

ORIGINAL ARTICLE

A new approach to etching low-carbon microalloyed steels to reveal prior austenite grain boundaries and the dual-phase microstructure

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Abstract

A modification to picric acid solutions has been undertaken to reveal the prior-austenite grain boundaries in microalloyed steels as a result of elemental segregation. It has been found the maximum addition of sodium dodecyl sulphate plus hydrochloric acid to fully reveal both the prior austenite grain boundaries and the final post-processed structures in these steels.

KEYWORDS

microalloyed steels, post-processed structures, prior austenite grain boundaries, sodium dodecyl sulphate

1 | INTRODUCTION

Determination of the prior-austenite grain size is of great importance in steel due to its strong influence on final microstructure, mechanical properties, and more.^{1–3} The process of revealing the prior-austenite grain size depends on several factors, such as the steel chemical composition, the heat treatments, and other variables that until now have not been well-identified.⁴ Low-carbon alloy steels have been reported as very difficult to etch, and some as ‘impossible to etch’ with picric acid solutions, so that several different reagents have been studied for this purpose.⁵ In this regard, several different approaches have been taken to identify the prior-austenite grain boundaries in microalloyed steels.^{5,6}

Multiple studies have shown that prior-austenite grain boundaries in quenched steels can be revealed using picric acid solutions plus wetting agents.^{7–10} This is because dur-

ing austenitisation and tempering, phosphorus and other trace solute atoms segregate to the grain boundaries.^{11,12} Wetting agents or surface-active agents (surfactants) are added to etchants to improve grain boundary delineation in steels acting on the etching speed or selectivity modification.⁷ Sodium dodecyl sulphate (SDS) has been used as a wetting agent in previous studies, showing good results with low and medium carbon steels.¹³ Other authors also reported that the addition of HCl increases the attack on the phosphorus-rich regions, better outlining the prior-austenite grain boundaries in steels.^{14–16}

In this research, chemical etching based on picric acid with additions of sodium dodecyl sulphate and some drops of hydrochloric acid (HCl) was investigated to reveal the prior-austenite grain boundaries in microalloyed steels at different normalisation temperatures after hot-rolling. Also, the same solution was used to reveal and contrast the bainitic and martensitic grain boundaries of the

TABLE 1 Chemical composition (wt.%)

Steel	C	Mn	Si	Al	V	Mo	Cr	N	Nb
V	0.12	1.11	0.23	<0.01	0.2	0.47	–	–	–
CrV	0.13	1.56	0.19	<0.005	0.21	0.5	0.51	–	–
CrNbV	0.13	1.42	0.25	0.016	0.21	0.51	0.48	–	0.03
AlCrNb	0.25	1.90	0.20	0.04	0.2	0.5	0.25	–	0.06

TABLE 2 Austenitisation temperature of the post-processed steels (wt.%)

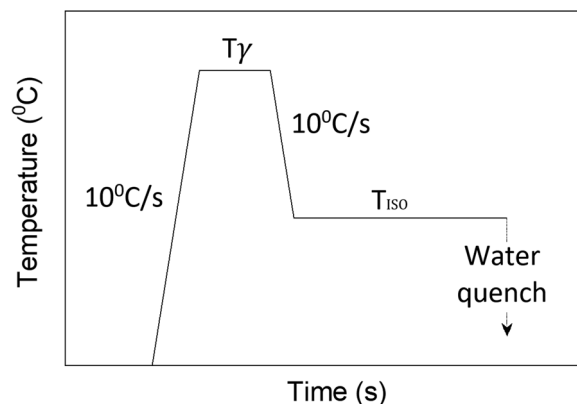
Alloy	Austenitisation temperature
V	1245°C
CrV	1200°C
CrNbV	1245°C
AlCrNb	1200°C

post-treated steels. Results indicate a high-quality delination on microalloyed steels and the possibility for future research on other alloys.

2 | EXPERIMENTAL PROCEDURE

Table 1 lists the chemical composition of three microalloyed steels with different chromium and niobium content. They were vacuum-induction melted in ingots of 80 mm × 80 mm × 100 mm at the University of Sheffield. The ingots were cut to 40 mm thick and homogenised at 1300°C for 2 h, then hot worked in several passes to 7.6 mm thick plates. Specimens of 12 mm × 12 mm × 7.6 mm were cut from the plate's mid-section and then heated in an argon atmosphere from 950°C to 1300°C. The samples were then cut in half, mounted in bakelite and prepared for metallographic analysis to observe the microstructure in the plane of the rolling direction/normal direction.

For the post-treated results, samples of 150 mm long × 15 mm wide × 7.6 mm thick were machined from the plates for dilatometry along the rolling direction. These specimens were solution annealed at the temperatures listed in Table 2. The heat treatments were performed in a Dilatronic dilatometer at the University of Sheffield was used to conduct the heat treatment shown in Figure 1. Specimens were heated at a heating rate of 10°C/s to the austenitisation temperature (T_γ), which is the same as the solution annealing temperature, for 3 min. After that, the samples were cooled at a cooling rate of 10°C/s to the temperature of isothermal transformation, T_{ISO} , during 90 min followed by a water quench to room temperature.

**FIGURE 1** Heat treatment**TABLE 3** Chemical etchants

Chemical etchant	Description
E1	150 ml of distilled H ₂ O + 4.5 g of picric acid (C ₆ H ₃ N ₃ O ₇) + 20 ml of sodium alkylsulphonate ("Teepol") + drops of HCl
E2	150 ml of distilled H ₂ O + 4.5 g of picric acid (C ₆ H ₃ N ₃ O ₇) + between 0.85 and 1.15 g of sodium dodecyl sulphate (C ₁₂ H ₂₅ NaO ₄ S) as wetting agent + between 4 and 12 drops of HCl
E2 – mod 1	150 ml of distilled H ₂ O + 4.5 g of picric acid (C ₆ H ₃ N ₃ O ₇) + 1 g of sodium dodecyl sulphate (C ₁₂ H ₂₅ NaO ₄ S) as wetting agent + 5 drops of HCl

2.1 | Metallographic preparation

All the samples were polished using standard metallographic techniques. After the cutting with abrasive disk, samples were mounted in bakelite for further grinding with silicon carbide abrasive papers grades P400, P800 and P1200 for around 1 min each, followed by polishing with diamond suspension of 6 and 1 μm at low force, low speed for 10 min each. After each grinding samples were cleaned with running water and submerged in isopropanol to prevent oxidation. Table 3 lists the two reagents used to reveal the prior-austenite grain boundaries. Optical microscopy was carried out on a Nikon ECLIPSE LV150 microscope.

2.2 | Preparation of the reagent E2

After several trial-and-error experiments, adequate preparation of the reagent E2 was established. First, the acid and the wetting agent were added to the distilled water. Then,

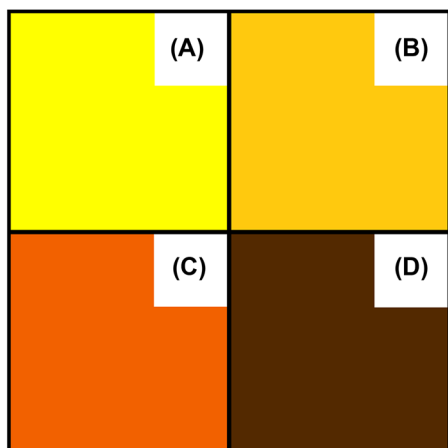


FIGURE 2 Colour evolution of the etching E2

the solution was heated between 75°C and 90°C. During this process, the solid particles dissolve, which changed the colour from (a) to (b) in Figure 2. When the solution reached the desired temperature, drops of HCl were added, followed by the addition of several dummy samples to reduce the solution's strength, and change the colour to match Figure 2C (around 5 dummy samples submerged in the solution for 5 min each). While the specimens etch, the colour of the etch becomes darker as shown in Figure 2D. The solution was found to work until crystals start to appear on the surface of the solution. After the etching process, the samples required a rapid deep clean with water + teepol and then submerge them in isopropanol to protect them from oxidation.

3 | RESULTS AND DISCUSSION

3.1 | Prior austenite grain boundaries revelation

Figure 3A shows prior-austenite grain size of V steel revealed with reagent E1. This solution showed poor results on all steels evaluated in this research.

Reagent E2 showed better results, but small variations in the quantity of each component of the etch show big differences in how well the prior-austenite grain boundaries are revealed. Excess of wetting agent, in this case sodium dodecyl sulphate, results in an inability for the picric acid to reveal the prior-austenite grain boundaries as reported by Nelson.¹⁷ This results in etch pits at the prior austenite grain boundaries (Figure 3B). This problem cannot be solved by the addition of more HCl, as shown in Figure 3C, which only increases the size of the etch pits but does not improve the delineation. Reagent E2 with 1.15 g of sodium dodecyl sulphate works for steels V, VCr and

VNbCr with different alloying additions but with the same carbon content.

Figure 4A shows the V Steel heat treated at 1200°C and etched with solution E2 with 9 drops of HCl for 10 s. The etch is light, with only some of the prior austenite boundaries revealed. In this case, no dummy samples had been etched, so the etchant was at full strength. The colour shown at the right corner of the micrograph corresponds to the colour of the solution when the etch had been completed. Figure 4B shows the effect of swabbing with a piece of cotton produces over the same sample, with the same solution as Figure 4A. The swabbing constantly removes the etch over the smoother intragranular region, but the etch concentrates in the etched grain boundary recesses resulting in better delineation of the grain boundaries compared to the standard immersion approach. If the prior-austenite grain boundaries are not fully revealed as Figure 4C, adding more HCl drops and then reducing the strength of the acid by etching more dummy samples results in all of the grain boundaries being revealed as shown in Figure 4D. An excess of HCl causes very dark lines over the grain boundaries, making them very difficult to measure (Figure 4E).

For steels with 0.1C, the reagent E2 shows very good results at 80°C. At higher temperatures, the delineation of the prior-austenite grain boundaries increases, especially for steels with relative big grains, but the pitting effect appears in form of dark lines along the micrography as shown in Figure 5A and B. Figure 5C shows how the etch E2 delimitates all the prior-austenite grain boundaries at ~95°C, but the pitting stains are much bigger than the ones left by the same solution at lower temperature.

The reagent E2 with 8 drops of HCl at 80°C successfully reveals the prior-austenite grain size of steels with 0.1C at all solution annealing temperatures, even with massive grain growth. Figures 6 and 7 give evidence of the success of this solution to reveal the prior austenite-grain boundaries in steels V, CrV and CrNbV.

3.2 | Revealing bainite and martensite in the post-processed steels

Figure 8 shows the etching of the V steel heat treated at 1245°C T_γ followed by isothermal transformation at 610°C T_{ISO} comparing the E2 reagent and Nital. Figure 8A shows how etching with E2 with 9 drops of HCl at 80°C, applied by swabbing energetically with cotton, produces a well-defined delineation of the grain boundaries of heat-treated steels. Not only the allotriomorphic ferrite which boundaries the prior-austenite grains is revealed with this reagent, but also the martensitic and bainitic regions at grain boundaries. It represents a good improvement from

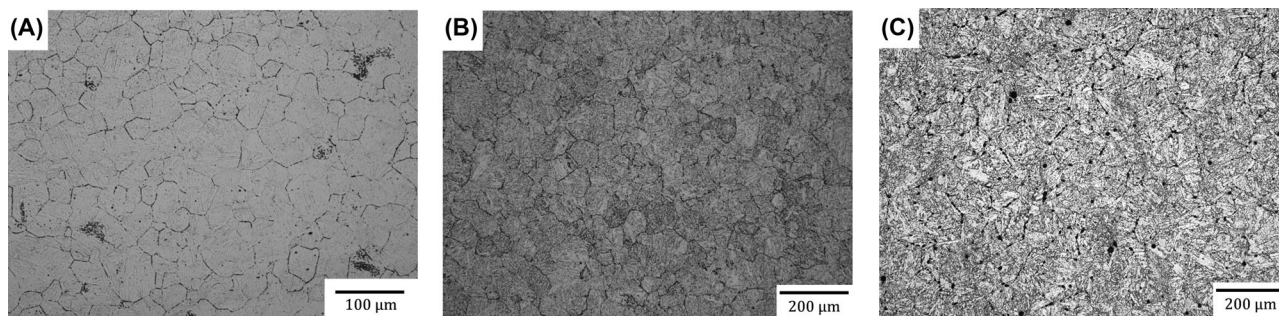


FIGURE 3 V Steel (A) 1000°C T_γ etched with solution E1 for around 60 s, (B) 1250°C T_γ etched with solution E2, 1.22 g sodium dodecyl sulphate + 8 drops of HCl for around 60 s, (C) 1250°C T_γ etched with solution E2, 1.22 g sodium dodecyl sulphate + 12 drops of HCl for around 60 s

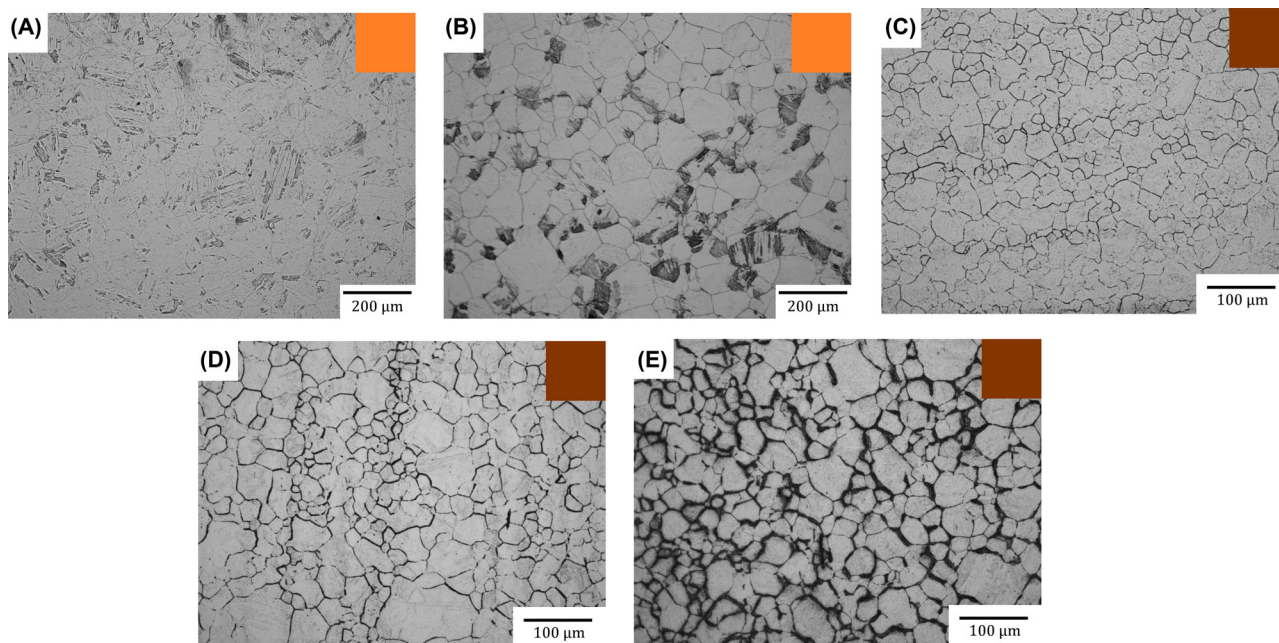


FIGURE 4 V Steel (A) 1200°C T_γ etched with solution E2 – 9 drops of HCl, submerging the sample for 10 s, (B) 1200°C T_γ etched with solution E2 – 9 drops of HCl and swabbing with cotton for around 60 s, (C) 1000°C T_γ etched with solution E2 – 6 drops of HCl and swabbing with cotton for around 60 s, (D) 1050°C T_γ etched with solution E2 – 9 drops of HCl and swabbing with cotton for around 60 s, (E) 1050°C T_γ etched with solution E2 – 12 drops of HCl and swabbing with cotton for around 60 s

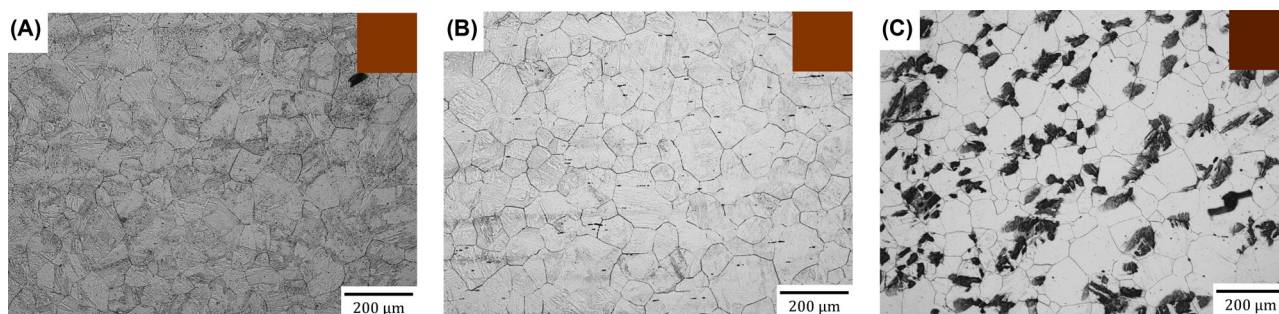


FIGURE 5 Effect of the temperature of the etch E2 over V steel samples treated at 1250°C T_γ , (A) at 70°C for 40–60 s, (B) at 80°C for 40–60 s, (C) at 90°C for 40–60 s

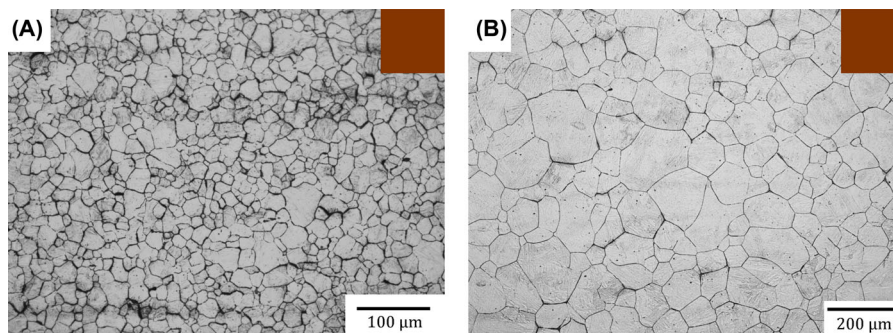


FIGURE 6 Steel CrV etched with solution E2 for 40–60 s austenitised at (A) 1000°C T_γ and (B) 1300°C T_γ

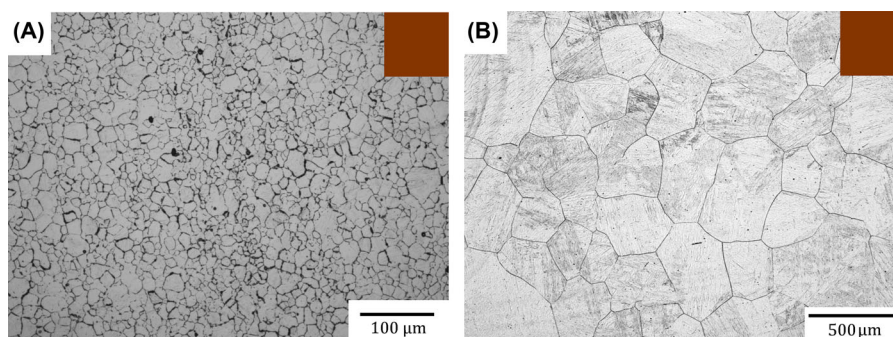


FIGURE 7 Steel CrNbV etched with solution E2 for 40–60 s austenitised at (A) 1000°C T_γ and (B) 1300°C T_γ

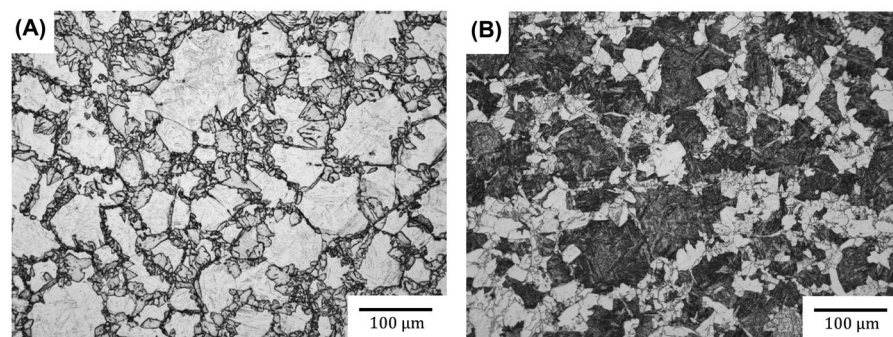


FIGURE 8 Steel V heat treated at 1245°C T_γ and 610°C T_{ISO} etched with (A) E2 reagent for 40–60 s and (B) Nital 2% for 5–15 s

the Nital 2% etch, which with the cotton swabbing delineates the ferrite, and produces a high contrast with other phases (Figure 8B).

The 2% Nital etch does not give much information about phases such as martensite or bainite, so without the E2 etch, evaluation of the microstructure would require much more expensive techniques such as scanning electron microscopy (SEM) or Electron Backscatter Diffraction (EBSD). The Nital etch gives a well-defined ferrite grain boundaries in steels with much higher ferrite volume fraction, for example, Figure 9, or in steels with fine grains and very low ferrite transformation (Figure 10). In Figure 11, it

is clear how a slight repolish (which does not remove all the previous etch) after etching with this reagent partially removes the grain area etching, but the intragranular detail remains, revealing the prior-austenite grain boundaries in steels with high percentage of transformation.

Samples of a steel with relative similar addition of carbide-former elements with a similar heat treatment but more than the double carbon addition¹⁸ were used to observe the effectiveness of the solution E2 on higher carbon steels. By contrasting the images with the results of etching E2 on V, CrV and CrNbV steels, it was determined a reduction in the amount of HCl was required in solution E2

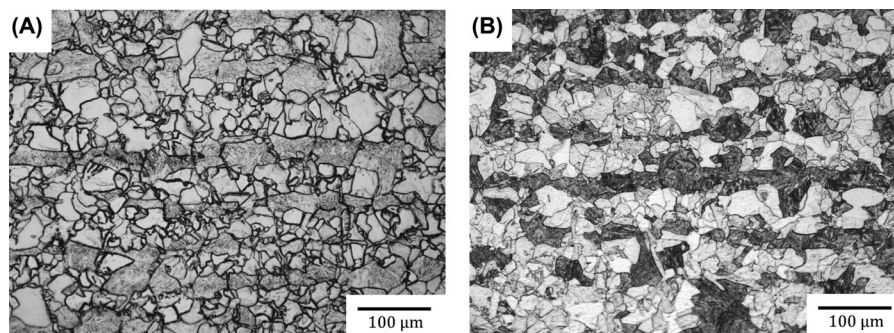


FIGURE 9 Steel CrV heat treated at 1100°C T_γ and 600°C T_{ISO} etched with (A) E2 reagent for 40–60 s and (B) Nital 2% for 5–15 s

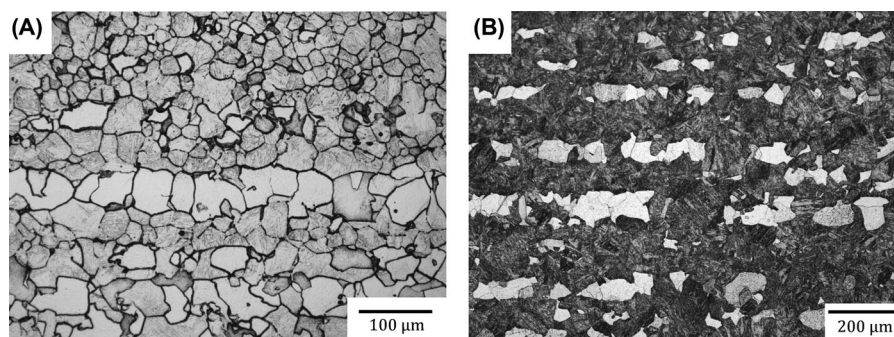


FIGURE 10 Steel CrNbV heat treated at 1245°C T_γ and 610°C T_{ISO} etched with (A) E2 reagent for 40–60 s and (B) Nital 2% for 5–15 s

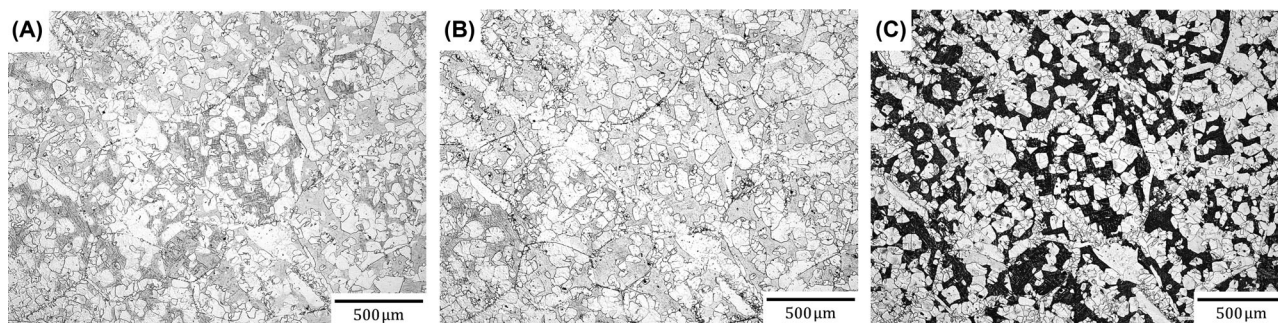


FIGURE 11 CrV steel heat treated at 1300°C T_γ and 625°C T_{ISO} etched with (A) E2 reagent for 30 s; (B) back polished from the first etchant and then re-etched with the same solution for another 30 s; and (C) etched in 2% Nital for 5–15 s (all the images had been taken in the same region of the sample)

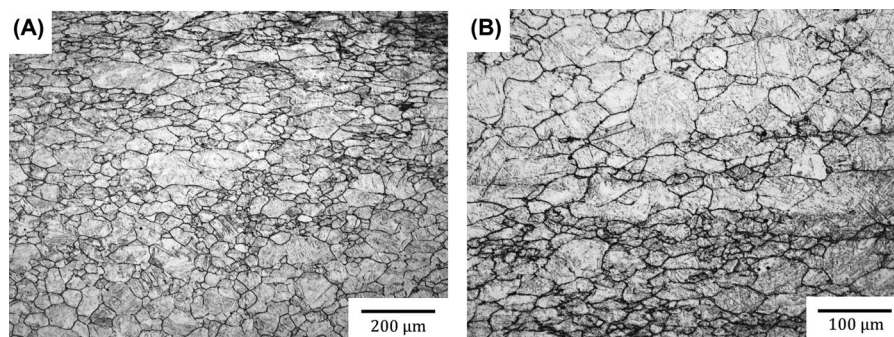


FIGURE 12 AlCrNb steel etched with a modification of solution E2 – mod 1 for 15–30 s

to obtain good micrographs. It is known that the amount of HCl required is inversely proportional to the carbon content in the alloy.⁹ Figure 12 presents the images obtained from etching the steel with a modification of the etching E2 (E2 – mod 1): 1 g sodium dodecyl sulphate + 5 drops of HCl, showing that not only a reduction in the HCl but also in the wetting agent.

4 | CONCLUSIONS

1. A methodical approach allowed the optimisation of the etching of low carbon steel to provide a comprehensive view of the microstructure that was not possible with standard etches. The new etching procedure reveals at once the different features of the microstructure in steel with a wide range of prior heat treatments.
2. 1.15 g is the maximum possible addition of sodium dodecyl sulphate to reveal the prior-austenite grain boundaries of microalloyed steels with 0.1%C content.
3. With higher carbon content in the alloy, the wetting agent impedes the acid to etch all the high segregation areas, affecting the selectivity of the reagents and then the prior-austenite grain boundary delineation. For this reason, wetting agents which work on low carbon steels need to be reduced and studied to analyse their capability to produce clean etching of the microstructure and grain boundaries.

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