}$$ \hspace{1cm} (6)

where $\alpha$ is $1/3$ [15], and $\rho$ represents the dislocation density. This equation is valid if internal stresses are absent. In heavily deformed materials the internal stress takes up about 80% of the applied stress [16].
Therefore, the effective contribution to the flow stress amounts one fifth of the value calculated with the equation above, resulting in a value of $2 \times 10^{-4} \mu$ for a dislocation density of $10^{9} \text{m}^{-2}$. It has to be realized that singling out the forest cutting mechanism to account 20% of the flow stress, the rest being due to internal stress is arbitrary since the internal stress in [16] may still be proportional to the square root of the dislocation density.

The third contribution to the flow stress, caused by the presence of silicon precipitates, is given by the Orowan stress [17]:

$$\tau_{\text{prec}} = \frac{0.84 \mu b \ln(2R_s/r_0)}{2\pi(1 - v)\sqrt{L - 2R_s}}$$  \hspace{1cm} (7)

where $R_s$ and $r_0$ are the particle and dislocation core radius, respectively.

During the shotpeening the measured concentration of silicon in solid solution significantly decreases, and silicon precipitates appear. This low temperature precipitation must then be assisted by pipe diffusion. Because the capture radius of the dislocations is undoubtedly small compared to the initial dislocation spacing, a lot of deformation is needed. This is confirmed by X-ray measurements and by TEM.

To calculate the contribution of the precipitates to the flow stress, their average spacing is needed. This is a difficult task because especially the small precipitates are easily overlooked. This is caused by the random orientation of the precipitates and the heavily deformed condition of the material. Therefore only an estimate of $0.1 \mu$ is used here. This value results in an Orowan stress of $4 \times 10^{-3} \mu$.

Comparison of the calculated contributions to the flow stress indicates that the high hardness values after laser melting and shotpeening are caused mainly by precipitation hardening and to a less extent by solid solution hardening. The dislocation–dislocation interaction seems not to be the predominant factor. It does not mean that the dislocation strengthening mechanism has to be ruled out completely. Indeed after long shotpeening times, when most of the silicon has come out of the solid solution, the flow stress is still slightly increasing. However, this is considered as of minor importance in explaining the predominantly acting hardening mechanisms.

The considerations mentioned above do not include any possible changes in cross slip behaviour. Furthermore we have not yet discussed an explanation of the large difference in dislocation density in samples treated at low and high laser scan velocity. Examination of the experimental results indicates that a changed cross slip behaviour might be responsible for this phenomenon.

An increase of hardness can be achieved if one could eliminate or postpone the onset of cross slip (stage III). From that point on the work-hardening rate is decreasing with increasing strain. In our samples we see that after an initial period of approxi-

mate linear hardening, the work hardening rate also decreases, but the peening time at which the saturation starts increases with increasing laser velocity. This indicates that the onset of cross slip might be postponed by an increased laser velocity. This observation is in line with the observed higher dislocation density in samples treated at high laser scan velocity. In the present case the cross slip behaviour can be affected in various ways.

First, the introduction of impurity atoms affects the stacking fault energy and therefore the stress necessary to constrict the partial dislocations to cross slip. In the case of aluminium the stacking fault energy is in the order of $200 \text{mJ/m}^2$. This high value results, applying linear elasticity, in an equilibrium separation less than one Burger vector for a screw dislocation. Since in our samples the maximum of silicon impurities is $2\%$, it is not very likely that the stacking fault energy is lowered by such an amount that the cross slip behaviour changes significantly.

A second mechanism by which the cross slip behaviour can be altered in our case is to do with the prerequisite of the cross slip process to occur, namely that the dislocation is in pure screw orientation over some distance. When impurities with sufficient stress fields are present the dislocations will show deviations from straightness [18], and the activation energy for cross slip will apparently be raised.

A study of the coarse slip bands after deformation can reveal whether this second mechanism plays a dominant role or not. Small additions of copper or magnesium in aluminium, elements that cause a significant misfit, have shown to increase the stress for the onset of cross slip [19] whereas addition of silver has no such effect. Since there is almost no size difference between aluminium and silver this is in line with the second mechanism described above. As already mentioned before there is a large misfit in the case of silicon in aluminium so that it is likely that cross slip is hindered by this mechanism in our case.

**CONCLUSIONS**

In conclusion we can state:

— Laser surface melting of as cast Al–12Si, leads to a very fine dispersion of silicon in aluminium.

— The tensile stresses induced by the laser treatment are completely reversed by the shotpeen process.

— The laser as well as the shotpeen process extend to comparable depths, enough to allow for further machining.

— The high quench rates cause a high concentration of silicon to be present in solid solution, contributing to the high hardness values after the laser treatment.

— The silicon in solid solution results in a changed cross slip behaviour which in turn results in a higher dislocation density.
Shotpeening of the laser-etched material leads to the formation of small silicon precipitates, leading to a further hardness increase.

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