

M. ROZMUS-GÓRNIKOWSKA¹, S. DYMEK¹, M. BLICHARSKI¹,
Ł. CIENIEK¹, J. KUSIŃSKI¹

MICROSTRUCTURE OF 309 AND 310 AUSTENITIC STAINLESS STEEL CMT OVERLAYS ON THE 16Mo3 PRESSURE VESSEL STEEL

The aim of this work was to characterize the changes in microstructure and chemical composition of the austenitic overlays on a pressure vessel steel that occur in the vicinity of the interface between the overlay and the base material. The investigations were carried out on a 16Mo3 boiler pipes weld overlaid by 309 and 310 steels.

The microstructural examinations were performed on longitudinal cross-sectioned samples. The qualitative and quantitative chemical composition analyses on metallographic samples were determined on Scanning Electron Microscopy (SEM) by means of Energy Dispersive Spectrometry (EDS).

The article analyzes the influence of the solidification sequence in both types of steel on final microstructure.

Keywords: 309 austenitic steel, 310 austenitic steel, weld overlay coating, CMT, SEM, EDS

1. Introduction

The protection of natural environment become nowadays a great challenge for rapidly developing industry. In this context, the reduction in emission of the harmful nitrogen oxides NO_x and sulfur compounds by fossil power as well as waste incineration plants is an important issue that must be taken into account in further development. The NO_x is the primary constituent of smog and attributes to acid rains. The decrease of air pollution with NO_x constitutes an important problem all over the world [1]. The easiest way of reducing the amount of nitrogen oxides, and also supreme from an economical point of view, is to carry out combustion at lower temperatures (below 1300°C). This is realized by delaying the mixing of fuel with oxygen. Less amount of oxygen in the combustion atmosphere decreases the burning process temperature. However, the reducing rather than oxidizing atmosphere speeds up corrosion of boiler elements, like pipes or walls, that are usually made of relatively inexpensive boiler steels. Also sulfides, chlorides and other compounds deriving from combustion processes accelerate corrosion of steel-made construction components. That is why, these components are overlaid by higher resistant materials like nickel alloys or less expensive austenitic stainless steels. The main element in these alloys that assures their corrosion resistance is Cr, while the

appropriate content of Ni grants the austenitic structure. Such overlays are produced by welding methods, usually conventional gas metal arc welding (GMAW).

The candidates for this application are 309 and 310 austenitic stainless steels. Though the austenitic stainless steels are less expensive than nickel alloys they have to comply severe requirements to serve as a replacement of Ni-alloys [2]: the amount of ferrite must be less than 8%, the overlay hardness can not exceed 200 HV10, the hardness of heat affected zone should not be lower than 350 HV10, the amount of Cr in 309 and 310 overlays should not be lower than 20% and 24,5% respectively. Additionally, the beads overlapping should be at least 50% and the overlays should be metallurgically tied to the base steel without microcracks, voids or pores. The small amounts of ferrite in the weld overlays is beneficial since it eliminates the susceptibility to solidification cracking, however, larger amounts of ferrite (above about 10%) decrease corrosion resistance, ductility and fracture toughness. For that reason, if the content of austenite former elements in 309 steel, like Ni, C, N, is too small, too much ferrite may appear in microstructure. On the other hand, the 310 steel is fully austenitic and its corrosion resistance is high, however it is susceptible to solidification cracking unless the cumulative sulfur and phosphorus content $S + P < 0.002\%$.

¹ AGH UNIVERSITY OF SCIENCE AND TECHNOLOGY, FACULTY OF METALS ENGINEERING AND INDUSTRIAL COMPUTER SCIENCE, AL. A. MICKIEWICZA 30, 30-059 KRAKOW, POLAND

* Corresponding author: rozmus@agh.edu.pl



The another issue that should be considered in the case of austenitic steel overlays is mutual dissolution of the overlaid steel and base material that occur in melted metal during the cladding process. This mutual dissolution decreases the chromium content in the overlay and thus deteriorates its corrosion resistance. This may take place during conventional GMAW process. However, newly developed cold metal transfer (CMT) process seems to be an appropriate technique for producing stainless steel overlays. The CMT is a low thermal input process that limits the diffusion of constituent elements in dissimilar welding (overlying can be regarded as dissimilar welding) as well as produces only modest microstructural changes in the base material [3,4].

This study deals with circumferential CMT overlay welding of boiler pipes by 309 and 310 austenitic stainless steels. The main goal was to characterize the changes in microstructure and chemical composition of the austenitic overlay that occur in the vicinity of the interface between the overlay and the base material. In particular, the influence of the solidification sequence in both types of steel on final microstructure is analyzed.

2. Material and experimental procedure

The 16Mo3 steel pipes clad by 309 and 310 stainless steel were investigated. The weld overlays were produced by the CMT technique in a circumferential manner. The cladding was performed in SEFAKO company. The chemical composition of 16Mo3 steel and 309 and 310 steel wires used in this study are shown respectively in Table 1 and Table 2. The diameter of wires used for cladding was 1.2 mm. The overlays were subjected to standard metallographic examinations on sections parallel to the pipe axis and perpendicular to the pipe surface. The polished metallographic sections were subjected to two-step etching: initially the base materials was etched in 2% nital and then the overlay was electrolytically etched in a 10% solution of CrO_2 in water at 1.7 V for 10 seconds. The investigation was carried out on a Axio Imager MAT.M1m Carl Zeiss light microscope and on scanning electron microscopes: Hitachi S-3500N with a Noran EDS spectrometer and FEI Nova NanoSEM 450 with a EDAX Apollo EDS spectrometer. The ferrite content in the investigated samples was measured by Fischer Ferritoscope FMP30 device. The metallographic sections served also for

TABLE 1

Chemical composition of 309 and 310 steel, wt. %

Steel	C	Cr	Ni	Mn	Si	N	Fe
Steel 309	0.022	23.36	13.82	1.98	0.7	0.086	balance
Steel 310	0.009	26.6	20.5	1.53	0.39	0.022	balance

TABLE 2

Chemical composition of 16Mo3 steel, wt. %

Steel	C	Si	Mn	Cr	Mo	Ni	Fe
16Mo3	0.16	0.34	0.65	0.30	0.30	0.30	balance

hardness and microhardness measurements. The measurements were done on a Wilson Wolpert Tucon 2500 tester using 1 kg and 10 kg loads.

3. Results and discussion

The microstructure of 310 steel in the vicinity of fusion line is shown in Fig. 1. Three different zone can be distinguished in microstructure: the heat affected zone (HAZ) in the overlaid pipe, the intermediate zone, i.e. transition zone and fully mixed zone (composite zone). The HAZ microstructure is not uniform. The regions of partly refined and fully refined microstructure as well as the region with well defined grain coarsening can be found in the very vicinity of the fusion line. The austenite that appear in the HAZ during welding transforms upon cooling on the mixture of bainite and ferrite. That is why, the HAZ microstructure is the same as in the welded low alloy steel.

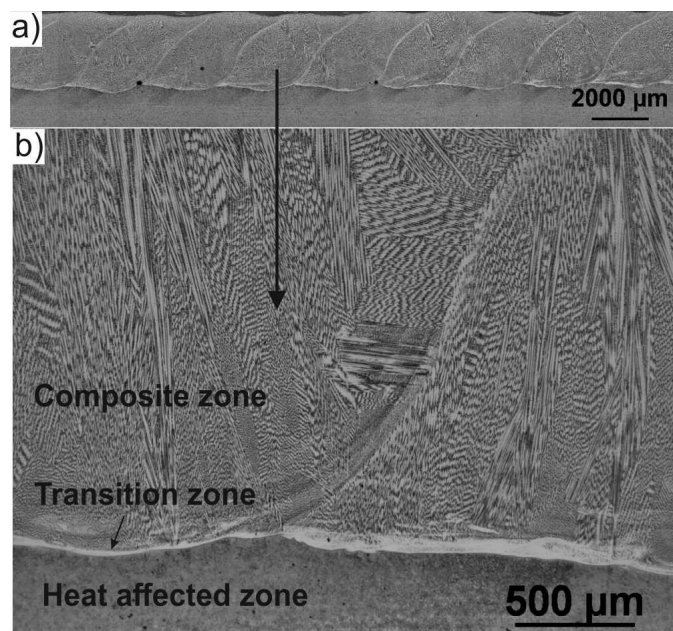


Fig. 1. The microstructure of the 310 steel in the vicinity of the fusion line

The changes in chemical composition in the 309 and 310 overlays as a function of the distance from the fusion line are depicted on Fig. 2. It is clearly visible that the changes from the composition of the base material to the composition of the overlaid steel are initially rapid and then become more gently. The width of the transition zone was about 30 μm in both cases, however the part of the transition zone when the composition changes were the fastest was about 7 μm . The microstructure outside the intermediate zone (composite zone) was austenitic with a small amount of ferrite. The amount of ferrite measured by the Fischer Ferritoscope was about 7% for the 309 steel overlay and less than 0.5% for the 310 overlay.

The 310 steel overlay is characterized by a clear cellular-dendritic microstructure (Fig. 3a). On the other hand, the mi-

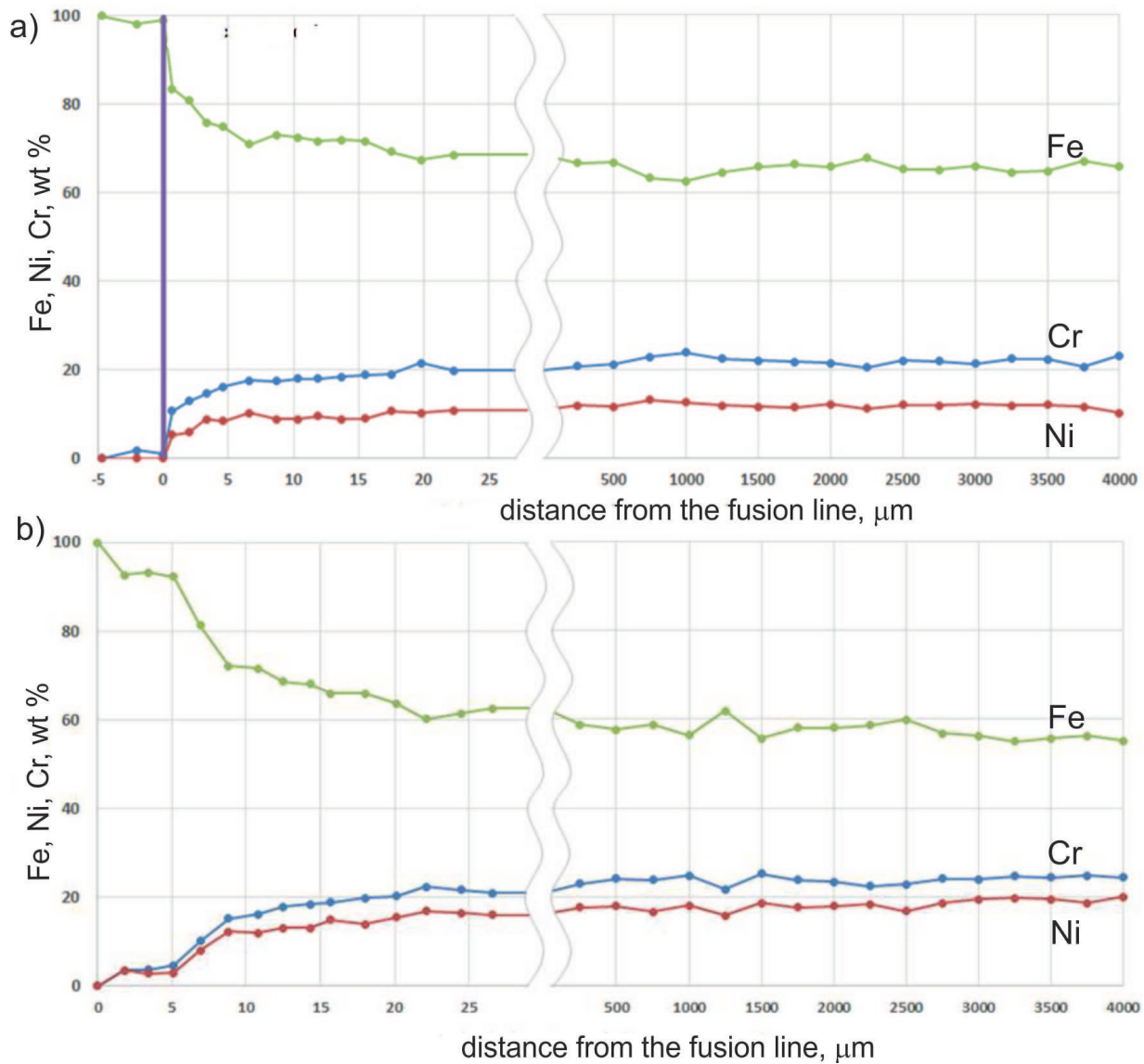


Fig. 2. Distribution of Fe, Ni, Cr (wt. %) as a function of the distance from the fusion line (a) 309 steel; (b) 310 steel

crostructure of the 309 steel overlay is different – the cells or dendrites are not always well-defined (Fig. 3b). There are several reasons for the formation of different microstructures in different austenitic steels, however, it is commonly accepted that the solidification microstructure depends on the ratio of chromium equivalent (Cr_{eq}) to nickel equivalent (Ni_{eq}) [5]. The values of Cr_{eq} and Ni_{eq} can be calculated using the Hammar-Svensson equations:

$$Cr_{eq} = Cr + 1.37Mo + 1.5 Si + 2Nb + 3Ti$$

$$Ni_{eq} = Ni + 22C + 14.2N + 0.31Mn + Cu$$

The ratios of Cr_{eq} to Ni_{eq} for the investigated 309 and 310 steels are equal to 1.51 and 1.27 respectively. The difference in values of Cr and Ni equivalents suggests that both steel will solidify in a different manner. In terms of the Cr_{eq}/Ni_{eq} ratio four different solidification modes can be distinguished in austenitic steels. In the first mode, referred to as “austenitic solidification”, austenite dendrites formed as a primary phase

and δ -ferrite is either absent or appear as a secondary interdendritic phase [6]. This mode of solidification occurs when the Cr_{eq}/Ni_{eq} ratio is smaller than 1.48. The other mode, referred to as “ferritic-austenitic solidification”, occurs when the Cr_{eq}/Ni_{eq} ratio takes a value from the range 1.48-1.95 [7,8]. In this mode, δ -ferrite nucleates as a primary phase in the form of dendrites but austenite appears yet before completion of solidification as a result of eutectic or peritectic reaction. For the Cr_{eq}/Ni_{eq} ratio greater than 1.95 the solidification is “ferritic”, i.e. ferrite is a leading phase during solidification and austenite forms only after completion of solidification [9]. The examined steels belong to first (steel 310 – the Cr_{eq}/Ni_{eq} ratio about 1.27) and second category (steel 309 – the Cr_{eq}/Ni_{eq} ratio about 1.51). The differences between solidification modes of the 310 and 309 steels may explain the formation of different microstructures that form in the both grades of stainless steel overlays. During solidification of the 310 steel overlay the austenite is formed as a primary phase. This austenite remains stable upon cooling to room temperature. Thus, no microstructural changes occur

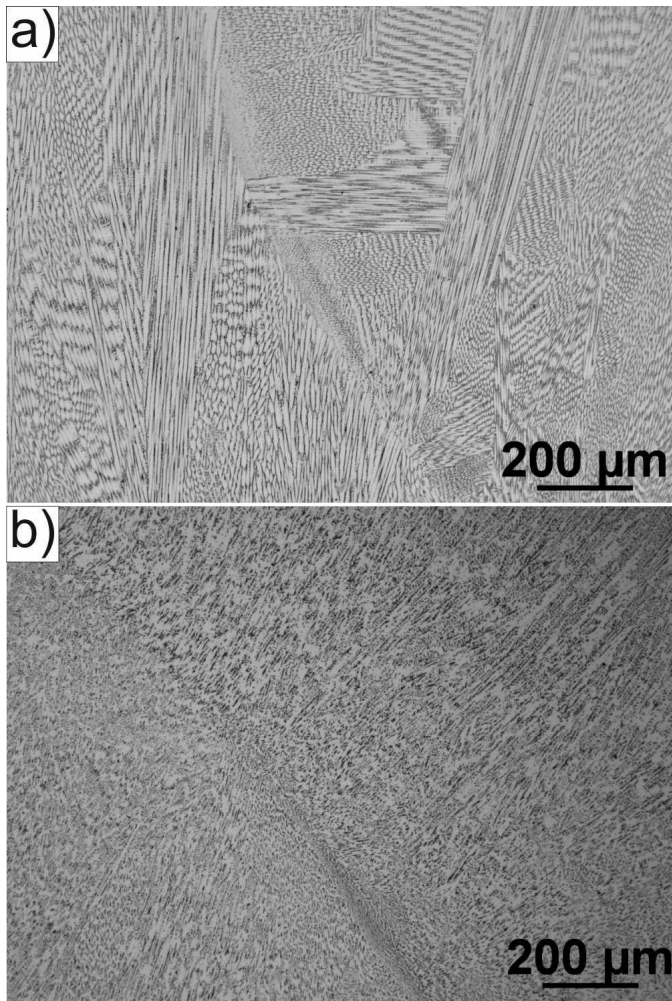


Fig. 3. Microstructure of the weld overlay (a) 310 steel; (b) 309 steel

in this steel and the cellular-dendritic microstructure is easily noticeable. On the other hand, the first phase that crystallizes from the liquid state in the 309 steel overlay is ferrite. The austenite is formed later – initially from the liquid and then, in the solid state when the solidification is completed, form ferrite. That is why the microstructure of the 309 steel overlay (in room temperature) is composed of austenitic matrix and ferrite islands (skeletal ferrite) that were not transformed to austenite. This is the only retained ferrite, though at elevated temperature a large fraction of dendrites were build from ferrite. Thus, the microstructure of the 309 steel overlay is composed of austenite matrix that was not transformed ferrite. Ferrite is in the skeletal (vermicular) and sometimes in a lacy (lathy) form. The formation mechanisms of these morphological forms of ferrite is still unclear. Inoue et al. [10] analyzed the solidification behavior of austenitic stainless steels that solidify in the ferritic-austenitic mode from the crystallographic point of view and attempted to shed new light on the formation mechanisms of the two different types of ferrite morphology. The authors concluded that the cellular austenite as a secondary phase is formed at the dendrite boundaries of the preceding primary ferrite (nucleated on the base metal austenite) during solidification, however, the ferrite and austenite grow independently, in terms of crystallographic

orientation during the solidification, and this growth manner was named by the authors as “independent two-phase growth”. The formation of the vermicular ferrite or the lacy ferrite is primarily determined by the crystallographic orientation relationship between the ferrite and austenite. When the parallel relationship between close packed planes, rather than the Kurdjumov-Sachs (K-S) orientation relationship, is satisfied between the ferrite and the austenite at the solidification stage, the ferrite/austenite interface is planar during post-solidification cooling, and this leads to vermicular ferrite morphology. When the K-S orientation relationship is established between the ferrite and the austenite at the solidification stage, the plate-like austenite grows into the ferrite epitaxially along the habit plane during the post-solidification cooling and this leads to the formation of lacy ferrite [10].

The formation of microstructure in austenitic steel weld overlays can be better understand when chemical microsegregation occurring during solidification is taken into consideration. The microstructure of each weld overlay is a typical cast microstructure of a complex alloy in which the chemically homogeneous liquid phase transforms upon solidification into solid that is no longer homogeneous. The redistribution of elements dissolved in the liquid occurs during solidification. This behavior is governed by thermodynamics and phase diagrams. In addition, this redistribution is influenced by kinetics, i.e. diffusion, overcooling, liquid metal mixing etc. The parameter that describes the redistribution of alloying elements is the equilibrium distribution coefficient k (k_i , for the i th component), defined as the ratio of the composition of solid and liquid at the solid/liquid interface: $k = c_s/c_l$, where c_s and c_l stand for concentrations of a given element in solid and in liquid on the interphase solid/liquid boundary. For weld overlays, especially those produced by the CMT method, solidification is very fast. That is why, it can be assumed that diffusion within the solid phase is negligible compared with diffusion in the liquid. As such, an assumption that the content of an alloying element in dendrite (cell) cores determined in post-solidification condition, i.e at room temperature, corresponds to a value resulted from the equilibrium distribution coefficient k is fully justified. That is why, the values of k can be calculated from EDS measurements performed on appropriate overlay sections. For this purpose, the chemical compositions in dendrite cores c_{cor} were measured and the values of k were calculated from the relation $k = c_{cor}/c_o$ (assuming additionally that Ni + Cr content is constant), where c_o stands for an average content of a given element in the alloy. The chemical composition was measured in SEM as well in TEM. The values of the partition coefficient k calculated for Cr and Ni are: $k = 1.21$ for Cr ($k > 1$) and $k = 0.67$ for Ni ($k < 1$). The results show that dendrite cores are enriched with Cr and depleted with Ni. It is evident that a significant amount of microsegregation is present on completion of solidification with the cell core approaching about 30% Cr while in the adjacent regions the Cr content fell to about 21%. It is interesting that these values correspond closely to the results presented by Brooks et al. [9] who calculated concentration profiles across solidification

cell in a GTA weld of the Fe-23Cr-12Ni alloy (similar to the 309 steel) solidifying as ferrite. The authors predicted a significant amount of microsegregation that was present on the completion of solidification with the cell core containing about 26% Cr and the cell boundary containing about 19% Cr. Though, Brooks et al. pointed out that after solidification and cooling, the solid state diffusion has resulted in a fairly homogeneous chemical composition in the retained ferrite, the relatively high concentrations of Cr found in the present investigation may indicate that microsegregation during solidification rather than solid state diffusion during cooling determined the distribution of particular elements in the overlay. Thus, unlike to Brooks et al. conclusion, the composition of ferrite cores may be regarded as representative for the original solidifying structure [9]. This is likely due to low energy CMT cladding method that largely restricts the diffusion in solid state.

The similar EDS measurements and calculation were performed in the 310 overlays. The analysis of the chemical composition showed that during solidification the interdendritic regions were considerably enriched with Cr and Mn and depleted in Fe. The distribution of Ni in the weld overlay was relatively uniform.

The hardness of 309 and 310 weld overlay were about 170 HV. However, in both cases an abrupt increase of hardness was observed on the interface between the base metal and overlay. As an example the nanohardness of a 310 weld overlay as a function of the distance to the fusion line is presented in Fig. 4. The likely reason for the increase of hardness on the interface between the base metal and overlay is the presence of martensite. According to the Schaeffler diagram, when nickel alloy or austenitic stainless steel is used to clad low-alloyed ferritic steel, between the weld overlay and the steel base, the martensite may form in the transition zone close to the base material [11].

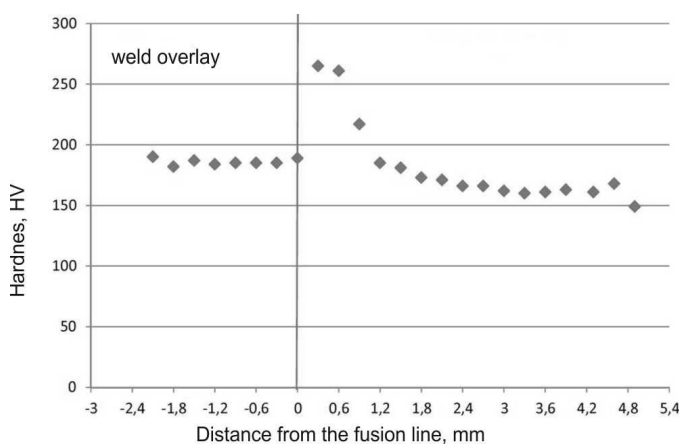


Fig. 4. Hardness profile on the cross section of the 310 weld overlay

4. Summary

- The investigations showed that the 309 and 310 overlays consisted of the following microstructural zones: composite zone, intermediate zone (transition zone) and the heat affected zone.
- In both investigated weld overlays the microstructure of composite zone was austenitic with a small amount of ferrite. The amount of ferrite was about 7 % for the 309 steel and less than 0,5 % for the 310 overlay.
- In case of 309 weld overlay the dendrite cores are enriched with Cr and depleted with Ni. Solidification of 310 steel overlay brings about substantial microsegregation of Cr, Mn and Fe. The interdendritic region were considerably enriched with Cr and Mn and depleted in Fe while the distribution of Ni was relatively uniform.
- In case of 309 and 310 steel an increase of hardness was observed on the interface between the base metal and overlay.

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