The effect of cladding speed on phase constitution and properties of AISI 431 stainless steel laser deposited coatings

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ABSTRACT

Shorter processing time has given impetus to laser cladding technology and therefore in this research the AISI 431 martensitic stainless steel coatings are laser deposited at high cladding speeds, i.e. up to 117 mm/s. The analysis of phase constitution and functional properties of the coatings are performed by optical microscopy, Scanning Electron Microscopy (SEM), and hardness and sliding wear tests. The outcome of this research shows that an extreme refinement of the solidification structure will influence the phase constitution of the coatings by lowering the Ms temperature and hence stabilizing the austenite which results in lower hardness values and increased wear rates. These results confirm that the structural refinement obtained by higher cladding speeds is not helpful for improving the hardness and wear properties of laser deposited martensitic stainless steel coatings.

1. Introduction

Austenitic stainless steels are extensively used in structural components primarily because of their high resistance to corrosion and oxidation. However, they usually exhibit a poor sliding wear and cavitation erosion resistance which may result in material transfer, mechanical mixing and oxidation between sliding bodies and cavitation erosion in machinery such as hydro-turbines, pumps and valves. A possible solution to the above-mentioned wear problems is to coat the austenitic stainless steel parts by a layer of martensitic stainless steel with a good combination of corrosion resistance and high hardness and erosion resistance using laser cladding process [1–4].

Laser cladding is a technique to produce dense and metallurgically bonded protective layers on metallic substrates to improve surface properties like corrosion, wear and thermal fatigue resistance [5,6]. In comparison to competitive technologies such as thermal spray or conventional weld overlay, laser cladding has many advantages e.g. lower heat input and workpiece distortion, limited dilution, smaller HAZ and greater precision [7]. On the other side, it is quite a slow process due to the track-wise generation of clad layers, and the process suffers from low energy efficiency [8]. Recent studies [5,8] show that increasing the cladding speed not only reduces the processing time, but also improves the energy efficiency by decreasing heat loss. As a result of increasing costs of energy, the process efficiency is becoming more important and if the added value of shorter processing time is also taken in to account, it becomes clear that there is a great motivation to increase the scan velocity of the laser cladding process.

High demands on the quality of clad layers make it necessary to have a thorough understanding of phase constitution and functional properties of the coatings deposited at higher cladding speeds. In the case of stainless steel coatings, this seems to be necessary because it has been shown before that the high cooling rate during solidification alters the microstructures and phases of stainless steel weld deposits [9–11]. In other words, rapid solidification of stainless steels may produce deposits with properties different from those observed during conventional solidification which can strongly affect the final mechanical, chemical and technological characteristics of stainless steel deposited coatings [12,13].

In this research, effects of laser cladding velocity on phase constitution, hardness and wear rate of AISI 431 martensitic stainless steel laser deposited coatings are examined and controlling mechanisms are explained. The motivation for selecting AISI 431 as the coating materials was its optimal combination of corrosion and wear resistance. In addition, this alloy has been previously studied as a candidate material for repair applications by laser cladding [14].

2. Materials and methods

A continuous wave IPG fiber laser with a wavelength of 1.07 μm, Beam Parameter Product (BPP) of 22.5 mm-mrad and a variable power up to 3.3 kW was employed to deposit commercial 42C powder from Sulzer Metco (equivalent to AISI 431) with particle size in the range of −140 to +325 mesh on 40 mm diameter rods of AISI 304 austenitic stainless steel. In all experiments, the laser beam was defocused to obtain a laser spot size of 3.3 mm on the surface.
Chemical compositions of the cladding and substrate materials are presented in Table 1. The powder feeding system consisted of Metco Twin 10C powder feeder, argon as the carrier and shielding gas and an ALOtec Dresden GmbH Cu-based side cladding nozzle with a cyclone and 2 mm nozzle opening. Single-layer and five-layer samples were deposited at scanning speeds (V) of 5, 25, 58 and 117 mm/s.

Solidification structures were studied by optical microscopy on the samples prepared by standard mechanical grinding/polishing and etched with Kalling 1 reagent for 5–10 s. The percentage of solid state transformation products was determined by Orientation Imaging Microscopy (OIM) with a Philips XL30 FEG Scanning Electron Microscope (SEM). As the distorted lattice of untempered martensite makes it difficult to get good quality Electron Backscatter Diffraction (EBSD) patterns, using a suitable sample preparation method which produces minimal surface relief was essential. In our current research, the surface preparation procedure recommended by Struers Co. for EBSD analysis of ferrous alloys was used. This procedure consisted of mechanical grinding with SiC-paper number 320 and 9 μm diamond suspension, polishing with 3, 1 and 0.25 μm diamond suspensions and the final polishing with OP-AA suspension [15]. By using this preparation method, the percentage of indexed data was higher than 95% in all of the OIM measurements. EBSD data were obtained by TSL OIM Data Collection 5 and analyzed by TSL OIM Analysis 5.31 software.

Mechanical properties were determined using the Vickers micro-hardness measurement (CSM Revetest) and the pin-on-disk dry sliding test (CSM Tribometer) at room temperature. Pin shape samples with a 6 mm diameter hemispheric head for wear test were cut from the clad layers by wire Electric Discharge Machining (EDM). Pin samples were cleaned with ethanol in an ultrasonic bath and tested against a disk with the hardness of around 970 HV0.5 at a sliding speed of 100 mm/s each for a distance of 1000 m while a normal force of 10 N was being applied. Prior to the test, the disk was polished to a mirror-like finish. The wear volume was calculated by using the equation for a spherical worn cap according to [17]:

\[ V = \frac{\pi d^4}{64R} \]

where \( V \) is the worn volume, \( d \) is the wear scar diameter and \( R \) is the radius of the wear sample tip (3 mm in our case). The wear rate, \( K \) defined as the worn volume (\( V \)) per unit of sliding distance (\( L \)) and of applied force (\( F_N \)) was determined using Eq. 2:

\[ K = \frac{V}{LF_N} \]

Table 1
Nominal composition of the coating and substrate materials (wt.%)[16].

<table>
<thead>
<tr>
<th>Alloy</th>
<th>C</th>
<th>Mn</th>
<th>Si</th>
<th>Cr</th>
<th>Ni</th>
</tr>
</thead>
<tbody>
<tr>
<td>AISI 421</td>
<td>0.2</td>
<td>1</td>
<td>1</td>
<td>15–17</td>
<td>1.25–2.5</td>
</tr>
<tr>
<td>AISI 304</td>
<td>0.08</td>
<td>2</td>
<td>1</td>
<td>18–20</td>
<td>8–10.5</td>
</tr>
</tbody>
</table>

Fig. 1. (a) Effect of cladding speed on cell spacing of single and multi layer deposits. Dashed lines show the fit for \( V^{-0.5} \) dependence, (b) dendritic structure of the coatings with epitaxial growth, (c) and (d) effect of cladding speed on the amount of \( \delta \) (visible as white islands).
3. Results

3.1. Effect of cladding speed on solidification microstructure

Fig. 1a shows the effect of cladding speed on cell spacing in single and multi layer deposits. The higher cladding speeds produced smaller cell spacing with values down to around 9 μm in five-layer and 3 μm in single-layer deposits. A variation of 15% is included in the data of Fig. 1a to account for changes in cell spacing from the bottom to the top of the coating because of local variations in solidification conditions [18]. The difference in cell spacing values of single and multi layer deposits (in spite of their similar cladding speeds) can be attributed to the heat accumulation in multi layer claddings. In both cases, cell spacing followed the empirical power law \( V^{-0.5} \) (\( V \) being the cladding speed) reported previously [18]. Fig. 1b shows an example of cellular dendritic structure of the coatings with an epitaxial growth of the dendrites across the track interfaces and Fig. 1c and d show the effect of cladding speed on the amount of delta ferrite (\( \delta \)). It can be seen, especially at track overlapping areas, that by increasing the cladding speed less \( \delta \) (visible as white islands) was formed.

3.2. Variations in hardness and wear rate

Figs. 2 and 3 represent the hardness and the wear rate of single and multi layer samples deposited at different cladding speeds. The hardness of single-layer claddings was more homogeneous than that of multi-layer deposits. It is obvious from Figs. 2 and 3 that while the properties of five-layer deposits were not sensitive to the cladding speed, higher deposition rates decreased the hardness and increased the wear rate in single-layer samples. The correlation of hardness and wear rate can be explained by the inverse relationship between these two properties when the wear mechanism is constant [19]. It should be mentioned that because of the similar setup and environmental conditions during the wear testing, it is reasonable to compare the wear performance of the test samples. As properties like hardness and wear rate directly depend on the phase constituents of the material, these changes can be regarded as an indication of different phase formation behaviors during solid state cooling. According to the TTT diagram of AISI 431 stainless steel [20], this type of steel has a very high hardenability and to form any transformation product other than martensite, such slow cooling rates are needed that take \( 10^3 \)–\( 10^4 \) s to reach from austenitizing temperature to around 600 °C. Under our processing conditions, for both single- and multi-layer deposits, having these slow cooling rates is virtually impossible and only the transformation of austenite to martensite can occur. This means that different values of hardness or wear rate are indications of different proportions of martensite (as the hard and wear resistant phase in the coating material) and consequently retained austenite as discussed in the following section.

3.3. Quantitative determination of phase constituents

Quantities of retained austenite and martensite were measured in single and multi layer coatings deposited at two extreme cladding speeds, namely 5 and 117 mm/s. Results of these measurements are presented in Fig. 4 which shows that the sample with the lowest hardness and highest wear rate (single layer deposited at highest speed) contains the highest amount of retained austenite. Referring back to Section 3.1, this sample has the smallest value of cell spacing. It has been shown [18] that the refinement of dendritic structure during solidification will stabilize austenite which results in less
martensite, lower hardness and higher wear rates. In the case of current work, such a correlation was available only in single-layer claddings with very fine solidification structures. This is an indication for a threshold above of which the cell spacing has no influence on the solid state transformation of austenite to martensite.

4. Discussion

As mentioned before, by increasing the cladding speed two general trends in the properties of the coatings under investigation were observed: refinement of the solidification structure (smaller cell spacing), and stabilization of retained austenite. In addition, while the refinement of dendritic structure was obvious in both the single- and the multi-layer deposits, noticeable changes in hardness and wear rate were observed only in single-layer coatings with dendritic structures much finer than their multi-layer counterparts. This implies that there is a connection between cell spacing and austenite stabilization which shows itself below some threshold.

It is known that during cooling of austenite, the transformation to martensite does not start until reaching the martensite start temperature \( M_s \), and the extent of transformation at a certain temperature below \( M_s \) depends on the difference between \( M_s \) and that temperature \([21]\). In other words, if there is any parameter that can affect the extent of martensitic transformation at room temperature, it should affect the \( M_s \) temperature. Higher amounts of retained austenite, as observed in the single-layer coatings with a very fine dendritic structure, show that the smaller cell spacing values obtained by faster solidification at higher cladding speeds stabilize the austenite and delay the transformation to martensite by lowering the \( M_s \) temperature.

According to the model proposed by Jiang et al. \([22]\) the dependence of \( M_s \) on the austenite grain size may be related to the probability of finding nucleation sites for martensite embryos which are formed by the overlapping of stacking faults and can be described as a function of grain size reciprocal as the following equation:

\[
M_s = M_s^0 \exp \left( \frac{-B}{D} \right)
\]

in which \( M_s^0 \) is the martensite start temperature calculated based on alloy composition, \( B \) is a constant related to material (which is mentioned to be \( \approx 1 \) for Fe–Cr–Mn–C alloys and not very sensitive to compositional changes) and \( D \) is the value of austenite grain size in \( \mu m \). Using the Andrews equation \([23]\), the \( M_s \) of AISI 431 is calculated to be 195 °C. By plotting Eq. 3 with \( B = 1 \) and \( M_s^0 = 195 \) °C, the graph of Fig. 5 will be obtained which shows that with austenite grain sizes smaller than around 10 \( \mu m \), \( M_s \) temperature quickly decreases.

The underlying mechanism of the reduction of \( M_s \) in a structure with smaller grain size can be explained by the schematic diagram of Fig. 6. According to the theory of martensitic transformation \([24]\), the energy barrier for the formation of a martensitic lath or plate mostly consists of the strain energy required to initiate two types of plastic deformation; a simple shear parallel to the habit plane (the common, coherent plane between austenite and martensite) and a uniaxial expansion (dilation) normal to the habit plane. This means that to initiate the martensitic transformation, austenite should be deformed and consequently, the yield stress of austenite will play a major role in determining the energy barrier of martensitic transformation as this energy barrier is the strain energy necessary to reach the required level of plastic deformation which in turn will be higher for materials with a higher yield stress.

Several researchers have reported a reduction in \( M_s \) temperature as a result of the refinement in primary austenite grain size \([25–28]\). Different explanations ranging from segregation of the active martensite nuclei into limited number of grains \([25]\) to burst transformation of austenite to martensite within a very small temperature interval \([26]\) have been proposed to explain this phenomenon. One popular explanation is that in a coarse grain austenitic structure, the strength of austenite and hence the martensite start temperature \( (M_s^c) \) primarily depends on the chemical composition but in a fine grain austenitic structure, the extra energy barrier \( (\Delta G_{\text{pt}}) \) caused by an increase in yield stress of the material as given by the Hall–Petch relationship \([29]\) requires a greater driving force \( (\Delta G_{\text{pt}}) \) which translates into a lower \( M_s \) temperature. In other words, the strengthening effect of the grain refinement on the parent austenite will make the martensite nucleation and growth more difficult \([27]\).

The question is whether cell spacing can be regarded as grain size. Microstructural investigation of the studied coatings by SEM and OIM showed that martensite lathes are stopped by the dendrite boundaries in various locations. Fig. 7 shows examples of this observation for one of the single-layer deposits. It can be seen that martensite lathes are stopped at dendrite boundaries which means that dendrite boundaries act as effective obstacles against the growth of martensite lathes. From this point of view, cell spacing can be regarded as austenite grain size because of the same functionality \([18]\). In fact, since martensite growth relies on glissile interfaces which need a certain level of coherency with the parent austenite, the misorientation across dendrite boundaries effectively hinders the growth of martensite lathes or plates \([24]\). In this case, the transfer of slip across grain

Fig. 5. Dependence of AISI 431 \( M_s \) temperature on austenite grain size.

Fig. 6. Schematic representation of the Gibbs free energy changes in martensitic transformation and the contribution of austenite grain refinement.
boundaries as described by Hall–Petch model is not possible and the growth of the martensite crystals will be suppressed [26].

5. Conclusions

The effect of cladding speed on the phase constitution and the final properties of AISI 431 martensitic stainless steel coatings deposited by fiber laser at cladding speeds up to 117 mm/s was studied. The increase in solidification rate at higher cladding speeds decreases the cell spacing down to 9 μm in multi-layer and 3 μm in single-layer deposits. A refinement of the solidification structure did not significantly affect the phase constitution of multi-layer deposits and consequently, the hardness and wear rate of these coatings were not altered. But in single-layer claddings, the significant refinement of dendritic structure stabilizes the parent austenite phase which reduces the hardness and increased the wear rate of single layer coatings deposited at higher cladding speeds. These results show that the structural refinement induced by high speed laser cladding has no effect or even a negative effect on the enhancement of hardness and wear resistance of martensitic stainless steel coatings.

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References