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Microstructural development during laser cladding of low-C martensitic stainless steel

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Abstract

Heat input plays an important role in the microstructural development of 12%Cr martensitic stainless steel. The microstructure of low-C 12%Cr martensitic stainless steel resulting from laser cladding was investigated. For 410L a ferritic microstructure is predicted according to the modified Schaeffler diagram for laser welding. Experiments were performed which included the addition of Ni and Mo to in order to obtain a fully martensitic microstructure. Electrolytic etching with oxalic acid indicated that sensitisation occurred at the ferrite grain boundaries for the 410L but no sensitisation occurred with the fully martensitic microstructure of the modified 410L.

Introduction

Sensitisation of low-C 12%Cr steels occurs at the ferrite-ferrite grain boundaries during low heat input welding. Sensitisation is avoided if the austenite potential is high enough to form a continuous martensite network on the ferrite grain boundaries or by increasing the heat input to allow more time for austenite transformation [1]. The heat input during laser cladding ranges typically between 25 – 250 J/mm. Ideally a fully martensitic structure would be required to avoid possible sensitisation during laser cladding. The microstructure of laser cladded 410L is expected to be fully ferritic according to the modified Schaeffler diagram [2]. The addition of Ni, Mo and Co to 410L base alloy to obtain a fully martensitic microstructure was investigated. Mo is added to increase the pitting corrosion resistance (**Eq 1**), but will also stabilise ferrite. Nickel is added to stabilise austenite to avoid ferrite formation and Co will increase the Ms temperature and therefore stabilise martensite (**Eq 2**).

$$PRE = Cr + 3.3Mo + 30N \qquad \text{(Eq 1)}$$

$$Ms\ (°C) = 550 - 350C - 40Mn - 20Cr - 10Mo - 17Ni - 8W - 35V - 10Cu + 15Co + 30Al \qquad \text{(Eq 2)}$$

Rapid solidification during laser cladding results in very fine substructures with interdendritic spacing of typically 2 – 10 micron. The Ms temperature was shown to be a function of the interdendritic spacing as shown in Eq. 3 [3].

$$Ms = Ms(calculated) \times e^{-(1/S)} \qquad \text{(Eq 3)}$$

where S = interdendritic spacing in micron

Experimental procedure

Chemical compositions of laser cladded low-C martensitic stainless steel are shown in **Table 1**. Low-C martensitic stainless steel alloys laser cladded (welded) onto a mild steel substrate. Cladding was performed with a Rofin Sinar DY044, 4.4 kW Nd:YAG laser coupled to a Kuka KR60L30 articulated arm robot and equipped with a Precitec YW50 welding head and coaxial cladding nozzle. A focal length of 300 mm was used and a bead width of 4 mm was obtained by defocusing the laser beam to a distance of 40 mm above from the focal position. Cladding parameters for a layer thickness of 1.0 mm are shown in **Table 2**. The process efficiency factor for Nd:YAG laser cladding is 0.5. Therefore the effective heat input was calculated to be 57 J/mm.

Table 1 – Chemical composition, calculated Ms temperature and Cr and Ni equivalent of the alloys under investigation

Material	C	Cr	Ni	Mn	Si	Mo	Co	*Ms (deg C)	Cr-eg	Ni-eg	PRE
410L	0.03	12.1	-	0.13	-	-	-	239	12.1	1	12
410L + 3%Ni	0.03	12.1	3	0.13	-	-	-	198	12.1	4	12
410L + 5%Ni	0.03	12.1	5	0.13	-	-	-	168	12.1	6	12
410L + 5%Ni + 1.1%Mo	0.03	14.3	5	0.715	0.25	1.1	-	106	15.8	6.3	18
410L + 5%Ni + 2.5%Mo + 5.5%Co	0.03	11.6	5	0.12	0.2	2.5	5.5	225	14.4	6	20
410L + 5%Ni + 5%Mo + 11%Co	0.03	11.1	5	0.1	0.4	5	11	280	16.7	6	28

*Modified Ms temperature for laser cladding

Table 2 – Laser cladding parameters for modified 410L alloys

Alloy	Laser power (W)*	Travel speed (m/min)	Powder feed rate (kg/h)	Carrying gas (l/min)	Comments
410L alloys	2250	1.2	0.9	Ar (4)	Coaxial nozzle, step over 2.0 mm

* Laser power at work piece

Metallographic evaluation and hardness testing was performed on as-welded samples. Electron backscatter diffraction was performed on the 410L+5Ni+2.5Mo+5.5Co cladded sample.

Results and discussion

Microstructural evaluation

The microstructure of the 410L base alloy is primarily ferritic and the microstructures of the modified 410L alloys are fully martensitic as can be seen in **Figures 1 to 6**. Electrolytic etching with 10% oxalic acid @ 4 V for 10 s revealed ditched ferrite grain boundaries of the 410L base alloy indicating possible sensitisation (**Figure 1**) as well as possible sensitised prior austenite grain boundaries of 410L+3%Ni (**Figure 2a**). No sensitised grain boundaries were observed for the 410L+5%Ni alloys when Mo and Co were added (**Figures 3–6**). Post weld heat treatment was performed at 480˚C for 3 hours and at 600˚C for 1 hour. Typical microstructures of 410L+5%Ni+2.5%Mo+5.5%Co and 410L+5%Ni+5%Mo+11%Co are shown in **Figures 8 and 9** respectively.
Shown in **Figure 9** are the predictions of the microstructures for the compositions shown in **Table 1** according to the modified Schaeffler diagram [2].

No delta ferrite was observed for the modified 410L alloys (3%Ni & 5%Ni) and good correspondence was found with the predicted fully martensitic microstructures. The addition of Mo and Co to the 5%Ni 410L alloys also resulted in fully martensitic microstructures. This is also in agreement with the modified Schaeffler diagram except for the 410L+5%Ni+5%Mo+11%Co alloy where the predicted microstructure is a mixture of ferrite and martensite. Co is expected to stabilise austenite at high temperature and to avoid primary ferritic solidification as shown in **Figure 10**. The Ni-equivalent factor for Co, according to the Schaeffler diagram, is expected to be 0.5.

Previous work on type 414 martensitic stainless steel indicated that the presence of ferrite is detrimental to the corrosion resistance due to formation of Cr-depleted zones in the ferrite. No sensitisation occurred for the 410L+5%Ni alloys during laser cladding with a calculated net heat input of 57 J/mm. Due to the fully martensitic structure, carbon is distributed more evenly and carbide precipitation on the prior austenite grain boundaries is not expected. However, if delta ferrite was present, sensitisation could occur in the overlap areas (HAZ on previous weld bead) even at extremely low heat input.

The modified 410L alloys were subjected to post weld heat treatment @ 480˚C for 3 hours and at 600˚C for 1 hour to determine the effect of secondary hardening (due to the possible precipitation of Ni_3Mo (480˚C)) and sensitisation (due to Cr-rich carbide precipitation (600˚C)). As shown in **Figure 7**, no carbide precipitation was observed for the 410L+5%Ni+2.5%Mo+5.5%Co alloys after PWHT at 480˚C or 600˚C. Carbide precipitation and possible sensitisation of the prior austenite grain boundaries occurred after PWHT at 600˚C for the 410L+5%Ni+5%Mo+11%Co alloy as shown in **Figure 8b**.

Hardness

Vickers hardness measurements were performed across the width of the clad layer, 0.5 mm from the top surface with a load of 1 kg. Hardness results are shown in **Figures 11 to 16**. The hardness of the 410L alloy is around 250HV due to the predominantly ferritic microstructure. Addition of 3 and 5% Ni resulted in a fully martensitic structure with an increased hardness of 370 – 380 HV. Addition of 5%Ni+1.1Mo and 5%Ni+2.5%Mo+5.5%Co also resulted in a fully martensitic structure with a hardness of 380 HV. Addition of 5Ni+5Mo+11CO resulted in a fully martensitic structure with a slightly lower hardness of 340 HV compared to the 5%Ni+1.1%Mo and 5%Ni+2.5%Mo+5.5%Co alloys. The lower hardness of the 5%Ni+5%Mo+11%Co alloy is probably due to the coarser prior austenite grain size.

The average hardness of the 410L base alloys prior and after post weld heat treatment is shown in **Table 3**. The hardness values were lower after post weld heat treatment except for the 410l+5%Ni+5%Mo+11%Co alloy where secondary hardening occurred. Secondary hardening observed is probably due to Ni_3Mo precipitation.

Table 3 – Average hardness of modified 410L alloys after PWHT

Alloy	**HV_{1kg} (as welded)**	**HV_{1kg} (PWHT 480˚C, 3h)**	**HV_{1kg} (PWHT 600˚C, 1h)**
410L+3%Ni	367	-	289 (-78)
410L+5%Ni	376	-	295 (-81)
410L+5%Ni+1.1%Mo	384	-	323 (-61)
410L+5%Ni+2.5%Mo+5.5%Co	385	368 (-17)	305 (-80)
410L+5%Ni+5%Mo+11%Co	340	413 (+73)	372 (+32)

Electron back scatter diffraction

The 410L+5%Ni+2.5%Mo+5.5%Co alloy was analysed with electron back scatter diffraction to determine the possible presence and distribution of retained austenite . Previous work performed on laser cladding of martensitic stainless steel revealed interdendritic retained austenite resulting from segregation during rapid solidification. EBSD was performed on a field emission gun scanning electron microscope equipped with an Oxford back scatter detector. Analysis was performed at 30kV with a working distance of 8 mm. Small isolated areas of retained austenite were observed. Shown in **Figure 17** is the typical distribution of retained austenite within the martensitic matrix. Less than 1% austenite was observed with 9% of the pixels not being indexed.

Conclusion

- Fully martensitic microstructures were obtained for the 410L+5%Ni with additions of Mo and Co. No delta ferrite was observed
- Sensitisation of the modified 410L alloys in the as-welded condition did not occur
- Secondary hardening was observed for the 410L+5%Ni+5%Mo+11%Co alloy after PWHT @480˚C for 3h and 600˚C for 1 h
- No carbide precipitation on the prior austenite grain boundaries was observed after PWHT except for the 410L+5%Ni+5%Mo+11%Co alloy @ 600˚C for 1h

Acknowledgement

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References

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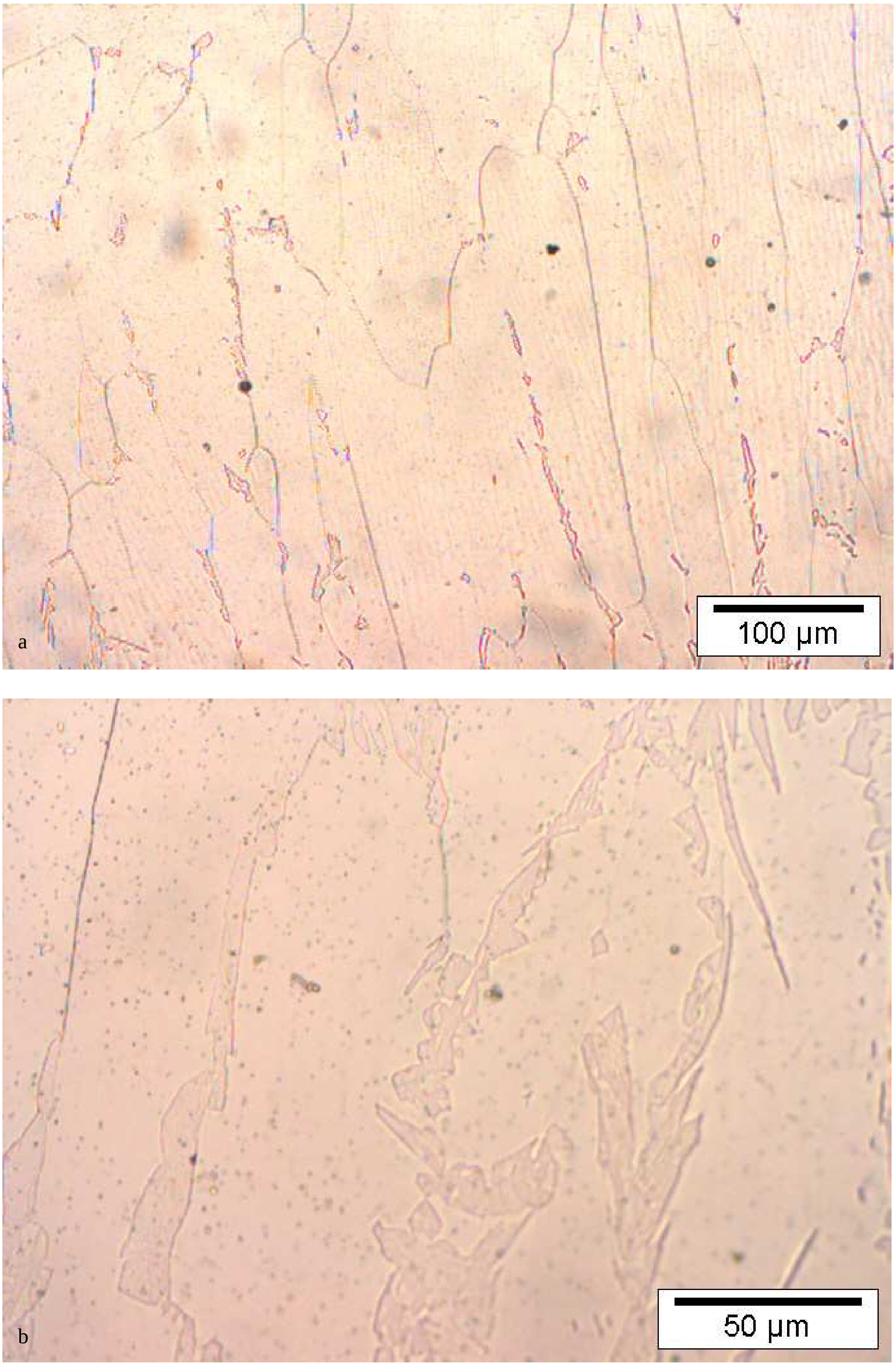


Figure 1 – Microstructure of 410L, oxalic acid, 4V, 10s, a) 200X, b) 500X

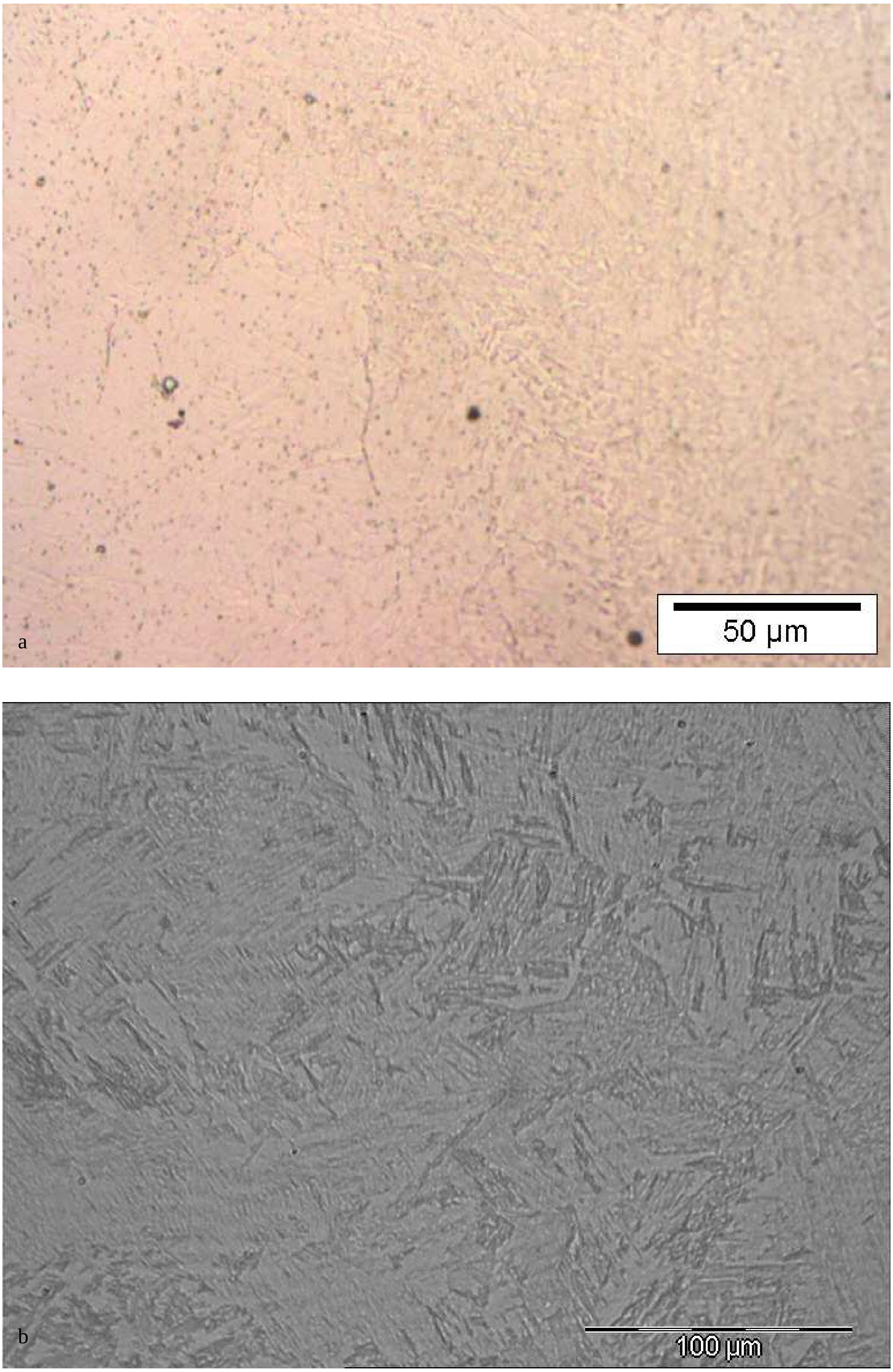


Figure 2 – Microstructure of 410L+3%Ni a) oxalic acid, 4V, 10s, 500X, b) Modified Fry's reagent, 500X

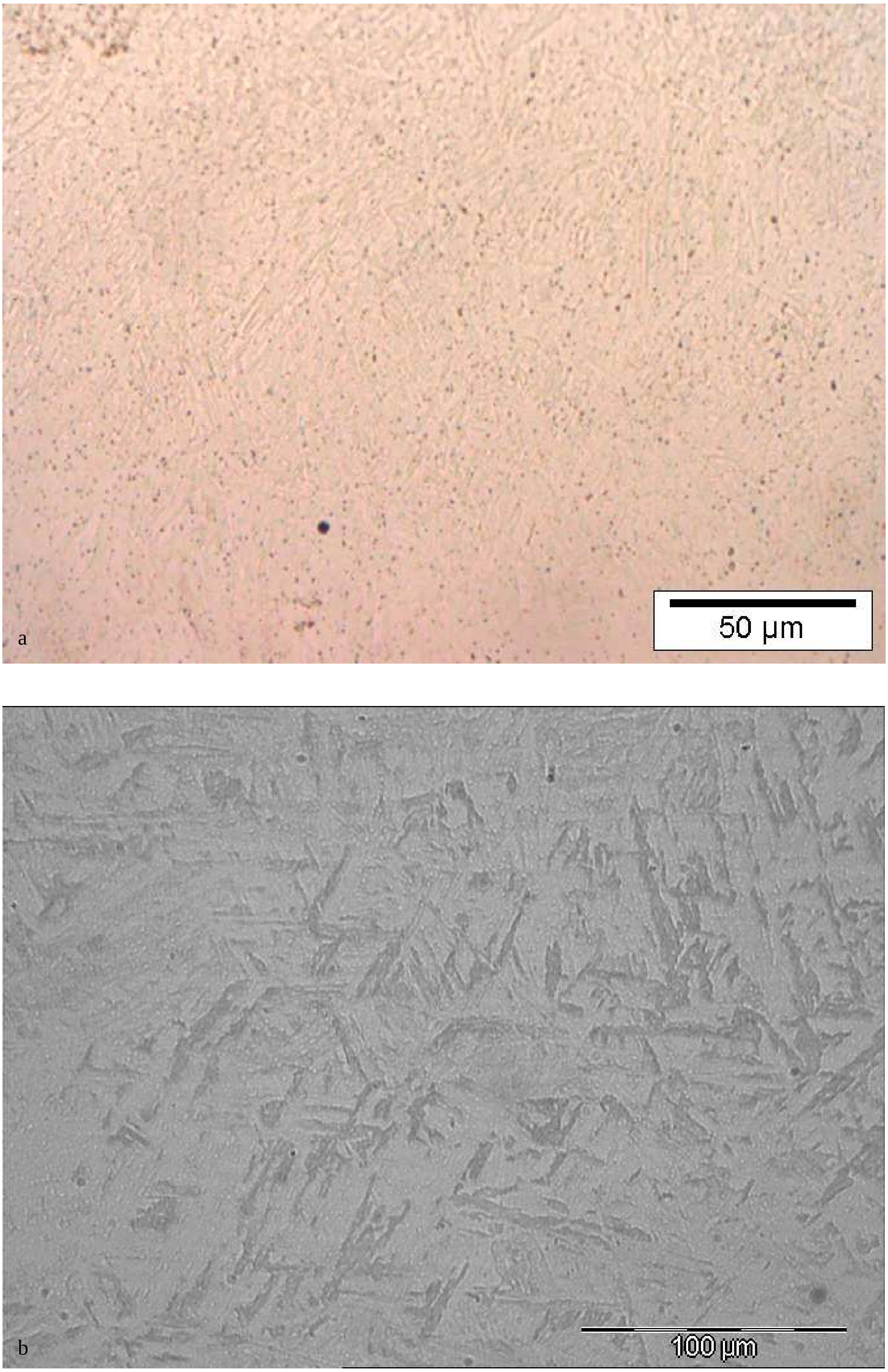


Figure 3 – Microstructure of 410L+5%Ni a) oxalic acid, 4V, 10s, 500X, b) Modified Fry's reagent, 500X

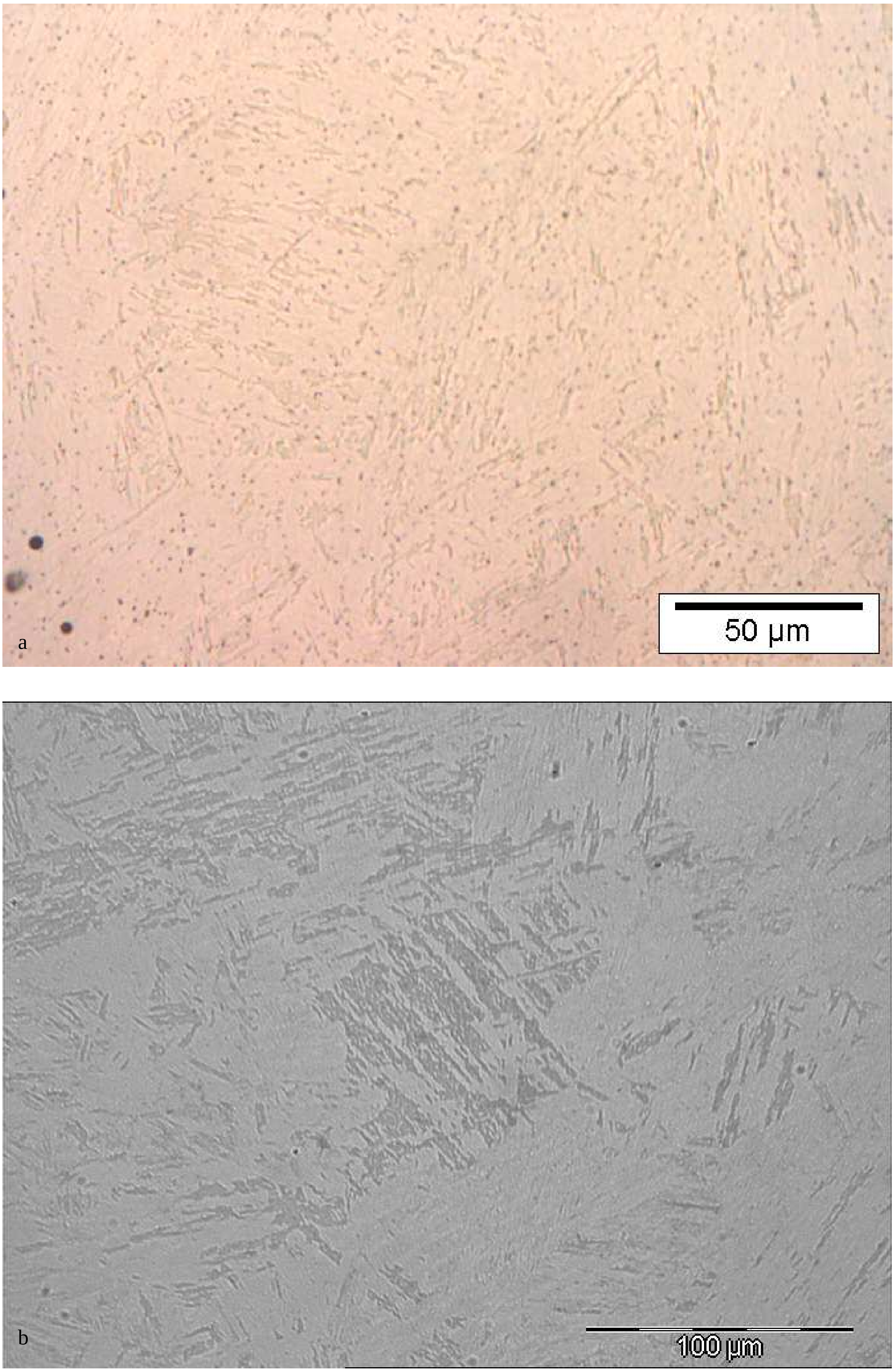
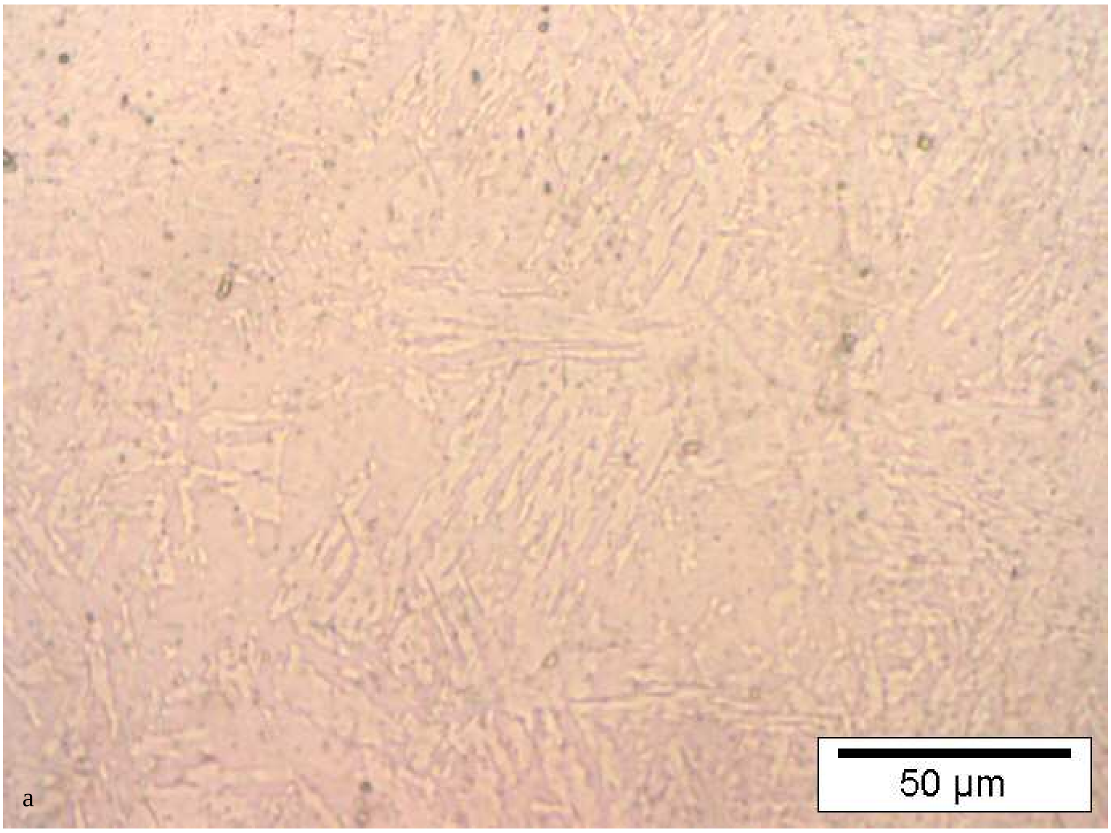


Figure 4 – Microstructure of 410L+5%Ni+1.1%Mo a) oxalic acid, 4V, 10s, 500X, b) Modified Fry's reagent, 500X



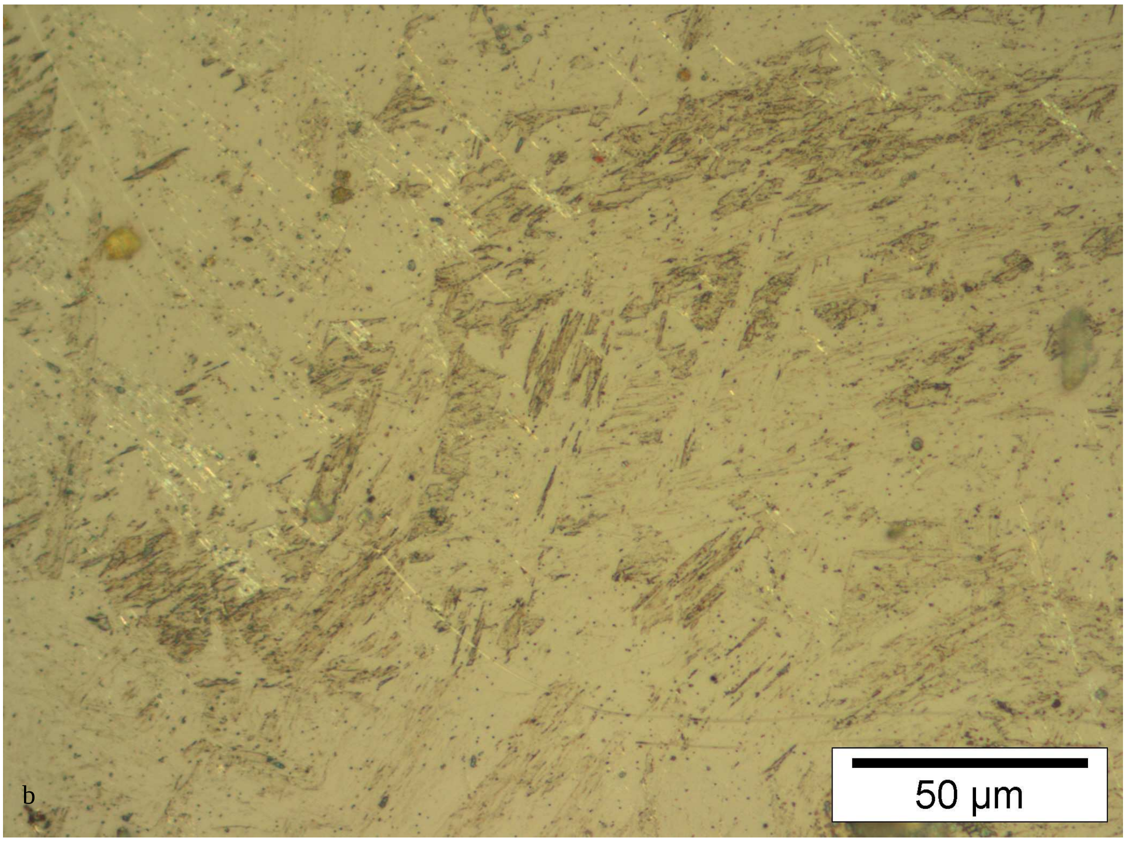


Figure 5 – Microstructure of 410L+5%Ni+2.5%Mo+5.5%Co a) oxalic acid, 4V, 10s, 500X, b) Modified Fry's reagent, 500X

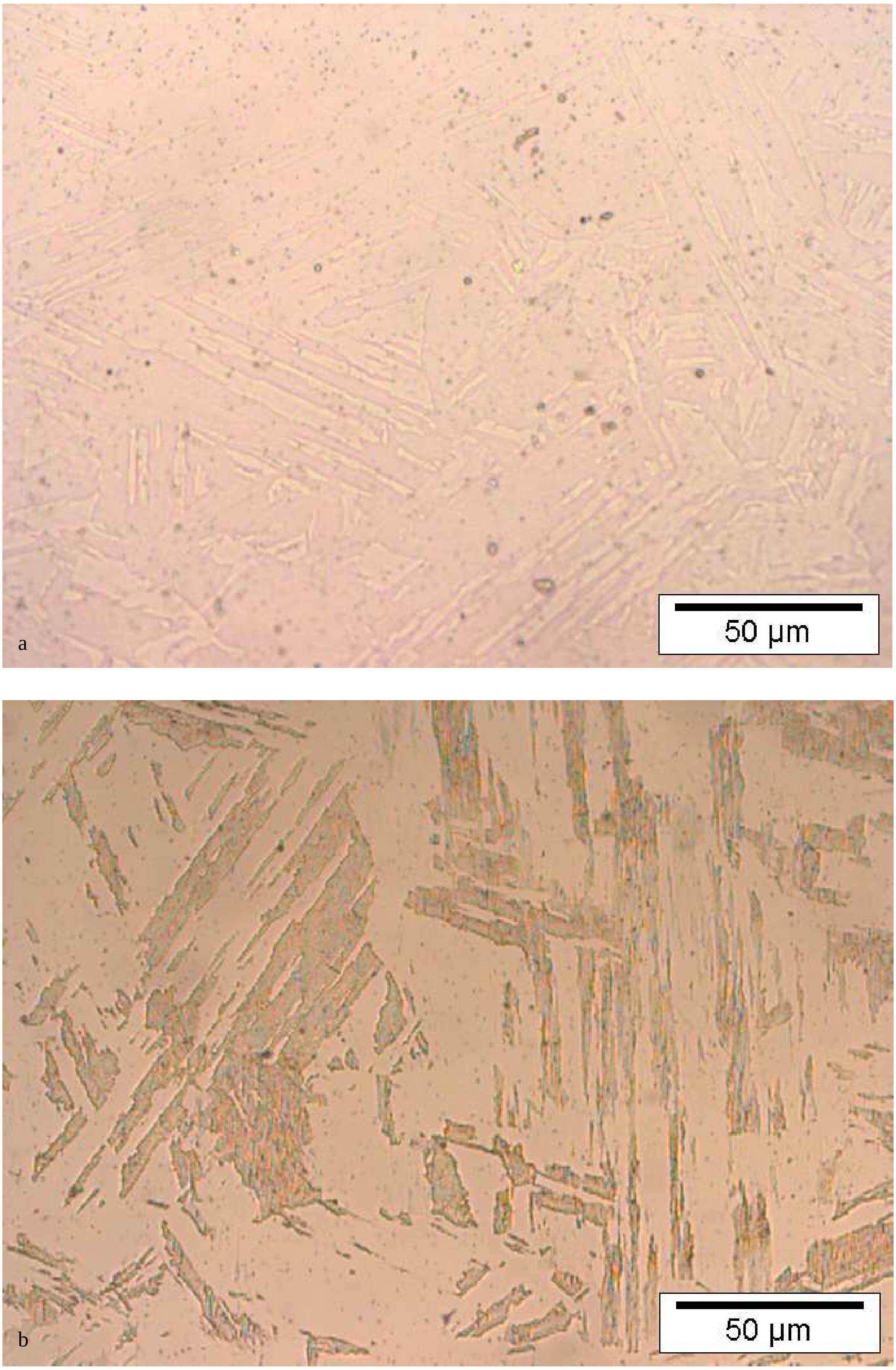


Figure 6 – Microstructure of 410L+5%Ni+5%Mo+11%Co a) oxalic acid, 4V, 10s, 500X, b) Modified Fry's reagent, 500X

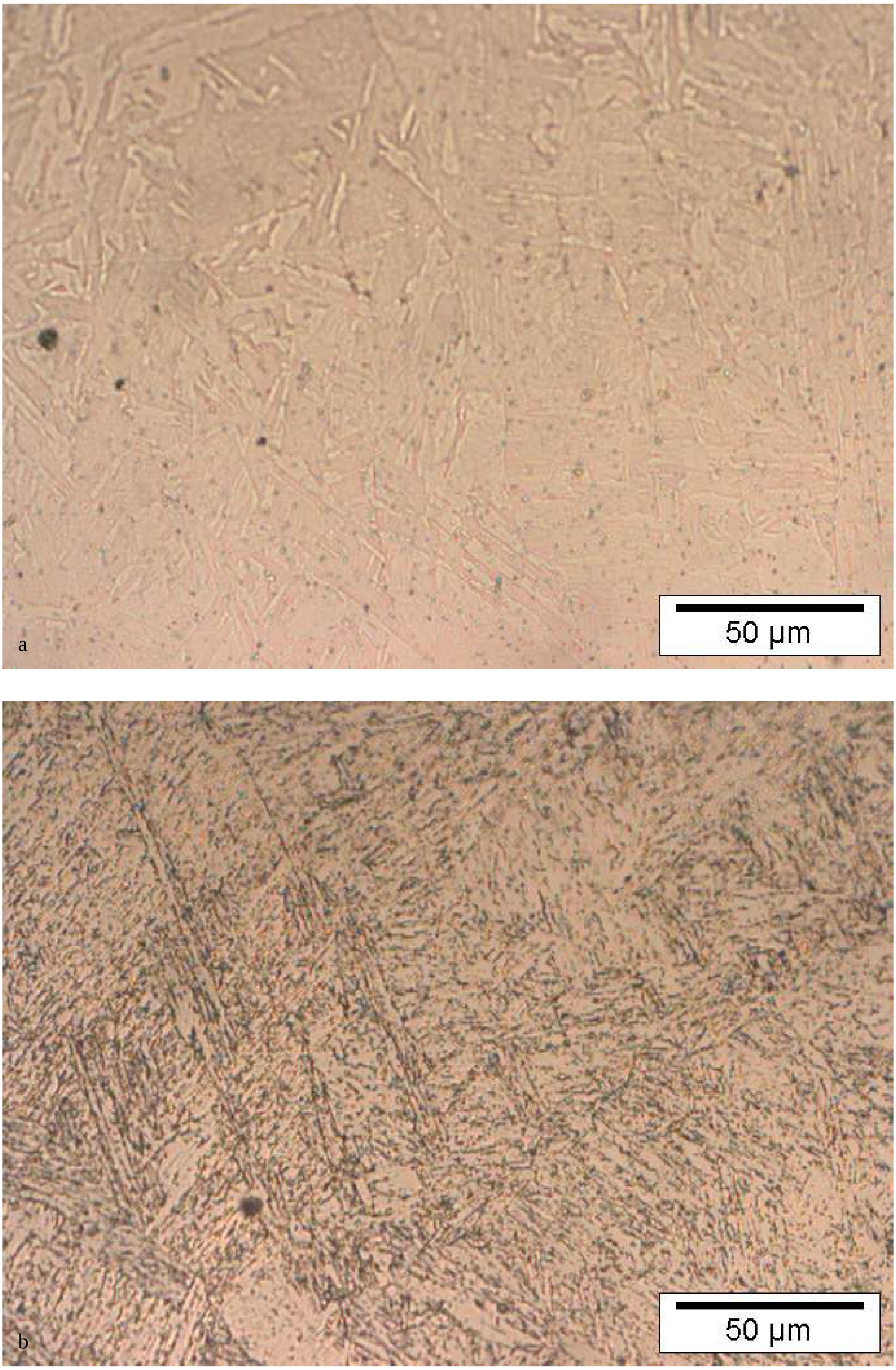


Figure 7 – Microstructure of 410L+5%Ni+2.5%Mo+5.5%Co, oxalic acid, 4V, 10s, 500X, a) PWHT @ 480˚C-3h, b) PWHT @ 600˚C-1h

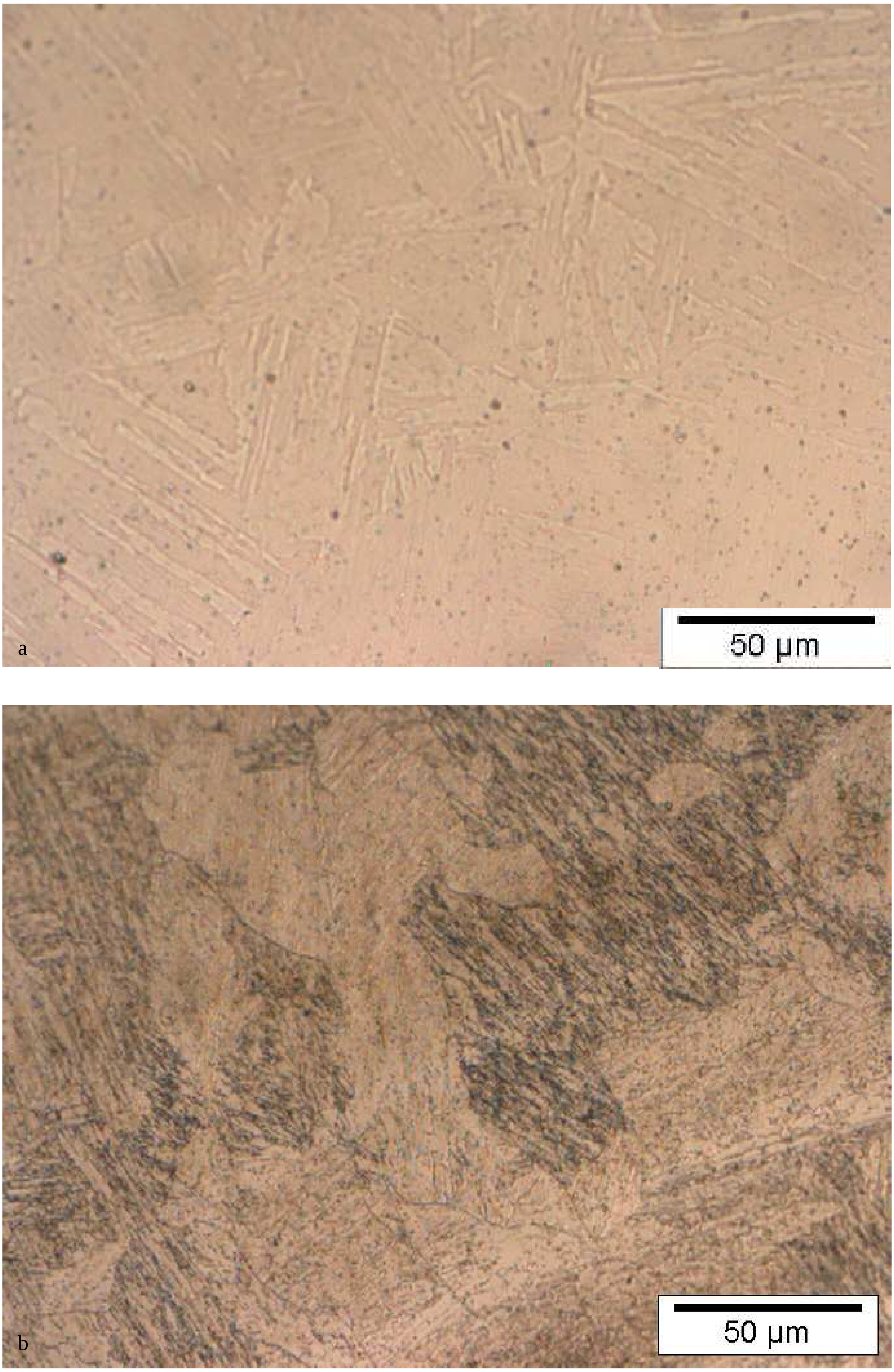


Figure 8 – Microstructure of 410L+5%Ni+5%Mo+11%Co, oxalic acid, 4V, 10s, 500X, a) PWHT @ 480˚C-3h, b) PWHT @ 600˚C-1h

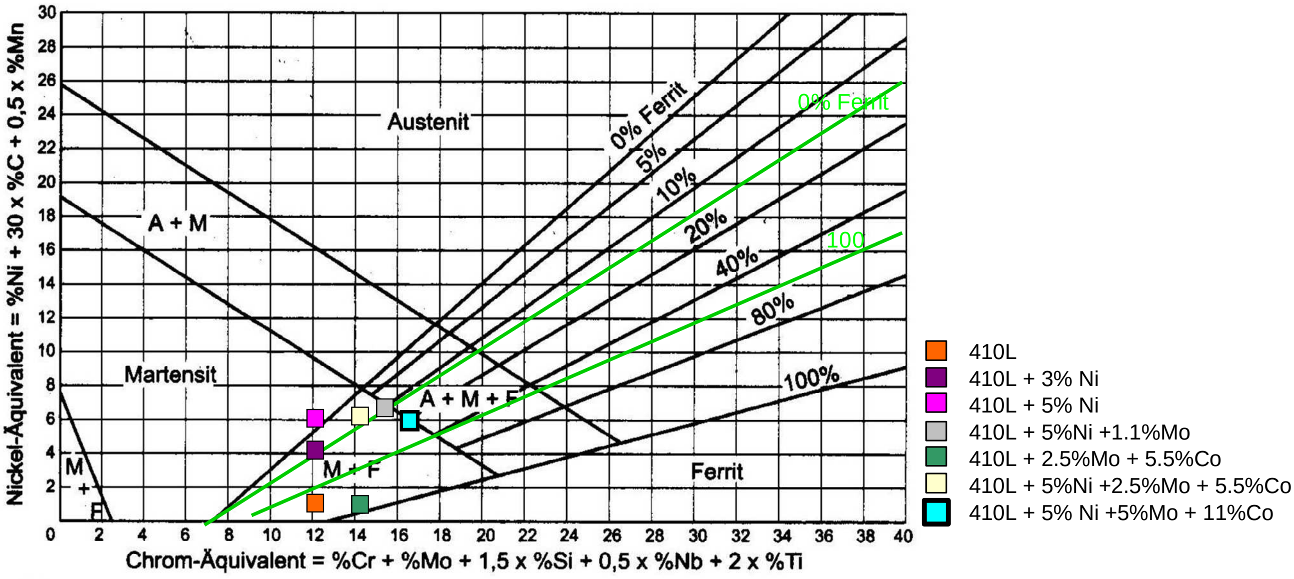


Figure 9 – Predicted microstructure of low-C martensitic stainless steel according to the modified Schaeffler diagram for laser welding [2]

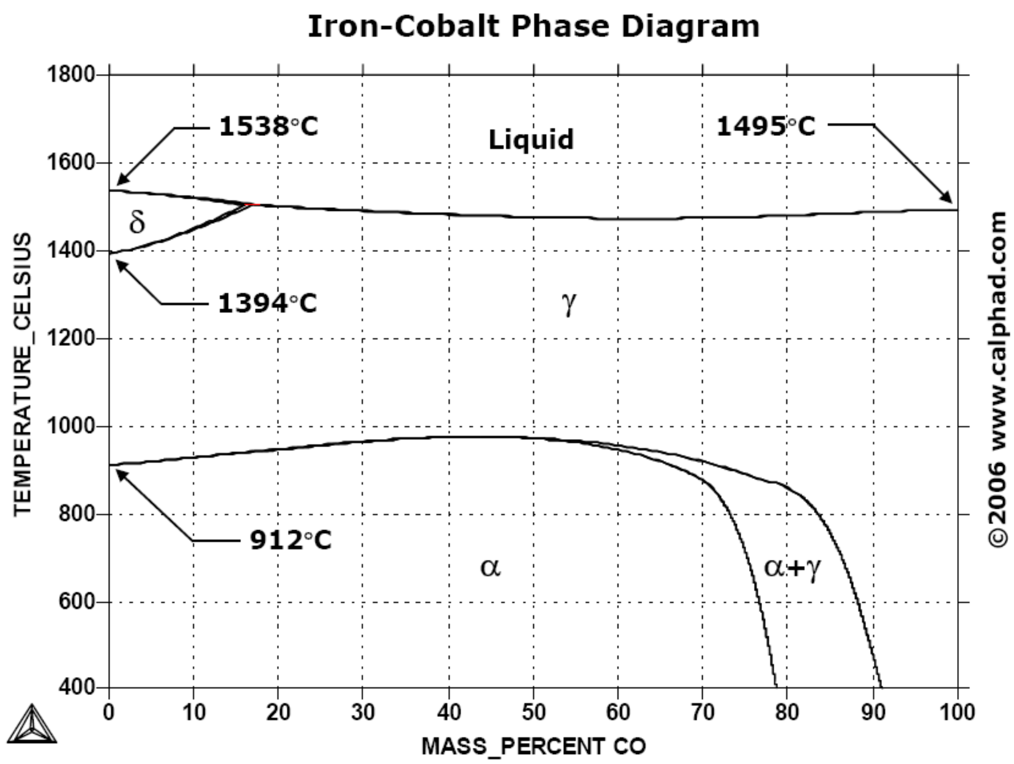


Figure 10 – Calculated Fe-Co phase diagram (Calphad)

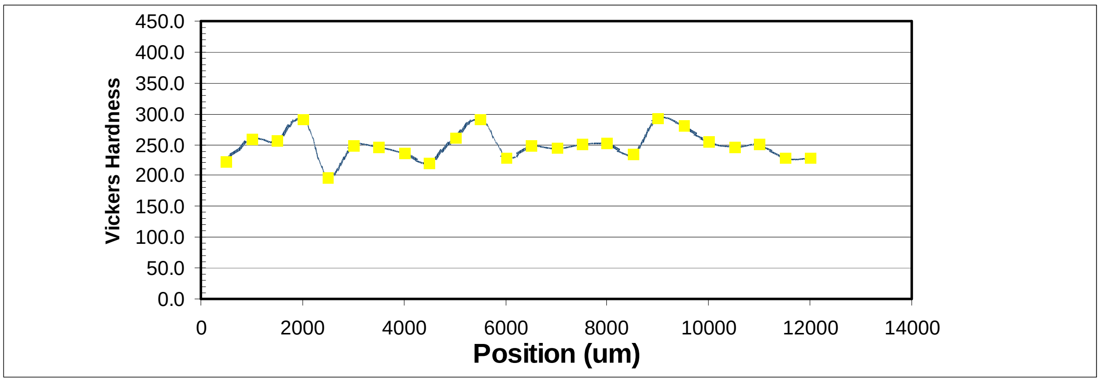


Figure 11 – Hardness of 410L, average 249HV$_{1kg}$

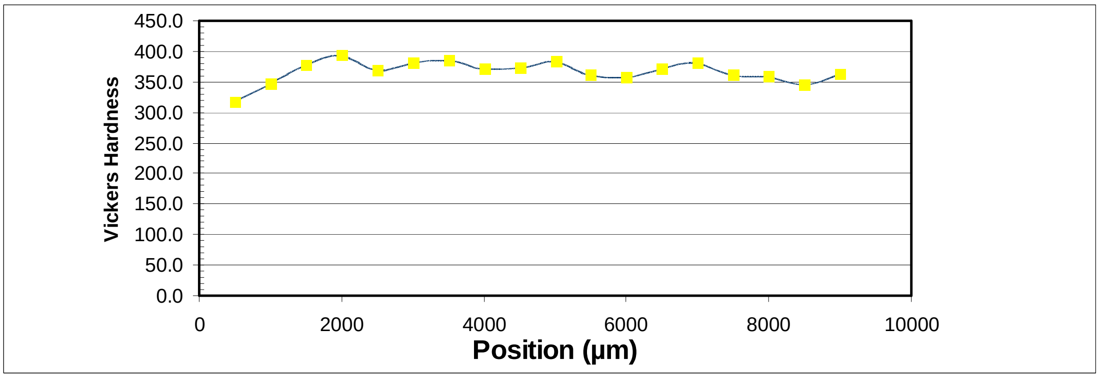


Figure 12 – Hardness of 410L+3%Ni, average 367HV$_{1kg}$

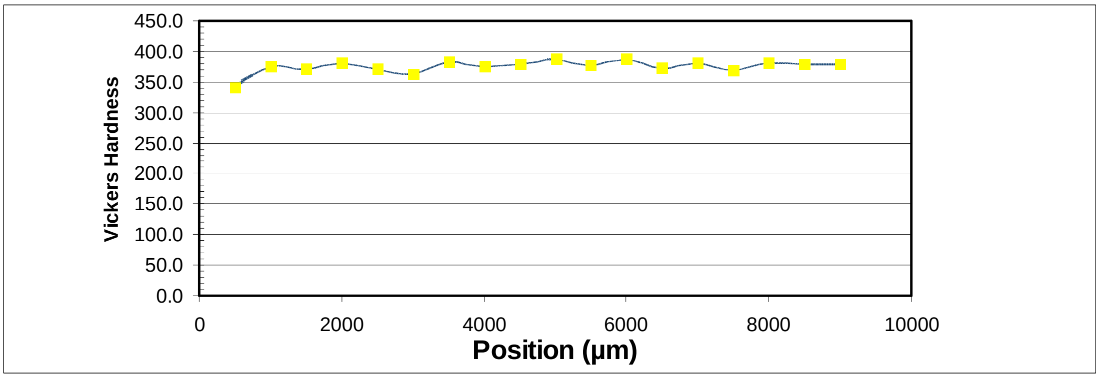


Figure 13 – Hardness of 410L+5%Ni, average 376HV$_{1kg}$

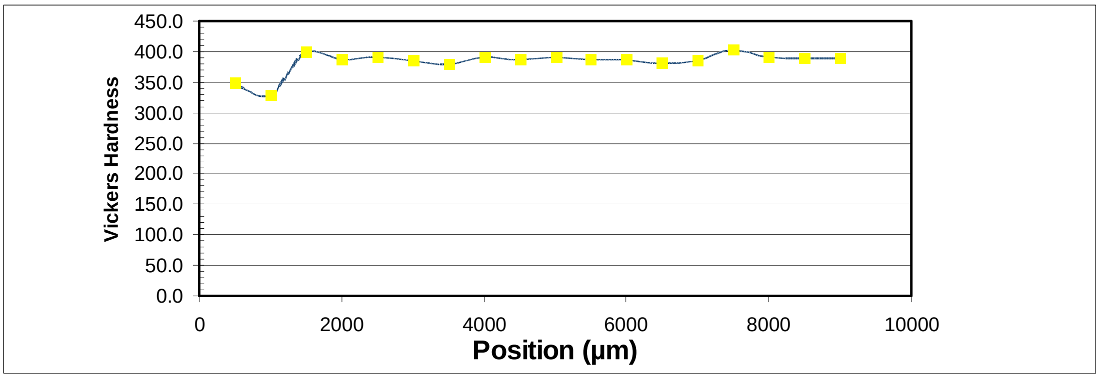


Figure 14 – **Hardness of 410L+5%Ni+1.1%Mo, average 384HV_{1kg}**

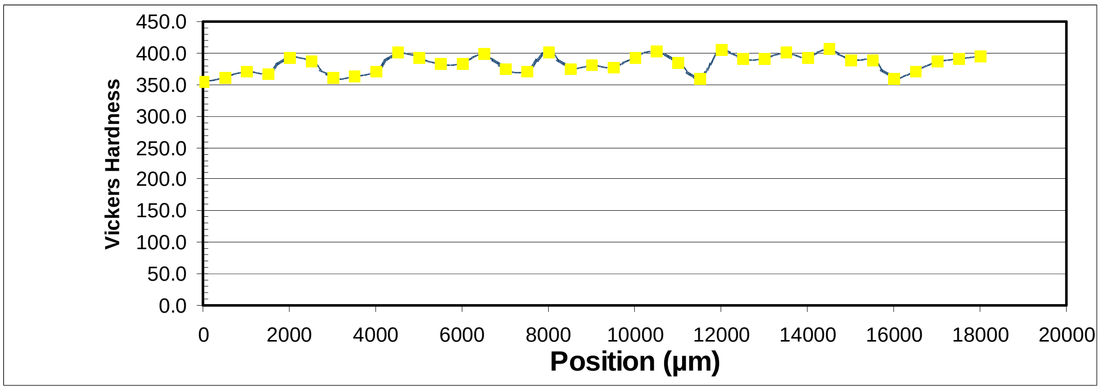


Figure 15 – **Hardness of 410L+5%Ni+2.5%Mo+5.5%Co, average 385HV_{1kg}**

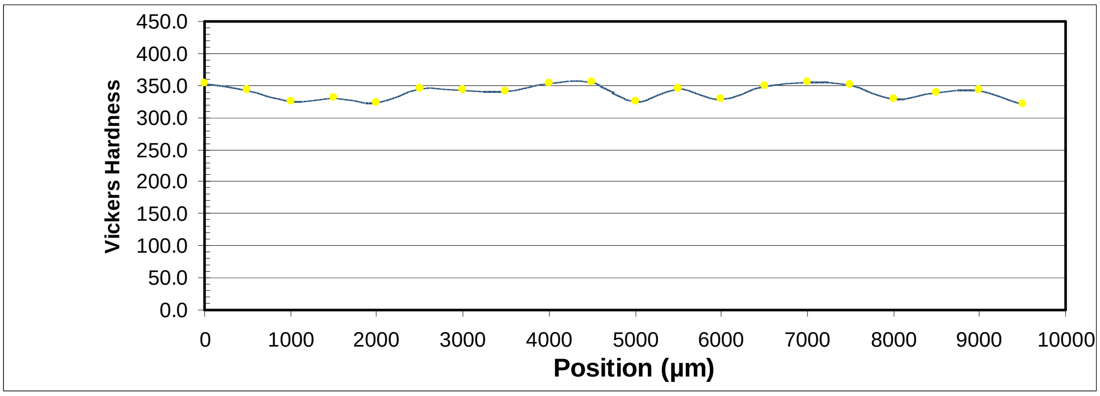
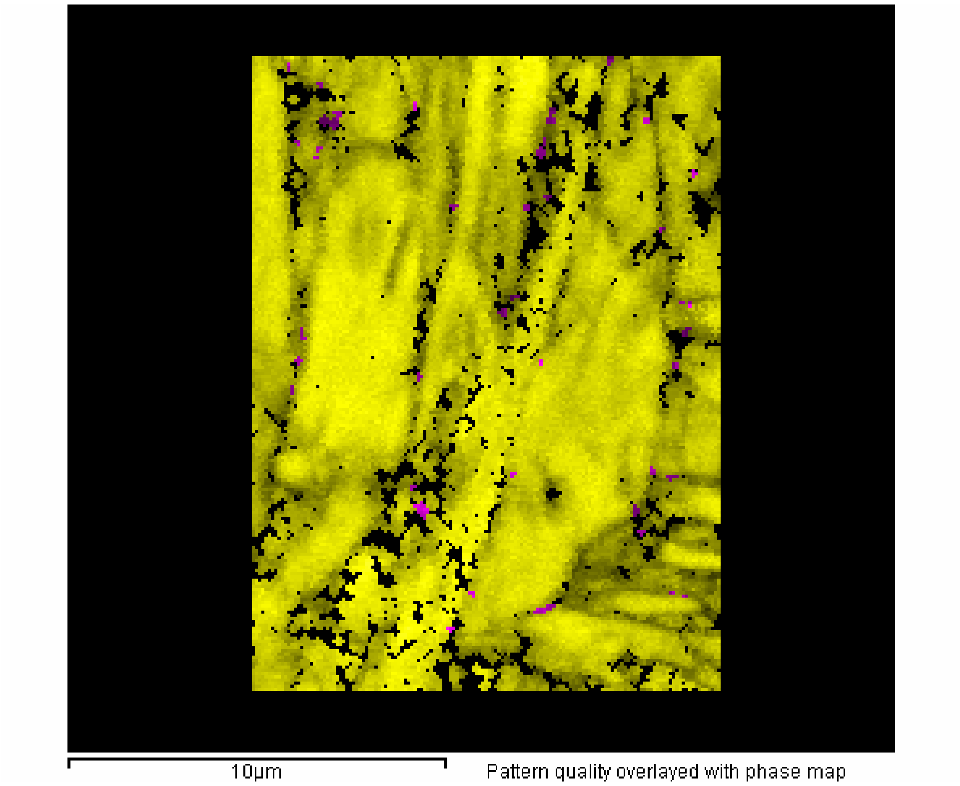


Figure 16 – **Hardness of 410L+5%Ni+5%Mo+11%Co, average 340HV_{1kg}**



Site area: 428.336 µm²
EBSD pixel size: 0.007 µm²
EBSD total pixels acquired: 28565
EBSD acquired area: 206.011 µm²

Phase	%	Count	Area µm²	Detail
None	8.6	2470	17.81	Unsolved points
Fe martensite	90.7	25897	186.77	Tetragonal, BODY
Iron Gamma.cif	0.7	198	1.43	Cubic, FACE

Figure 17 – EBSD phase map of 410L+5%Ni+2.5%Mo+5.5%Co, martensite (yellow) and austenite (pink)