Article

Manufactural Investigations on Dissimilar Laser Cladding and Post-Clad Heat Treatment Processes of Heat-Resistant Ni Alloy on Cu Substrate

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Abstract: Hardness of dissimilar laser clad samples of NiCrBSi alloy on a Cu substrate was investigated, with the aim of optimizing the manufacturing process for high-durability continuous casting molds for steelmaking. The performance of the clads is compared with that of samples prepared by thermal spray coating, and an optimal process is proposed. Dissimilar laser cladding between NiCrBSi alloy and Cu was achieved with a hardness of ~450 HV using a high-power diode laser, and no cracks and pores were observed. Post-clad heat treatment performed below the melting point of the Cu substrate (1357 K) using a furnace (1223 K for 500 min) resulted in a decrease in the hardness to 142 HV, which was attributed to the dilution of the alloy with the soft Cu substrate and changes to the microstructure; the solidification microstructure was almost homogenized during the heat treatment, and secondary boride phases were formed and almost dissolved in the matrix phase. Laser surface heat treatment of the clad metal at 1323 K resulted in a decrease in the hardness (to 359 HV near the surface), with a heat treatment depth of ~1.3 mm. In contrast, the hardness of the as-sprayed coatings was 730–750 HV, which drastically increased to ~1200 HV after laser fusing because of the formation of finely distributed secondary phases. Therefore, to achieve high-durability continuous casting mold components, minimization of Cu dilution is preferentially recommended for the laser cladding of NiCrBSi alloy on Cu substrate. Furthermore, when it is difficult to minimize the Cu dilution during the laser cladding, thermal spraying in conjunction with laser fusing treatment appears to be sufficiently applicable for high-durability continuous casting molds.

Keywords: dissimilar laser cladding; post-clad heat treatment; heat-resistant Ni alloy; microstructure; mechanical property

1. Introduction

To extend the service life of high-performance materials exposed to extremely demanding environments, such as the high temperatures and pressures present in steelmaking, aerospace, and power plant applications, optimization of the local microstructure, and of the mechanical and chemical properties at the surface, is crucial. Therefore, studies on the surface modification of various high-alloy materials have been reported [1–6]. In recent years, the need for high-precision surface modification, such as heat treatment [7–9], surface melting [10,11], nitriding [12,13], shock peening [14,15], and cladding [16,17] based on lasers has also been highlighted.

Among these various studies on laser surface modification, Chun et al. [7] and Park et al. [9] reported that laser heat treatment is effective for die mold surface hardening. Further, Sim et al. [12] and Shin et al. [13] also suggested laser-assisted nitriding for the surface hardening of plastic injection mold steel, which is difficult to harden by martensitic transformation (such as Cu-bearing carbon steel). Yang et al. reported that rapid surface melting via laser enhances wear and fatigue resistance for cast iron brake hubs [10]. Ren et al. also investigated laser shock peening for surface hardening of gear transmission for
20Cr2Mn2Mo steel, and reported that shock peening improves hardness and wear resistance [14]. Furthermore, the laser also enables precise coating for dissimilar combinations of materials. Zhao et al. explored the laser cladding of high-entropy alloys on carbon steel, and reported enhanced wear resistance in NaCl solution as well as in air [17]. Most of these studies commonly emphasized that the advantage of surface modification using lasers is that it allows precise control of the microstructure and mechanical properties for only the required area, with effective productivity.

In the continuous casting process of the steelmaking industry, the molten steel flows from a tundish into the mold, where it solidifies. Therefore, the mold is a crucial component of the overall casting process, as it is subjected to high thermal loads, and also affects the initial shape and quality of semi-finished products (i.e., slabs, billets, and blooms) before they enter the rolling mill lines [18–21]. The continuous casting mold is usually made of Cu alloys, which provide an optimal combination of thermal and mechanical properties. However, because of the low slide wear resistance of Cu alloys when subjected to severe conditions—e.g., the high temperature and pressure during continuous casting—their durability is severely limited [18,21]. Therefore, it is highly important to apply appropriate surface-coating processes to the casting molds in order to improve their tribological properties, thus increasing the quality and repeatability of the steel product and reducing mold repair costs. In this regard, several cost-effective surface-coating processes, such as electroplating [22], thermal spraying [2,4–6,23], and infiltration techniques [24], have been applied. Using these coating processes, even though the wear resistance of the mold was enhanced, poor mechanical bonding at the interface between the coating layer and substrate became a serious problem during service. Previous studies by Chun et al. intensively investigated the surface coating of heat-resistant Ni alloys (NiCrBSi, NiWCrBSi) and Co alloys (Stellite) on a Cu substrate by thermal spraying to manufacture a high-durability continuous casting mold [2,4–6]. In particular, these studies evaluated the applicability of subsequent laser-assisted fusing treatment of the coating to further improve the surface performance and interface bondability. Laser-assisted fusing treatment resulted in the nanostructuring of the sprayed coating, and a considerable increase in hardness. It was also confirmed that the bondability was slightly enhanced by eliminating pores at the interface between the coating and the substrate. In particular, it is well known that cracks frequently occur during the subsequent laser fusing treatment of thermally sprayed coatings; further pre-heating processes are also required during fusing [6], which is regarded as a manufactural disadvantage during manufacturing of the casting mold.

Laser cladding is also considered to be a potential method for applying the surface coating of the casting mold to take advantage of high-energy beam processing and rapid solidification phenomena, which minimize the heat-affected zone and suppress microsegregation. In particular, during laser cladding, dilution with the substrate occurs, which sufficiently increases the bonding strength as compared with that of thermal spraying. However, laser treatment of Cu is difficult because of its high reflectivity of infrared wavelengths and high thermal conductivity [25]. For these reasons, surface coating by laser cladding for the continuous casting mold component has not been widely investigated. Especially, to the author’s best knowledge, there were no systematic investigations into post-clad heat treatment processes for control of microstructure and mechanical properties as compared with thermal spraying. Consequently, to optimize the surface-coating processes for manufacturing high-durability casting molds, investigation of dissimilar laser cladding of heat-resistant Ni alloys on Cu alloys should be performed.

Therefore, in this study, laser cladding and its dissimilar cladability (between NiCrBSi alloy and Cu) were fundamentally investigated with respect to the microstructure and mechanical properties. To this end, a high-power diode laser was used for cladding experiments, and the influence of post-clad heat treatments on the microstructure and surface hardness was systematically examined, and furnace and diode laser surface heat treatments were compared. The results are compared with data for thermal spray coating (from the
author’s previous studies), and an optimal surface-coating process for manufacturing high-durability continuous casting molds is proposed.

2. Materials and Methods

2.1. Materials

In this study, a NiCrBSi-based Metco-12C (Oerlikon®) commercial alloy was used as the powder material for laser cladding, and pure Cu was used as the substrate. The chemical composition of the cladding powder was 7.5 wt.% Cr, 3.5 wt.% Si, 2.5 wt.% Fe, 1.7 wt.% B, 0.25 wt.% C, and the balance of Ni.

2.2. Laser Cladding and Post-Clad Heat Treatments

As shown schematically in Figure 1, 10 passes of laser cladding were performed on a pure Cu substrate. The overlapping ratio between each pass was set at 40%. For laser cladding, a high-power diode laser (Laserline®, wavelength of 900–1070 nm) was used with a laser power of 6.5 kW and a cladding speed of 15 mm/s. During cladding, a defocused beam was used, and the diameter at the surface of the substrate was set to 5.5 mm (referentially, the focal length of the laser optics was set to 150 mm at the focal point). After cladding, post-clad heat treatment was performed via furnace or laser surface heat treatment methods, and the microstructural evolution and mechanical properties of the samples were compared. Furnace heat treatment was performed at 773, 873, 973, 1073, 1173, and 1273 K, considering the melting point of Cu (1357 K). The effect of the heat treatment temperature on the microstructural and mechanical properties of the clad part was evaluated by applying isothermal heat treatments at the target temperature for 20 min, followed by water quenching. The influence of the isothermal holding time was investigated by isothermal heat treatment at 950 °C for 60–500 min, followed by water quenching.

![Figure 1. Schematic description of the laser cladding and post-clad heat treatment methods (furnace and laser heat treatment).](image)

The laser clad metals were also subjected to laser surface heat treatment. Unlike the furnace heat treatment, which used temperatures below the melting point of the Cu substrate, the laser surface heat treatment produced temperatures above the substrate’s melting point. A diode laser (TeraBlade Laser, TeraDiode Inc., Wilmington, MA, USA; wavelength of 900–1070 nm) was used, and the laser’s beam dimensions were set to 24 × 1 mm², considering the width of the overall clad metal (to cover the entire clad metal at once). Laser beam irradiation was performed with temperature control applied in real time. The laser power was automatically controlled to maintain the surface temperature during the treatment. To monitor the heat treatment temperature at the surface of the clad metal, a pyrometer (LASCON®) was positioned coaxially with the laser beam. This
pyrometer was calibrated using a black body source. The surface temperature of the laser heat treatment was set to 1323 K, considering the solidus temperature of Metco-12C alloy (1324 K calculated by Thermo-Calc software), with a laser scan speed of 1.0 mm/s, and a focal length of 310 mm.

2.3. Microstructure and Mechanical Properties

The cross-sectional microstructures of the treated specimens were observed using optical microscopy (OM; Olympus, BX51M, Olympus, Tokyo, Japan) and scanning electron microscopy (SEM; SNE-4500M, SEC, Suwon, Korea). The microstructure and elemental distribution in the treated zone were analyzed using electron probe X-ray microanalysis (EPMA; JXA-8530F, JEOL, Tokyo, Japan). To confirm the effect of the post-clad heat treatment on the mechanical properties of the clad metal, Vickers hardness tests (Mitutoyo, HM-100) were performed with a testing load of 0.25 N and a dwell time of 10 s.

3. Results

3.1. Microstructure and Mechanical Properties of NiCrBSi Clads

Figure 2 shows the representative (a) surface appearance and (b) cross-sectional macrostructure after 10 passes of NiCrBSi laser clads on a Cu substrate. The overall dimensions of the clad metal at surface appearance were 110 × 25 mm². The ratio of dilution with the Cu base metal was approximately 35% based on a single deposit, and sound clad metal was obtained without cracks or pores. Figure 3 shows the microstructure of the clad metal observed by SEM, where each observation area (A–F) is marked on the schematic diagram of the laser clads. Near the surface of the clad metal (images A–C), the fine solidification structure consisted of columnar dendritic morphology. The average primary dendrite arm spacing was 10 µm, and the secondary dendrite arm spacing was 100 µm, and the secondary dendrite arm spacing was ~1 µm. Near the faying surface (images D–F), an unmixed zone between the NiCrBSi alloy and the Cu substrate was clearly observed.

![Figure 2. OM images: (a) top-view and (b) cross-sectional macrostructure of dissimilar laser clads.](image)

Figure 4 shows the results of EPMA analysis of the as-clad sample (a) near the surface of the clad metal (at region B indicated in Figure 3) and (b) near the faying surface (region E). In the clad metal (Figure 4a), solidification segregation behavior was confirmed for Ni, Cr, and Si, along with Cu. Therefore, the Cu from the substrate was highly diluted during the dissimilar cladding. Near the faying surface (Figure 4b), the unmixing behavior of the alloying elements from the NiCrBSi alloy and the Cu substrate was clearly observed (as shown in Figure 3).
Figure 3. SEM microstructures of dissimilar laser clads (backscattered electron images).

Figure 4. Cont.
Figure 4. Backscattered electron (BSE) image and elemental distribution maps analyzed by EPMA for the as-clad specimen: (a) near the surface, and (b) near the faying surface.

Figure 5 shows the hardness distribution of an as-clad specimen along the (a) transverse and (b) longitudinal directions, where the measurement points and directions are defined in the upper schematic. The hardness tended to slightly decrease from the first pass to the final pass, and the average hardness of the clad metal near the surface was 453 HV (Figure 5a). As shown in Figure 5b, a similar average hardness value (451 HV) was confirmed in the longitudinal direction within the clad metal; however, the hardness drastically decreased to 55 HV, which is the hardness of the soft pure Cu substrate. Therefore, the slight decrease in hardness with additional cladding passes was probably due to a continuous increase in the degree of dilution of the alloy with Cu.

Figure 5. Hardness distribution in the (a) transverse and (b) longitudinal directions for an as-clad specimen.
3.2. Influence of Post-Clad Heat Treatment on the Microstructure and Mechanical Properties of Clads

In this section, the influence of the two post-clad heat treatment methods (furnace and laser heat treatments) on the microstructure and hardness of the clad metal are compared, with the aim of optimizing the manufacturing conditions for dissimilar laser cladding. Furthermore, these results are compared with the author’s previous research on thermal spray coating of heat-resistant Ni alloys on Cu substrates [2,4–6].

3.2.1. Furnace Heat Treatment below the Melting Point of Cu

Figure 6 shows the relationship between the heat treatment temperature and the hardness of the clad metal, where the hardness measurement positions are defined in the upper schematic. Each hardness value shown in Figure 6 is the average of 10 measurements. As the heat treatment temperature increased, the hardness of the clad metal continuously decreased compared to average as-clad hardness of 453 HV (Figure 6a). In particular, as the isothermal holding time increased to 500 min at a heat treatment temperature of 1223 K (Figure 6b), the hardness of the clad metal decreased from 275 HV to 142 HV. The hardness of the clad metal near the surface was ~70% of the as-clad hardness.

Figure 7 shows EPMA results of the microstructure developed in the samples after post-clad heat treatment at (a) 1073 K for 20 min, (b) 1223 K for 180 min, and (c) 1223 K for 500 min. For the heat-treated clad metal at the 1073 K–20 min condition, a Ni-based matrix phase with secondary phases consisting of Cr-based borides and carbides were clearly confirmed, i.e., the solidification structure with columnar dendrite morphology (displayed in Figure 4a) was changed by the heat treatment. As the heat treatment temperature and time further increased, the microstructure of the clad metal changed, as shown in Figure 7b,c, respectively. Secondary phases formed and were almost dissolved into the matrix phase (Figure 7c), i.e., the solidification microstructure was nearly homogenized during the heat treatment used here. Furthermore, these microstructural variations are thought to be the cause of the drastic decrease in the hardness of the clad metal observed in Figure 6.
Figure 7. BSE images and elemental distribution maps determined using EPMA for clads near the surface, heat treated at: (a) 1073 K for 20 min, (b) 1223 K for 180 min, and (c) 1223 K for 500 min.

Figure 8 shows a representative hardness distribution around the faying surface between the clad metal and substrate, and its variation after the post-clad heat treatments. The corresponding measurement positions are marked on the upper schematic of the clad metal. For the as-clad specimen, hardness sharply decreased within the transition zone,
as also indicated in Figure 5b. Unlike the as-clad specimen, with a sharp decrease in hardness at the transition zone, the hardness decreased smoothly after heat treatment at 1223 K, probably due to the mixing of the alloy and Cu homogenizing the interface, as described by the EPMA microstructure shown in Figure 9. Compared with that of the as-clad specimen (Figure 4b), evidence of solute diffusion behavior was clearly observed after the heat treatment (region marked by the white dashed rectangle in Figure 9). Therefore, the smooth transition zone near the faying surface after the heat treatment could be due to solute diffusion.

![Figure 8](image8.png)

**Figure 8.** Effect of heat treatment on the hardness distribution along the longitudinal direction near the faying surface.

![Figure 9](image9.png)

**Figure 9.** BSE image and elemental distribution maps obtained by EPMA near the faying surface for heat-treated clads (1223 K for 500 min).
3.2.2. Laser Heat Treatment above the Melting Point of Cu

To evaluate the heat treatment characteristics above the melting point of Cu, laser heat treatment was performed. Figure 10 shows the typical history of laser power and surface temperature during laser beam irradiation for 100 s. The heat treatment temperature (1323 K) was constant, while the laser power changed over time. Figure 11 shows the hardness distribution along the (a) transverse and (b) longitudinal directions for the laser-heat-treated clad metal at 1323 K. The measurement positions are marked in the schematic, as also shown in the figure. The average hardness of the laser-heat-treated clad metal near the surface was 359 HV (Figure 11a), which was lower than that of the as-clad specimen (453 HV). As shown in Figure 11b, the heat treatment depth of the clad metal was ~1.3 mm, which was defined as the region with lower hardness than the as-clad specimen. It was also speculated that this loss of hardness was related to the microstructural evolution, as shown in Figure 7.

Figure 10. Trends of laser power and surface temperature during laser heat treatment of the clad metal (set temperature at surface: 1323 K).

Figure 11. Hardness distribution along the (a) transverse and (b) longitudinal directions for the clad metal laser heat treated at 1323 K.
3.3. Optimal Dissimilar Coating Process for High-Durability Continuous Casting Mold

The author’s previous studies reported the thermal spray coating of heat-resistant Ni alloys (NiCrBSi (Metco-16C) and NiWCrSiB (1276F)) to a Cu substrate combined with laser fusing treatment to manufacture a high-durability continuous casting mold component [2,4–6]. In this section, considering the results obtained, the dissimilar coatability between laser cladding and thermal spraying was analyzed from the viewpoint of mechanical property. Furthermore, a manufactural crucial point in the dissimilar coating processes was also suggested. These studies measured the hardness values of the as-sprayed coating at 730–750 HV, and the hardness was drastically increased up to ~1200 HV owing to finely distributed secondary phases (carbides and borides) after laser fusing. These hardening behaviors resulted in enhanced wear resistance of the coatings [2,4–6]. Therefore, post-thermal-spray heat treatment significantly increased the mechanical performance of the coatings. In contrast, for laser cladding of the NiCrBSi alloy (Metco-12C) with a Cu substrate together with post-clad heat treatments, the hardness of the clad metal decreased for both furnace and laser heat treatments, which could be regarded as being as a result of dilution with the much softer Cu substrate. In particular, in terms of the bonding strength between the coating and substrate, it is typically recognized that laser cladding has advantages over thermal spraying because of the dilution behavior. However, from the results of this study, the dilution of the heat-resistant Ni alloy with Cu during laser cladding was the reason for the observed softening of the coatings after heat treatment. In other words, minimized dilution of Cu is recommended for the laser cladding of NiCrBSi alloy on Cu substrate. Furthermore, by optimizing the laser fusing conditions, the author’s previous studies showed that laser fusing treatment slightly enhanced the bondability between the coating and the substrate by minimizing voids at the interface [2,4–6]. Consequently, when it is difficult to minimize the dilution of Cu during the laser cladding, thermal spraying in conjunction with laser fusing treatment also appears to be applicable.

4. Conclusions

The dissimilar laser cladding of the NiCrBSi alloy and Cu was investigated, considering their respective microstructures and mechanical properties before and after post-clad heat treatments, with the aim of optimizing the manufacture of high-durability continuous casting molds. The following conclusions were drawn:

(1) Successful laser cladding between NiCrBSi alloy and Cu was achieved using a high-power diode laser, and a sound clad metal without cracks or pores was obtained, with a hardness of ~450 HV.

(2) In the case of furnace post-cladding heat treatment, the hardness of the clad metal continuously decreased with increasing temperature to 142 HV (at 1223 K, 500 min), i.e., a 70% decrease compared to the as-clad sample. This was attributed to the dilution with the softer Cu substrate and the microstructural evolution during heat treatment. The solidification microstructure was almost homogenized during the heat treatment, and boride secondary phases formed and almost dissolved into the matrix phase.

(3) For the laser surface heat treatment of the clad metal at 1323 K, changes to the top ~1.3 mm of the sample were observed, and the average surface hardness was 359 HV. Compared to the hardness of the as-clad specimen (453 HV), the laser heat treatment also resulted in a much smaller hardness loss than the furnace heat treatment. In contrast, the hardness of the as-sprayed coatings (730–750 HV) increased up to ~1200 HV, which was correlated with the microstructural features of the finely distributed secondary phases (carbides and borides) after laser fusing treatment.

(4) In conclusion, considering the mechanical performance and microstructural features, minimization of Cu dilution is preferentially recommended for the laser cladding of NiCrBSi alloy on Cu substrate. Furthermore, when it is difficult to minimize the Cu dilution during the laser cladding, thermal spraying in conjunction with laser fusing treatment appears to be sufficiently applicable for high-durability continuous casting molds.
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