



Rare earth addition on SAF 2507 Super Duplex Stainless Steel: effect on microstructural evolution and mechanical properties

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ABSTRACT

The manufacturing of large duplex stainless-steel components commonly requires sand casting, which does not ensure sufficiently high cooling rates to prevent the formation of deleterious secondary phases, especially in thick sections. To restore a balanced ferrite-austenite microstructure free of secondary phases, a solution annealing treatment is required. This study investigates the role of rare earth elements as alloying additions in SAF 2507 super duplex stainless steel (X2CrNiMoN25–7–4). Small cerium additions were introduced to modify the precipitation kinetics of secondary phases and reduce segregation during solidification. Their effect on improving the microstructural stability of thick cast components was then evaluated. The first part of the study focused on solution heat treatment, with particular emphasis on the influence of temperature and holding time on microstructure, mechanical properties and corrosion resistance. A SAF 2507 sand casting was produced, and several specimens were subjected to isothermal heat treatments between 950°C and 1150°C with different holding times. Microstructural characterization was performed using optical and scanning electron microscopy, while image analysis was used to quantify phase fractions. Mechanical behaviour was evaluated through tensile, impact and hardness tests, and corrosion resistance was assessed by immersion tests. To investigate the effect of rare earth additions, two additional castings of the same alloy were produced with different cerium contents and subjected to identical heat treatments and characterization procedures, enabling direct comparison with the base alloy. The results confirmed the correlation between σ -phase content and the deterioration of mechanical and corrosion properties. Rare earth additions improved microstructural stability and overall performance by reducing the formation of deleterious phases, demonstrating the potential of combining alloying design with heat treatment optimization to produce large SAF 2507 cast components.

1. Introduction

Duplex Stainless Steels (DSS) are currently the most widely used materials in demanding applications that require both high mechanical strength and corrosion resistance [1]. These alloys exhibit a biphasic microstructure consisting of a ferritic matrix with uniformly distributed austenitic islands, a configuration that optimizes their overall properties [2,3]. The distribution of these phases depends on both the chemical composition of the steel and its thermal history [4]. Compared with ferritic and austenitic stainless steels, duplex grades show superior resistance to different forms of corrosion, including pitting, stress corrosion cracking, intergranular and crevice corrosion and an

exceptional balance of strength and toughness [5]. By tailoring the phase ratio via alloy composition and thermal processing, DSS offer an exceptional combination of strength, toughness, and corrosion resistance, making them key candidates for harsh offshore, marine, oil and gas, and desalination applications [6,7].

In duplex stainless steels, carbon and nitrogen act as interstitial austenite stabilizers, whereas nickel and copper are substitutional austenite stabilizers. Chromium, molybdenum and tungsten promote ferrite formation [4]. Keeping carbon content low limits carbide precipitation, whereas nitrogen additions simultaneously enhance mechanical strength and pitting corrosion resistance [8]. An appropriate balance of these alloying elements ensures an even phase distribution

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Fig. 1. Sand casting of STD SAF2507 SDSS.

and optimized material properties [9].

The alloy composition also determines the Pitting Resistance Equivalent Number (PREN), which characterizes the resistance to localized corrosion [10]. When the PREN exceeds 40, the material is classified as a Super Duplex Stainless Steel (SDSS), characterized by its excellent pitting corrosion resistance [11,12]. The most widely used SDSS is SAF 2507 (X2CrNiMoN25–7–4), containing 24–26 wt% chromium, 6–8 wt% nickel, 3–5 wt% molybdenum, less than 0.03 wt% carbon and up to 0.35 wt% nitrogen [13].

To preserve the superior properties of duplex stainless steels, it is essential to maintain the alloying elements in solid solution and prevent their precipitation as intermetallic phases, carbides or nitrides, which cause severe embrittlement and a marked reduction in corrosion resistance due to the depletion of chromium, molybdenum and nickel in the matrix [14,15]. At temperatures between 700°C and 1000°C, γ_2 phase and deleterious phases such as σ and χ can precipitate, along with chromium nitrides and carbides (Cr_2N , Cr_3C_6 , Cr_6C and Cr_7C_3) [16,17]. The γ_2 phase corresponds to secondary austenite formed by solid-state reaction rather than solidification, and it is consequently depleted in alloying elements, rendering it more susceptible to corrosion [14]. The χ -phase, a metastable ternary compound rich in chromium and molybdenum with a wide compositional range [18], transforms to σ -phase after prolonged aging [15,19]. The σ -phase is generally the most prevalent due to its rapid formation kinetics and high thermodynamic stability [20]. It contains 30 wt% chromium and 8 wt% molybdenum [21] and typically exhibits a lamellar morphology resulting from the eutectoid decomposition of ferrite according to the reaction $\delta \rightarrow \sigma + \gamma_2$. Several studies have demonstrated that even small amounts of σ -phase can drastically impair corrosion resistance and toughness [22]; when its volume fraction reaches 1–3%, resistance can decrease by more than 70% at ambient temperature [23,24]. The precipitation of secondary intermetallic phases occurs preferentially along ferrite-austenite phase boundaries [14,17]. Because these secondary phases consume substantial amounts of Cr and Mo, their rapid formation creates narrow chromium- and molybdenum-depleted zones in the immediately adjacent matrix [15]. This localized alloy depletion is the direct mechanistic cause of intergranular corrosion susceptibility, as the depleted grain boundary regions dissolve preferentially when exposed to aggressive media [17]. Furthermore, these Cr/Mo-depleted boundary regions act as primary nucleation sites for localized pitting attack, establishing an

intrinsic, mechanistic connection between intergranular corrosion phenomena and pitting degradation [15,23]. To eliminate such deleterious phases, a solution annealing heat treatment is required.

It is well known that the addition of rare earth elements to stainless steels refines the solidification microstructure and reduces dendritic spacing [25]. In particular, cerium and lanthanum can reduce element segregation, thereby suppressing σ -phase precipitation. Several studies have also reported that rare earth additions decrease the hardness of secondary phases. The introduction of rare earth elements can promote the formation of high-melting-point inclusions such as Ce_2O_3 and $\text{Ce}_2\text{O}_2\text{S}$ through reactions with residual oxygen and sulfur impurities present in the steel. Cerium additions between 0.011 wt% and 0.023 wt% have been reported to modify the inclusion population and significantly improve toughness [26]. Furthermore, cerium additions can promote the formation of complex Ce-containing oxides, together with manganese, chromium, silicon and aluminium oxides, which improve pitting corrosion resistance by reducing preferential interfacial initiation sites [27]. Another beneficial effect of rare earths in duplex stainless steels is the widening of the passive potential range and the formation of a denser, chromium-rich passive film [28].

Despite these known benefits of rare earth additions in wrought alloys, a major research gap remains regarding the quantitative impact of cerium alloying on the phase transformation kinetics and microstructural stability of thick-section sand-cast super duplex stainless steels. Conventional solution annealing heat treatments often require excessively prolonged holding times at high temperatures to fully dissolve σ -phase in thick sections, risking severe grain growth and energy inefficiency. While Ce is recognized for inclusion modification and passivity enhancement, its specific capacity to alter σ -phase precipitation and solubilization kinetics, retard intermetallic phase formation during cooling and assist phase balance restoration during solution annealing in thick cast components has not been systematically established. To address this research gap, the present study systematically investigates the coupled influence of cerium alloying additions and solution heat treatment parameters on a sand-cast SAF 2507 super duplex steel. By optimizing the parameters of solution annealing and evaluating the effects of rare earth alloying, this work aims to establish new, efficient, and sustainable strategies to enhance the performance of super duplex stainless steels. The outcomes of this study are expected to contribute not only to understanding phase transformations in these alloys but also to the practical development of more durable, energy-efficient, and cost-effective materials for critical industrial applications. Furthermore, the ability to slow down precipitation kinetics offers an additional technological advantage, as it enables the production of cast components with increased wall thickness by reducing the risk of detrimental phase formation during cooling.

2. Materials and methods

2.1. Analysed material

The reference material used in this study was a $\sim 500 \times 300$ mm sand casting made of SAF 2507 (X2CrNiMoN25–7–4) super duplex stainless steel illustrated in Fig. 1. The nominal chemical composition adopted as reference for the SAF 2507 grade is reported in Table 1 [29].

In addition to the standard alloy (STD), two sand castings were produced with different nominal additions of rare earth elements: 0.01 wt% of cerium for the low rare earth addition casting (L-RE) and 0.02 wt% of cerium for the high rare earth addition casting (H-RE), with only trace amounts of lanthanum, as confirmed by the chemical composition analysis reported in Table 2.

All materials were supplied by *Acciaieria Fonderia Cividale S.p.A.* and the sand castings were produced at *Inossman Fonderie Acciaio Maniago S.r.l.*, using a small induction furnace. Each melt consisted of 500 kg of SAF 2205 (X2CrNiMoN22–5–3) duplex stainless steel scrap, melted under a protective atmosphere at a nominal temperature of 1600°C for

Table 1

Nominal chemical composition of the SAF2507 SDSS.

Cr	Ni	Mo	Si	Mn	P	S	Al	Co	Cu
24.82%	6.85%	4.032%	0.963%	0.524%	0.0353%	0.003%	0.012%	0.0837%	0.235%
Nb	Pb	Sn	Ti	V	W	N	C	Ca	Fe
0.023%	0.0044%	0.0077%	0.0034%	0.0632%	0.037%	0.164%	0.012%	0.0003%	bal.

one hour. The melt temperature was monitored using *Heraeus Electro-Nite Positherm*® disposable immersion thermocouples, providing rapid spot measurements with an accuracy of $\pm 1.5^\circ\text{C}$. After the removal of slag, alloying additions were made to reach the target composition. For the STD melt, approximately 12.5 kg of ferrochromium, 0.7 kg of ferromolybdenum, and 1.8 kg of nickel were added. The temperature was held at 1600°C for 30 min to ensure homogenization by electromagnetic stirring. The melt chemistry was verified through sampling before adding about 1 kg of aluminium for deoxidation. Finally, the temperature was reduced to a nominal temperature of 1590°C , and the metal was poured into sand molds with a bottom-pouring system. The risers were covered with exothermic powders to control solidification. The L-RE and H-RE castings were produced following the same procedure, with the further addition of 0.25 kg and 0.55 kg of a commercial cerium-based ferroalloy during casting, assuming an efficiency of approximately 40%.

2.2. Chemical analysis

The chemical composition of each casting was analysed by *Acciaieria Fonderia Cividale S.p.A.* using Spark Optical Emission Spectroscopy (SOES) with a *SpectroLAB S01* spectrometer. The instrument was calibrated using certified reference materials and the optical system was checked and aligned to ensure measurement accuracy and repeatability. Samples were taken from dedicated extensions of the castings and a minimum of three measurements was performed on each specimen to ensure analytical reliability.

2.3. Heat treatments

All heat treatments were performed using a *Nabertherm N11/HR* muffle furnace integrated into the *Nabertherm Tool Shop Hardening System MHS 17* pilot plant. Isothermal solution annealing heat treatments were conducted on $30\times 30\times 250\text{mm}$ bars extracted from the different castings. Temperatures were selected within the typical range adopted for the solution heat treatment of this specific alloy [30], with narrower intervals in the most critical temperature range. In particular, heat treatments were performed at 950°C , 1000°C , 1025°C , 1050°C , 1100°C and 1150°C . Based on preliminary results, the holding times were set to 0 min, 15 min, 30 min, 60 min and 120 min for each temperature. The 0 min holding time was defined as the instant at which the specimen core reached the furnace set temperature, as determined by preliminary thermocouple measurements. The heating rate was set at 200°C/h . To ensure a rapid cooling, all specimens were water-quenched, maintaining continuous agitation to enhance heat exchange efficiency.

2.4. Microstructural characterization

Multiple $20\times 20\times 10\text{mm}$ specimens were extracted from each heat-treated bar of the different castings. Samples were sectioned by abrasive cutting under coolant flow and prepared following a standard metallographic procedure. Etching was carried out using Murakami's reagent, identified as the most effective for this class of materials, in accordance with a previous study [31].

All etched specimens were examined using a *Zeiss Axio Vert.A1* optical microscope equipped with a high-resolution *Zeiss AxioCam 208 Color* camera. For each sample, at least 10 representative micrographs were acquired in bright field at $100\times$ magnification to enable accurate

image analysis and quantitative phase evaluation as a function of the solution annealing parameters. Additional images highlighting specific microstructural features were captured at $200\times$, $500\times$ and $1000\times$ magnifications. The micrographs were processed using the *ImageJ 1.53a* software. The image analysis procedure was performed in accordance of the ASTM E562 standard [32], as described in detail in the referenced publication [31].

A more detailed examination of the microstructure was conducted using a *Zeiss Evo 40* Scanning Electron Microscope (SEM) equipped with an *Oxford INCA X-Sight* Energy Dispersive X-ray Spectroscopy (EDXS) probe. SEM analyses were performed at various magnifications to investigate the morphology of deleterious phases of specimens subjected to different heat treatment conditions. EDX mapping was also employed to evaluate the elemental distribution within the microstructure.

2.5. Mechanical characterization

2.5.1. Hardness tests

For hardness testing, samples were extracted from each heat-treated bar using the same geometry as those prepared for microstructural analysis. Sample preparation followed the same procedure, except that metallographic etching was not necessary. Particular attention was paid to ensuring that the surfaces to be analysed were plane-parallel.

Hardness was measured using a *Zwick-Roell Durscan 50* automatic durometer, in accordance with ASTM E92–17 standard [33]. Each sample was placed on a single-sample holder, and a series of sixteen indentations was applied uniformly across the surface using a load of 30 kgf. The high load was selected to account for the heterogeneous distribution of phases, particularly in partially solution-treated samples, ensuring that each indentation provided a representative hardness value.

The results were plotted as a function of σ -phase content. The measured hardness values were also compared with the limits specified in ASTM A240 standard [34].

To further investigate the influence of rare earth additions on the hardness of the individual phases, complementary Vickers microhardness measurements (HV0.1) were performed on fully solution-annealed specimens, thus avoiding any influence of secondary phases. Two specimens were analysed for each alloy condition (STD, L-RE and H-RE). For each alloy, fifty indentations were performed on both ferrite and austenite. The average hardness values and corresponding standard deviations were subsequently calculated and compared among the three alloy conditions.

2.5.2. Tensile tests

At least two specimens were extracted from each heat-treated bar for tensile testing. Specimen geometry was defined according to ASTM E8 standard [35]. Due to the bar dimensions, small-size specimens proportional to the standard were machined, with a calibrated diameter D of 6 mm, a gauge length A of 40 mm and an effective length LO equal to five times the calibrated diameter.

Tensile tests were performed using an *MTS 810* universal testing machine at ambient temperature. The tests were performed under strain control at an extensometer rate of 0.004 (mm/mm)/min until 0.7% strain, and then under displacement control at 1 mm/min until rupture. Instantaneous strain was measured using a 25 mm gauge-length knife-edge extensometer, allowing the construction of stress–strain curves and the determination of the elastic modulus E , yield strength R_p , and

Table 2
Chemical composition and PREN of the SDSS castings.

	Cr	Ni	Mo	Mn	Si	N	Cu	Co	V	Ti	Nb	P	C	W	Al	S	B	Ce	La	Fe	PREN
STD	24.32%	6.86%	4.02%	0.752%	0.483%	0.205%	0.131%	0.061%	0.052%	0.019%	0.017%	0.016%	0.013%	0.013%	0.0095%	0.0064%	0.0022%	0.0006%	0.0002%	bal.	40.87
L-RE	25.38%	6.59%	3.86%	1.25%	0.451%	0.285%	0.213%	0.119%	0.062%	0.005%	0.018%	0.024%	0.018%	0.041%	0.0018%	0.0017%	0.021%	0.0086%	0.0034%	bal.	42.68
H-RE	25.45%	6.51%	3.79%	1.27%	0.543%	0.272%	0.211%	0.118%	0.061%	0.005%	0.018%	0.025%	0.017%	0.042%	0.0045%	0.0015%	0.0024%	0.0162%	0.0058%	bal.	42.31

ultimate tensile strength R_m . Percent elongation at fracture $A\%$ was calculated by relating the displacement at fracture to the gauge length L_0 .

Average values and standard deviations were calculated for all measured parameters. The results were plotted as a function of σ -phase content and compared with the limits specified in ASTM A890 and ASTM A995 standards [30,36].

Fracture surfaces were analysed through macrographs acquired with a *Zeiss SteREO Discovery.V12* microscope equipped with a high-resolution *Zeiss Axiocam 208 Color* camera. Further fractographic analyses were performed on selected specimens using the previously described SEM at various magnifications to correlate fracture mechanisms with σ -phase content and the effects of chemical composition variations.

2.5.3. Impact tests

Specimen geometry for impact testing was defined according to ASTM E23 standard [37]. At least four 10x10x55 mm square-section specimens with a V-notch and a 45° apex angle were extracted from each heat-treated bar.

All Charpy impact tests were performed at ambient temperature at *Facs Fucine S.r.l.* using a *Galdabini CH/30* pendulum with a capacity of 295 J and an impact velocity of 5.5 m/s.

The results were plotted as a function of σ -phase content and compared with reference limits reported in the literature [38].

As for tensile testing, fracture mechanisms were investigated in relation to σ -phase content and alloying additions. Macrographs of fracture surfaces were acquired using a *Zeiss SteREO Discovery.V12* microscope, and detailed fractographic analyses were performed on selected specimens using the *ZEISS Evo 40* SEM at various magnifications.

2.6. Corrosion characterization

For the corrosion tests, all the 50x20x10mm specimens were extracted from the heat-treated bars and tested according to ASTM G48 *Method A: Ferric Chloride Pitting Test* [39]. The standard allows flexibility in specimen dimensions; the only precautions applied were rounding all edges and manually polishing the surfaces up to 1200-grit paper to minimize pit initiation at corners.

The tests were performed using a 6 wt% ferric chloride solution at 50°C for 72 h. The test temperature was maintained constant throughout the exposure. Weight loss results were plotted on a semi-logarithmic scale as a function of σ -phase content and compared with the limits specified in the NORSOK M-630 standard [40]. Samples were subsequently visually examined, and low-magnification stereomicroscope images were acquired. To complement the corrosion characterization, high-magnification SEM analyses were performed on the most representative specimens of each material, both on the surface and in cross-section.

In this study, localized pitting corrosion evaluated by immersion testing was used as an overall indicator of corrosion performance because it directly integrates and quantifies the macro-scale performance degradation resulting from matrix Cr/Mo depletion induced by σ -phase precipitation throughout the material.

3. Results and discussion

3.1. Chemical analysis

The chemical compositions of the analysed castings are reported in Table 2.

The chemical composition of the STD alloy is within the nominal range of SAF 2507 super duplex stainless steel, with sulphur and phosphorus contents below the limits prescribed by the NORSOK M-630 standard [40].

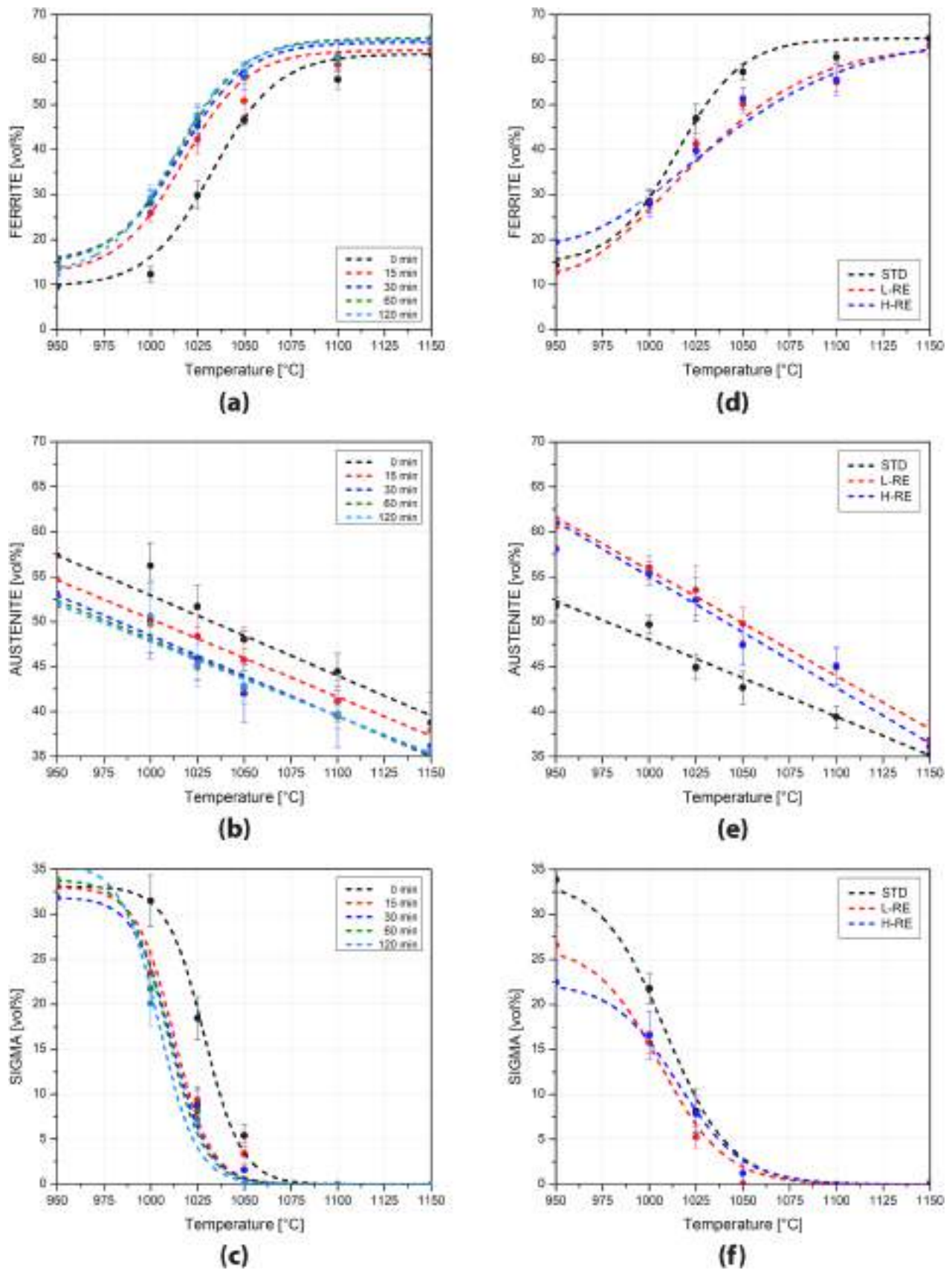


Fig. 2. Image analysis results: (a), (b), (c) STD casting samples for different holding times in the furnace, (d), (e), (f) comparison of STD, L-RE and H-RE casting samples with a holding time of 30 min.

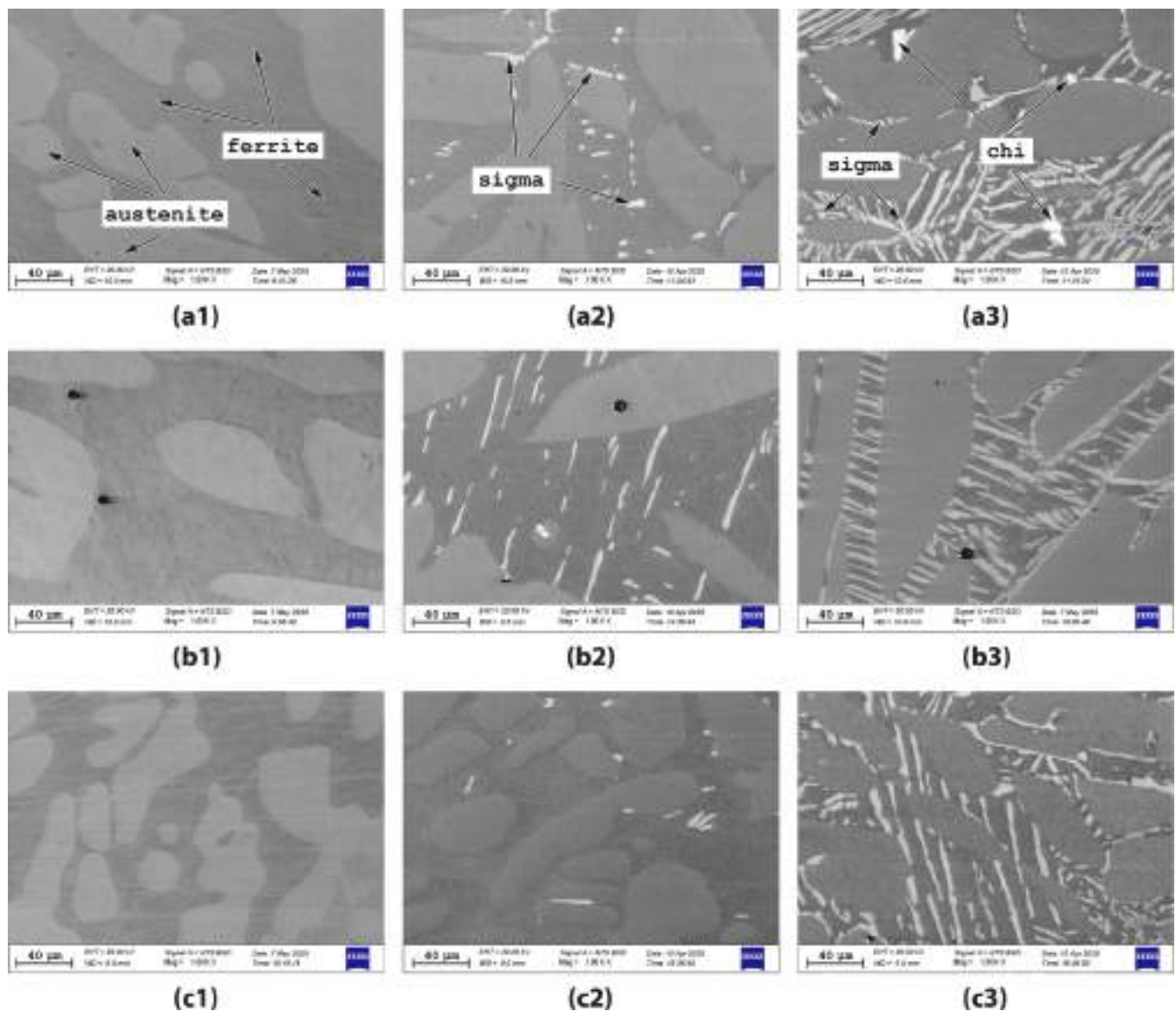


Fig. 3. SEM micrographs of some representative samples of the different castings analysed: (a-) STD casting, (b-) L-RE casting, (c-) H-RE casting, (-1) 0% σ -phase, (-2) 10% σ -phase, (-3) 20% σ -phase.

The L-RE casting consists of the same base alloy as STD with the addition of a small amount of rare earth elements, achieving 0.0086% Ce with minor La traces.

Similarly, the H-RE casting contains the same base alloy with nearly double the Ce content compared to L-RE. All alloying elements remain within the nominal composition ranges [29].

The pitting resistance equivalent number (PREN) was calculated according to the widely adopted expression $PREN = \%Cr + 3.3\%Mo + 16\%N$. The calculated values, reported in Table 2, are higher than 40 for all investigated alloys, confirming that the produced castings satisfy the compositional requirements for SAF 2507 super duplex stainless steel and comply with the minimum PREN specified by the NORSOK M-630 standard [40].

3.2. Microstructural characterization

Quantitative image analysis results are summarized in Fig. 2.

As shown in Fig. 2(a), the ferrite fraction in the STD casting increases with both temperature and holding time, following a sigmoidal trend consistent with Avrami-type phase transformation kinetics [41]. This

behaviour reflects two different mechanisms: the solubilization of σ -phase into ferrite and the shift in the ferrite–austenite equilibrium toward ferrite, as predicted by the duplex steel phase diagram. The transformation rate is highest between 1000°C and 1050°C and for holding times up to 30 min. Below this range, σ -phase dissolution is incomplete, while at higher temperatures the transformation slows once most of the σ -phase has been removed.

The austenite evolution, reported in Fig. 2(b), exhibits linear decrease with increasing temperature and time, reflecting the phase balance mechanism. The transformation kinetics are slower than for σ -phase solubilization. Austenite reaches approximately 50 vol% at 1000°C after 15 min or at 1050°C once the core temperature is reached, confirming the inverse relationship between temperature and time in phase transformations.

As shown in Fig. 2(c), the σ -phase fraction decreases quickly with both parameters. Complete dissolution occurs at 1050°C after 30 min or at 1100°C once the core temperature is reached. The incomplete dissolution of σ -phase at 1000°C and 1050°C for shorter holding times is mainly attributed to kinetic limitations associated with the diffusion-controlled redistribution of Cr and Mo. Increasing the holding time

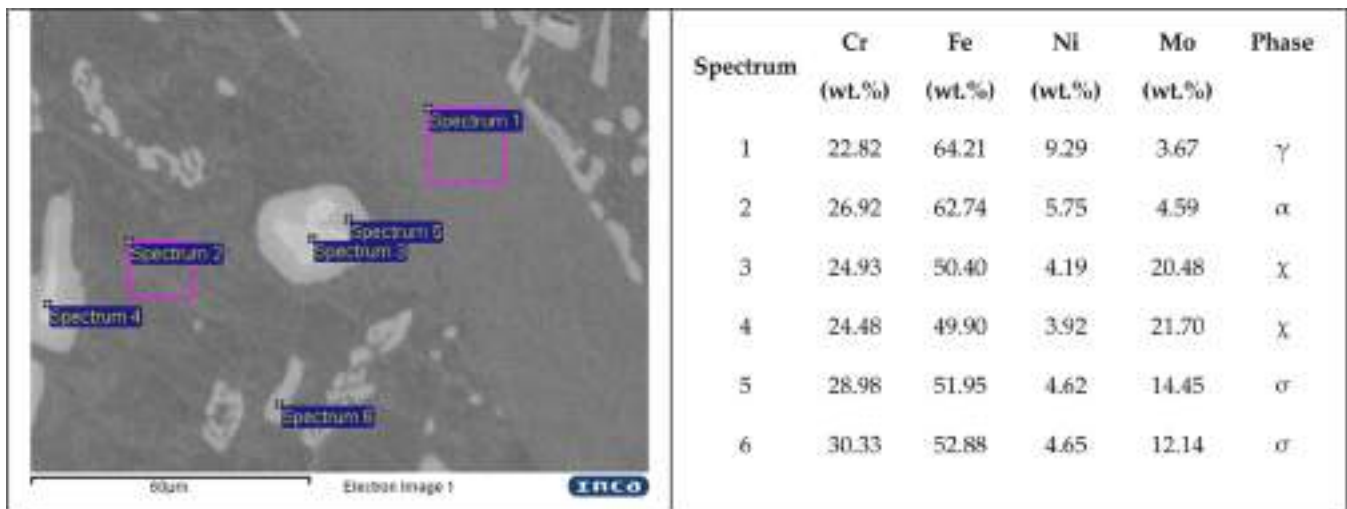


Fig. 4. EDX analysis of an STD casting sample containing 20% σ -phase.

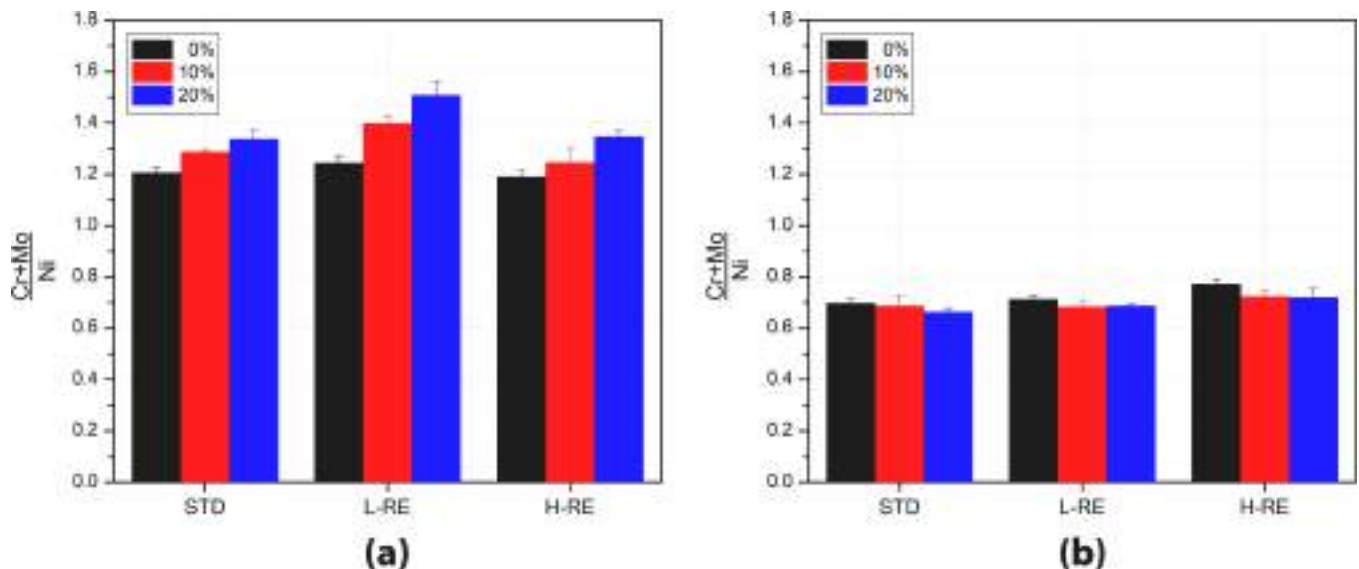


Fig. 5. Chromium, molybdenum and nickel ratio in the different castings analysed containing 0%, 10% and 20% σ -phase, calculated: (a) in the ferritic phase, (b) in the austenitic phase.

promotes σ -phase dissolution.

Fig. 2(d–f) report the results for the castings containing rare earth additions, at a representative holding time of 30 min. The rare earth-modified samples exhibit slightly lower ferrite contents and higher austenite fractions than the STD casting, confirming the austenite-stabilizing effect of rare earth [42,43]. The most significant difference concerns the σ -phase, reported in Fig. 2(f), which is markedly reduced in the rare earth alloys, especially at lower temperatures. This behaviour is probably caused by the slowdown of diffusion-controlled precipitation processes due to the presence of rare earths, which are known to fill lattice vacancies and limit the formation of σ and χ phases [26,44,45]. This effect enhances microstructural stability at elevated temperatures, potentially extending the service life of duplex stainless-steel components before σ -phase-induced degradation occurs. The differences between the L-RE and H-RE samples, characterized by different rare earth contents, fall within experimental uncertainty, suggesting that higher additions have only a marginal influence on phase balance.

Following the heat treatments and quantitative image analysis, representative samples of each alloy, corresponding to conditions of full solubilization, 10% and 20% of σ -phase content, were selected for

detailed microstructural characterization by scanning electron microscopy. In Fig. 3, backscattered electron images acquired at 1000 $\times$ magnification reveal the morphological evolution of the different microstructural constituents with increasing σ -phase fraction. Phase identification was supported by EDX analyses, reported in Fig. 4. The results confirmed the different chemical compositions of the secondary phases. In particular, the σ -phase exhibited a higher chromium content, whereas the χ -phase showed a significant enrichment in molybdenum compared with the ferrite and austenite phases.

In all alloys, σ -phase was observed to nucleate exclusively within ferrite grains. At approximately 10% of content, nucleation occurred preferentially along ferrite grain boundaries, progressing toward ferrite-austenite interfaces as precipitation advanced. This behaviour reflects the higher diffusivity of Cr and Mo in the ferritic matrix, consistent with literature findings [19,46]. The σ -phase exhibited a predominantly blocky morphology, with coral-like structures appearing only locally. The addition of rare earth elements has an influence on the morphology of the σ -phase, promoting its evolution toward more compact and linear configurations. In particular, increasing rare earth content enhances the continuity and regularity of the σ -phase, favouring the formation of less

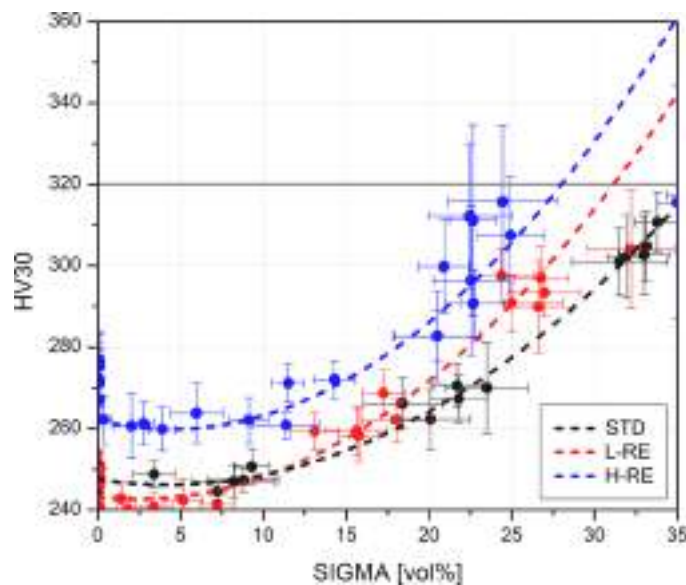


Fig. 6. Effect of σ -phase and rare earth on hardness.

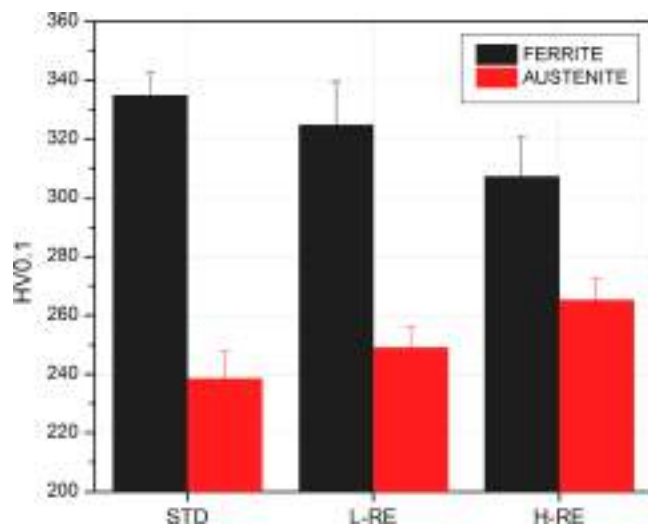


Figure 7. Effect of rare earth on hardness of ferrite and austenite.

irregular structures. The observed evolution is consistent with literature findings, which suggest that rare earth elements may affect the nucleation and growth of intermetallic phases through different mechanisms, including modification of interfacial energies, altered diffusion behaviour, and segregation phenomena at interfaces or grain boundaries [47]. Moreover, RE-containing oxides have been reported to potentially act as heterogeneous nucleation sites, influencing phase precipitation pathways and morphology. However, these mechanisms are proposed based on literature evidence, as direct characterization of RE segregation, oxide formation, or lattice parameter variations was not performed in the present study.

In the surrounding ferritic regions, small, brighter islands were identified as secondary austenite, formed through eutectoid reactions associated with local Cr and Mo depletion caused by σ -phase precipitation, resulting in Ni-enriched zones.

Elemental quantification of Cr, Mo and Ni in ferrite and austenite, reported in Fig. 5 provided insight into compositional variations as a function of σ -phase content. For the ferritic phase, the (Cr + Mo)/Ni ratio increased with higher σ -phase fractions, opposite to typical precipitation behaviour. This occurs because the samples were obtained

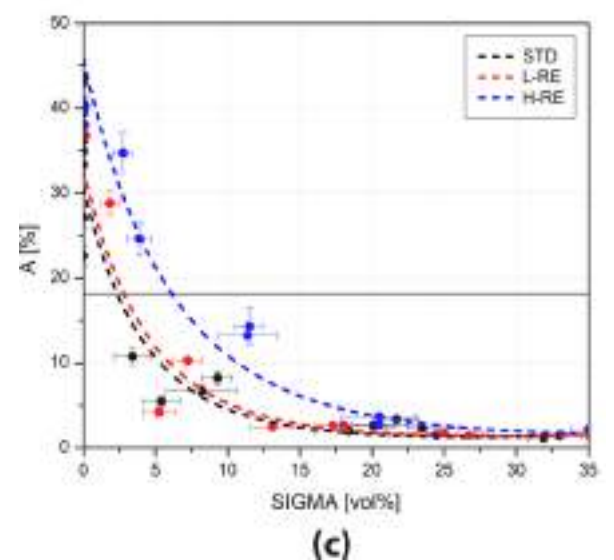
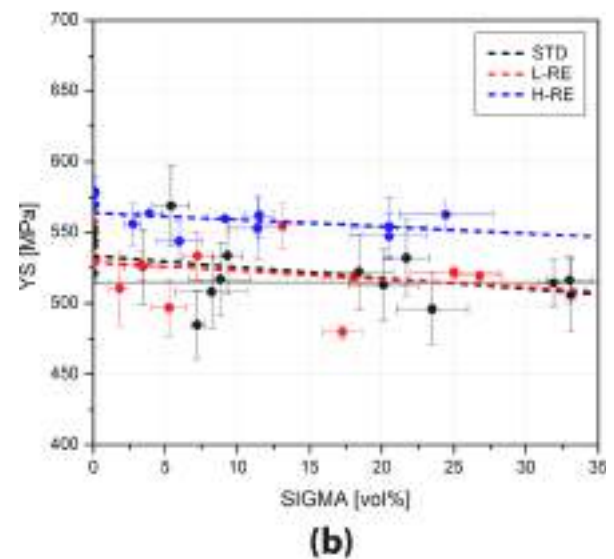
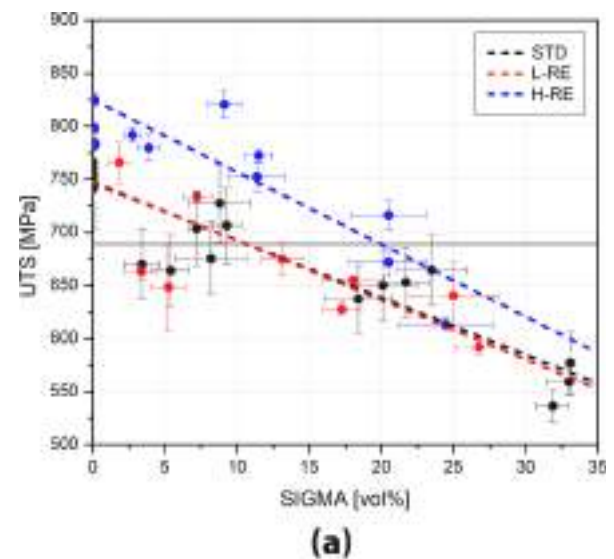


Fig. 8. Effect of σ -phase and rare earth on tensile tests of STD, L-RE and H-RE cast samples: (a) tensile strength, (b) yield strength, (c) elongation at break.

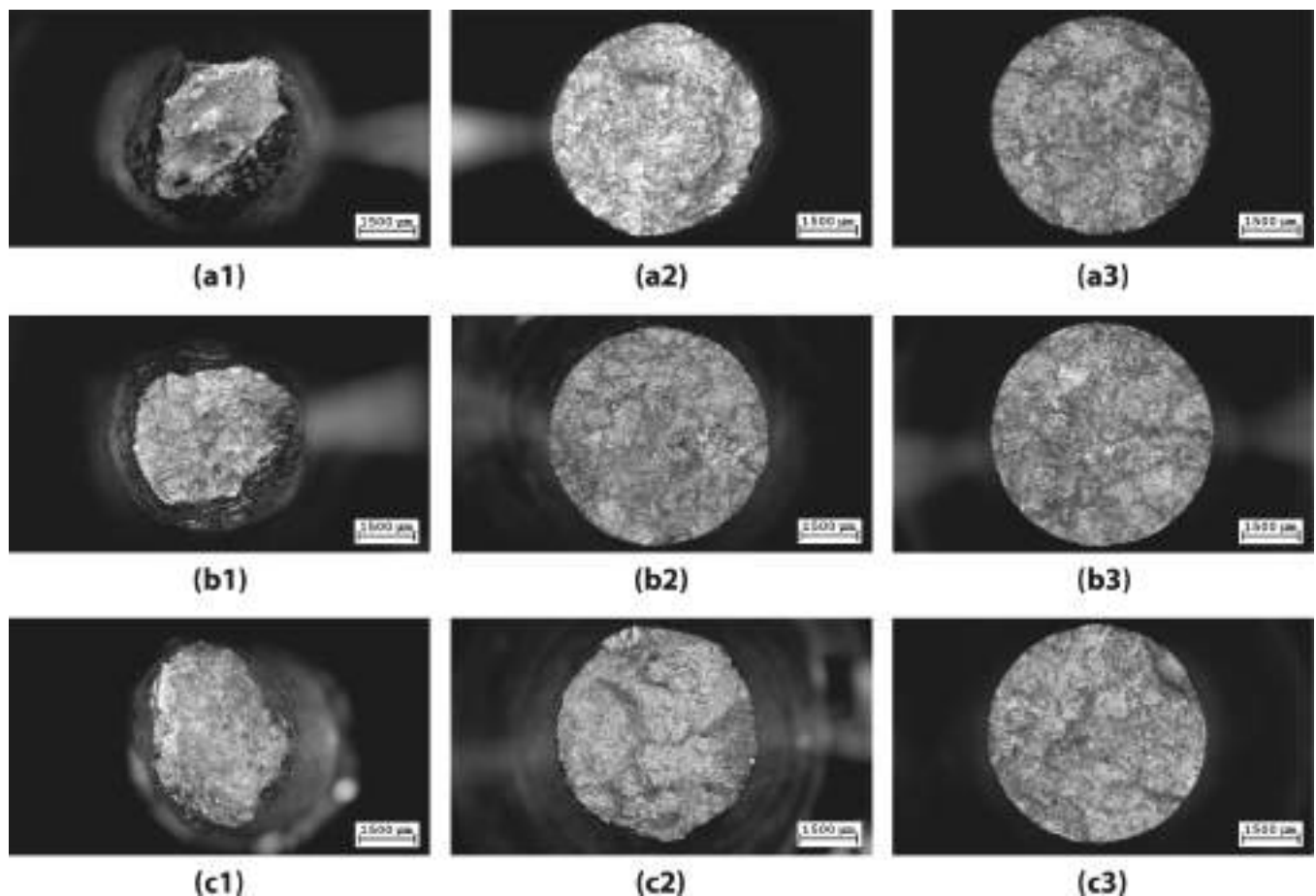


Fig. 9. Macro fractography of some tensile samples representative of the different castings analysed: (a-) STD casting, (b-) L-RE casting. (c-) H-RE casting, (-1) 0% σ -phase, (-2) 10% σ -phase, (-3) 20% σ -phase.

from progressively solution-treated conditions: during dissolution, Cr and Mo are reabsorbed into ferrite, enriching it and increasing the ferritizing-to-austenitizing element ratio. In austenite, no significant trend was observed, indicating that its composition remains largely unaffected by σ -phase presence.

With regard to rare earth additions, no measurable variations in elemental partitioning were detected by EDX analysis. This can be attributed to the intrinsic limitations of the technique, whose detection sensitivity is not sufficient to reliably quantify such low concentrations of rare earth elements. Despite this effect, the compositional trends shown remain valid, as they are governed primarily by the redistribution of major alloying elements (Cr, Mo and Ni) during σ -phase dissolution.

3.3. Mechanical characterization

3.3.1. Effect of σ -phase and rare earth on hardness

The hardness results for the three investigated castings subjected to different solution heat treatments are shown in Fig. 6, together with the ASTM A240 reference limit [34].

For the STD casting, the presence of σ -phase causes an evident increase in hardness, consistent with other findings [13]. This effect becomes significant only above approximately 10 vol% of σ -phase, while lower contents produce negligible changes. This behaviour can be attributed to the fact that, in multiphase materials, overall hardness generally reflects the weighted average of the hardness of the individual phases. Thus, small amounts of σ -phase, although intrinsically very hard, do not substantially affect the bulk hardness.

The L-RE casting exhibits a similar trend to the STD alloy. At low σ -phase contents, its hardness is slightly lower, likely due to its higher

austenite fraction, which is softer than ferrite. At higher σ -phase levels, however, the L-RE samples display slightly greater hardness, probably due to the presence of rare earth elements. Several authors have reported strengthening effects related to rare earth additions, including improved interphase cohesion and a more uniform molybdenum distribution within ferrite [42,48]. Furthermore, these elements promote solid solution and grain refinement strengthening [26] and reduce segregation during solidification [44], collectively contributing to the observed increase in hardness.

Similarly, the H-RE cast shows a comparable behaviour but with consistently higher hardness values for all σ -phase contents. This effect can reasonably be attributed to its higher rare earth concentration, which enhances the overall strengthening response of the material.

In all cases, even with significant σ -phase fractions, the measured hardness values remain below the maximum limits prescribed by the reference standard. It is also worth noting that at higher σ -phase contents the microstructure becomes markedly heterogeneous, leading to increased variability in local hardness measurements and consequently to larger standard deviations. Therefore, hardness testing alone does not represent a reliable method for detecting the presence of σ -phase in these alloys.

Phase-specific microhardness measurements, as reported in Figure 7, revealed opposite trends for ferrite and austenite with increasing rare earth additions. While the hardness of ferrite slightly decreased, the hardness of austenite progressively increased. This behaviour is consistent with the redistribution of the major alloying elements between the two phases. In particular, the increase in austenite hardness is in line with the modified partitioning behaviour promoted by rare earth additions, whereas the slight decrease in ferrite hardness may reflect a

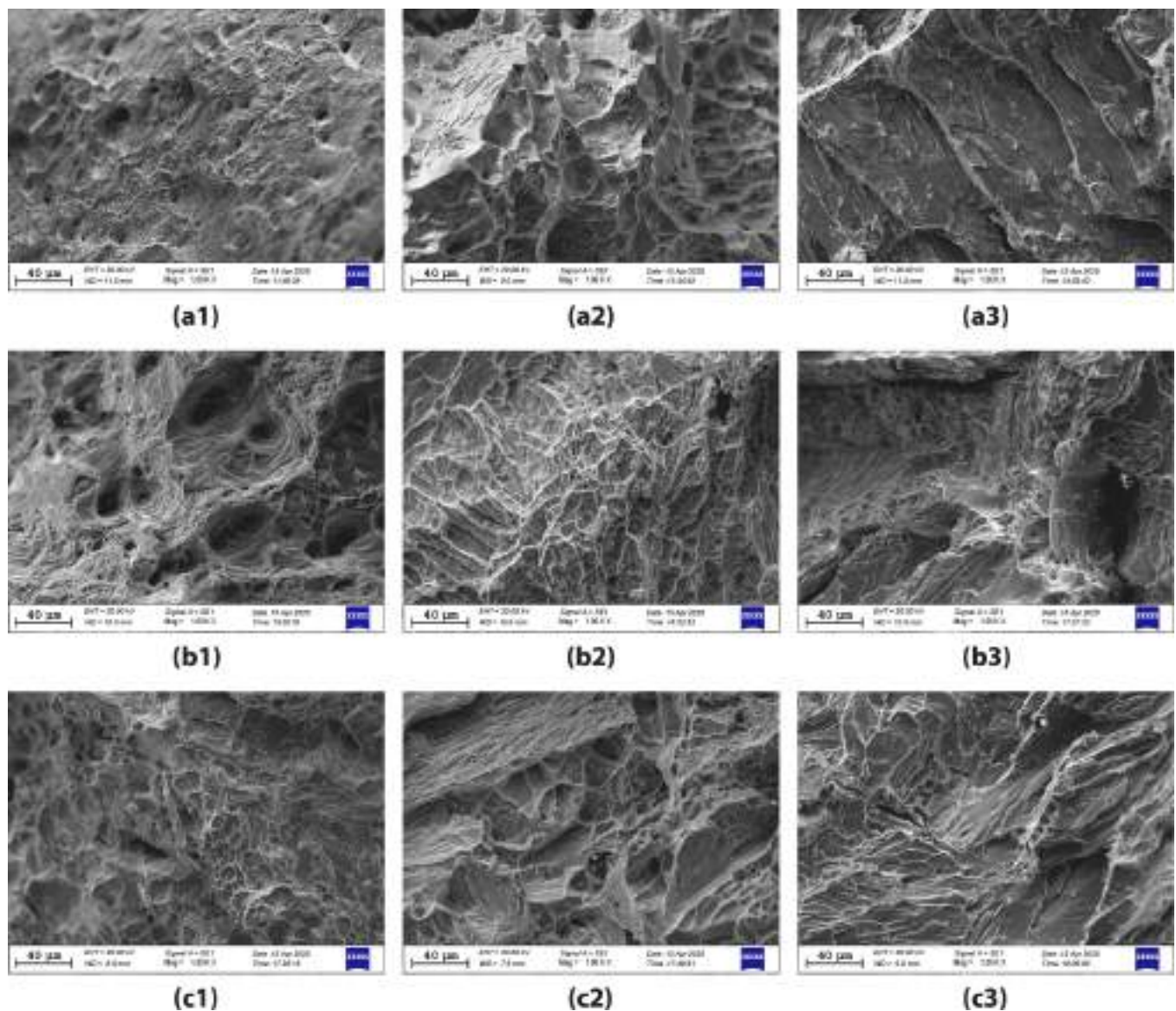


Fig. 10. SEM fractography of some tensile samples representative of the different castings analysed: (a-) STD casting, (b-) L-RE casting, (c-) H-RE casting, (-1) 0% σ -phase, (-2) 10% σ -phase, (-3) 20% σ -phase.

more homogeneous ferritic matrix resulting from the reduced segregation previously discussed. Overall, rare earth additions significantly reduced the hardness mismatch between ferrite and austenite, leading to a more balanced mechanical response of the duplex microstructure and an improvement in the mechanical properties observed for the H-RE alloy.

3.3.2. Effect of σ -phase and rare earth on tensile strength

The tensile test results of the samples extracted from the different casts and subjected to various solution heat treatment conditions are shown in Fig. 8 as a function of the σ -phase content. The graphs also report, in grey, the minimum tensile property limits prescribed by ASTM A890 and ASTM A995 standards [30,36], adopted as reference.

As illustrated in Fig. 8(a), the ultimate tensile strength decreases with increasing σ -phase content, clearly demonstrating the detrimental effect of secondary phases. This behaviour contrasts with the hardness results, where higher σ -phase fractions led to increased hardness values, as strength and hardness are generally correlated [49,50]. However, the hard and brittle σ -phase acts as a preferential crack initiation site. Its predominantly blocky morphology and distribution within the

microstructure promote stress concentration and facilitate crack propagation, resulting in premature brittle fracture and a reduction in tensile strength [51]. During tensile loading, plastic deformation is thus localized within the ductile matrix until a critical stress is reached, causing sudden failure.

As shown in Fig. 8(b), the yield strength does not exhibit a clear correlation with σ -phase content, confirming that this parameter is not particularly significant for identifying or quantifying σ -phase. On the other hands, the elongation at fracture, reported in Fig. 8(c), shows a pronounced reduction even with a few amounts of σ -phase. For all materials, elongation drops to critical levels at approximately 15–20 vol % of σ -phase, reflecting the limited ductility associated with its presence. Since σ -phase is non-deformable, the overall capacity of the alloy to accommodate plastic strain decreases proportionally with its volume fraction, resulting in degraded mechanical performance.

The addition of small amounts of rare earth elements does not significantly affect the tensile properties of the L-RE alloy compared to the standard composition, consistent with the hardness results. Neither the ultimate tensile strength nor the yield stress and elongation exhibit marked variations, suggesting that the RE content is insufficient to

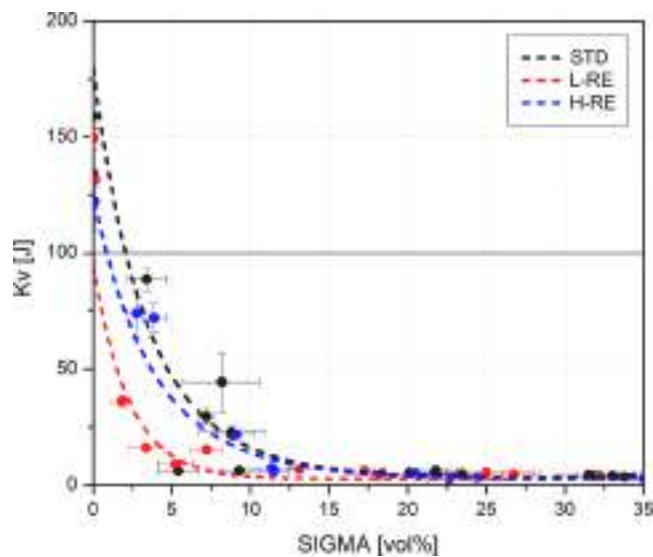


Fig. 11. Effect of σ -phase and rare earth on impact tests.

modify the tensile behaviour of the material appreciably.

In contrast, the H-RE alloy, containing a higher concentration of rare earth elements, shows an overall improvement in tensile performance. The ultimate tensile strength increases by about 75 MPa ($\approx 10\%$) relative to the other casts, consistent with the corresponding rise in hardness. Similarly, the yield strength exhibits an approximate 30 MPa

increase ($\approx 6\%$), while the elongation at fracture, particularly for σ -phase contents below 15%, nearly doubles. These results confirm that higher rare earth additions enhance the tensile response, likely due to the combined effects of microstructural refinement and solid-solution strengthening.

In all cases, only the fully solubilized samples exhibit tensile properties that meet the minimum requirements defined by the reference standards.

Macroscopic fracture surface analyses, reported in Fig. 9, support these observations. In the absence of σ -phase, the specimens display pronounced necking, typical of ductile behaviour, with a characteristic cup-and-cone fracture morphology. As σ -phase content increases, the material becomes progressively more brittle, with reduced necking and fully cleavage-dominated fracture surfaces. At the highest σ -phase fractions, plastic deformation prior to failure is nearly absent. From a macroscopic point of view, no substantial differences are observed with increasing rare earth content. The only noticeable difference is observed in the samples with the highest rare earth content, which, in agreement with the elongation results, still exhibit a certain degree of necking even in the presence of significant amounts of σ -phase.

This trend is confirmed by SEM fractography of Fig. 10. Fully solubilized samples exhibit numerous dimples, indicative of ductile rupture. In samples containing rare earths, EDXS analyses reveal inclusions within the dimples, identified as rare earth oxides. At intermediate σ -phase levels, a mixed fracture mode is observed, with both dimples and cleavage surfaces. As σ -phase content increases further, cleavage and intergranular cracking become dominant, confirming a transition to brittle fracture. Comparison among the different alloys at equivalent σ -phase levels shows no substantial differences, except for a general

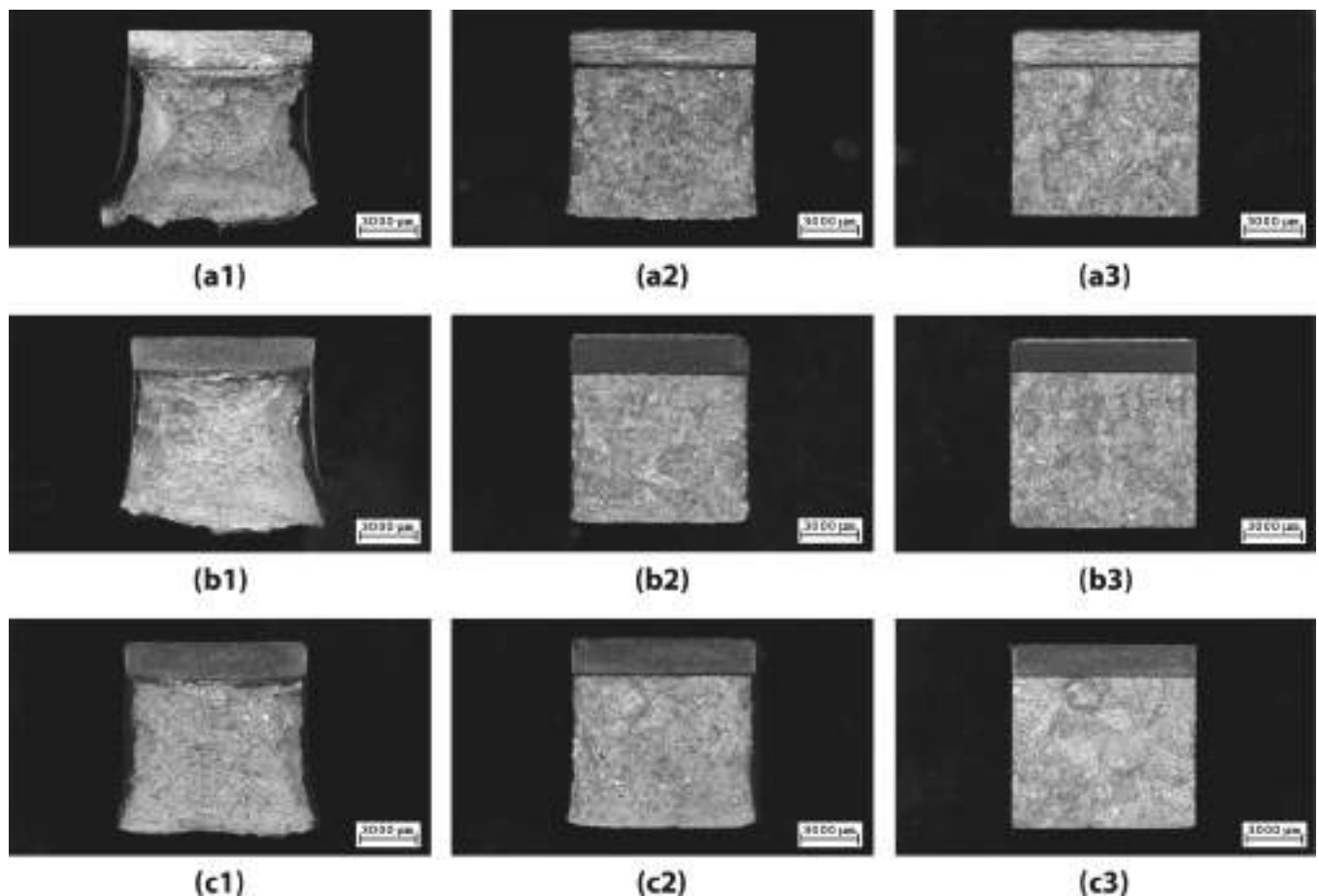


Fig. 12. Macro fractography of some impact samples representative of the different castings analysed: (a-) STD casting, (b-) L-RE casting, (c-) H-RE casting, (-1) 0% σ -phase, (-2) 10% σ -phase, (-3) 20% σ -phase.

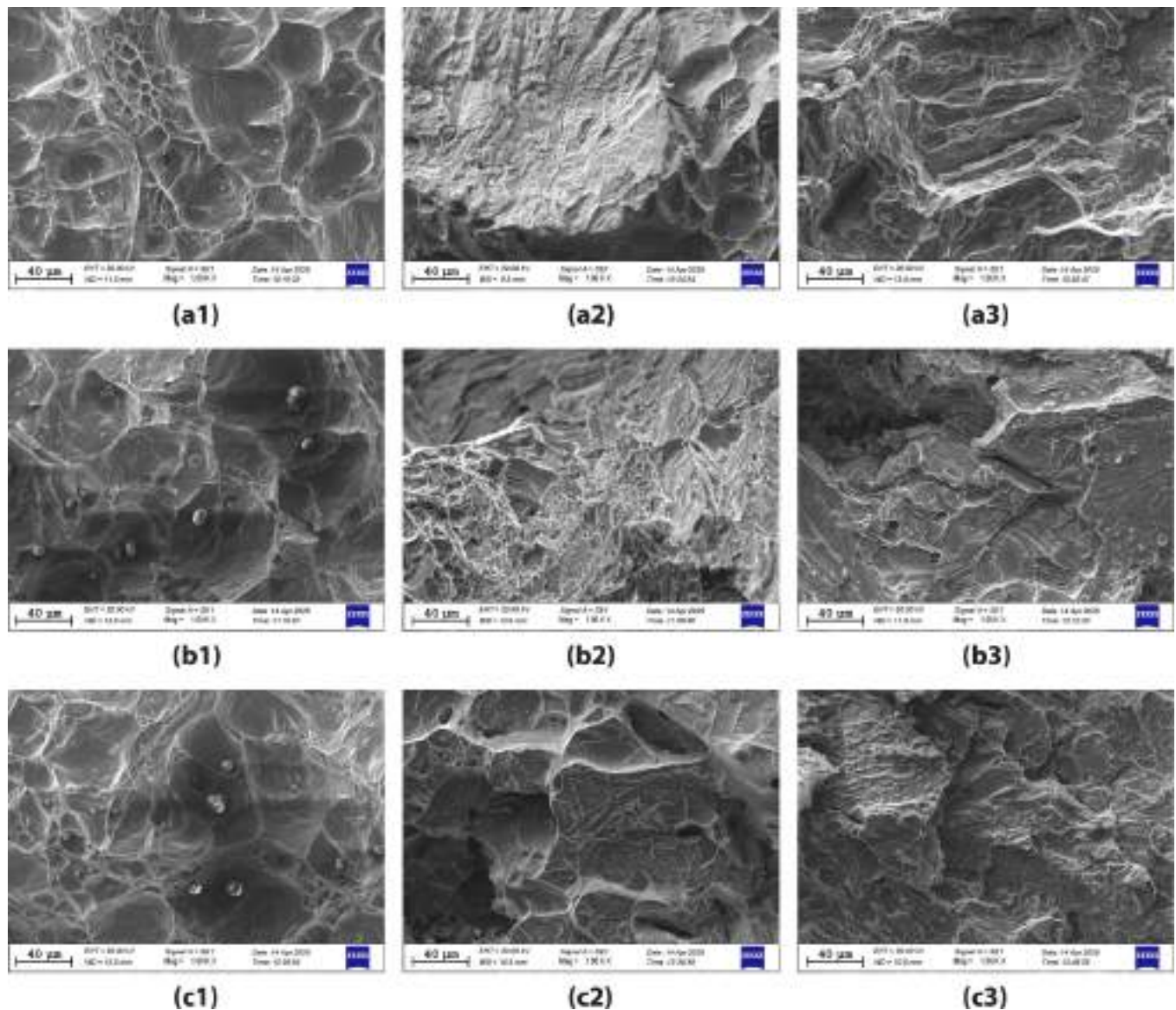


Fig. 13. SEM fractography of some impact samples representative of the different castings analysed: (a-) STD casting, (b-) L-RE casting, (c-) H-RE casting, (-1) 0% σ -phase, (-2) 10% σ -phase, (-3) 20% σ -phase.

refinement of the dimple morphology in rare earths-containing alloys, consistent with previous studies [26,44].

3.3.3. Effect of σ -phase and rare earth on impact strength

The results of the impact tests, shown in Fig. 11 as a function of the σ -phase content, confirm the trends observed in the other mechanical characterizations. The absorbed impact energy decreases with increasing amounts of this brittle secondary phase. Even a few percent of σ -phase cause an intense reduction in toughness, reaching values far below acceptable limits for practical applications [38,52]. This behaviour highlights the high sensitivity of impact testing as a diagnostic tool for detecting the presence of σ -phase in duplex stainless steels.

Comparing the results of the L-RE alloy with the STD cast reveals a similar trend. However, at low σ -phase fractions, the rare earths-containing alloy exhibits a slightly reduced impact energy, by several tens of Joules. This behaviour suggests that the RE addition in the L-RE alloy may not be sufficient to fully develop the beneficial effects associated with microstructural refinement and segregation control. Moreover, changes in the inclusion population and local microstructural heterogeneities introduced during solidification may partially

counteract the expected improvement in toughness [47,53]. When the σ -phase exceeds 15%, its embrittling effect becomes dominant, masking any influence of rare earth additions.

Conversely, specimens from the H-RE cast, characterized by a higher rare earth content, show an overall improvement in impact performance. This behaviour is consistent with previous studies reporting that sufficiently high RE additions can promote a more homogeneous solidification structure, reduce elemental segregation, modify the morphology and distribution of non-metallic inclusions and refine the microstructure [26,44,54]. These effects improve resistance to crack initiation and propagation, resulting in higher impact toughness, particularly at low σ -phase contents. It should be noted that these mechanisms are proposed based on literature evidence, as they were not directly investigated in the present study. In all cases, samples not fully solubilized exhibit impact energies below the reference limit, indicated by the grey line in Fig. 11.

Macroscopic fracture surface analyses of Fig. 12 provide clear visual evidence of the embrittling influence of the σ -phase. Fully solubilized specimens exhibit highly ductile fracture surfaces with significant plastic deformation and the typical three-dimensional morphology. For

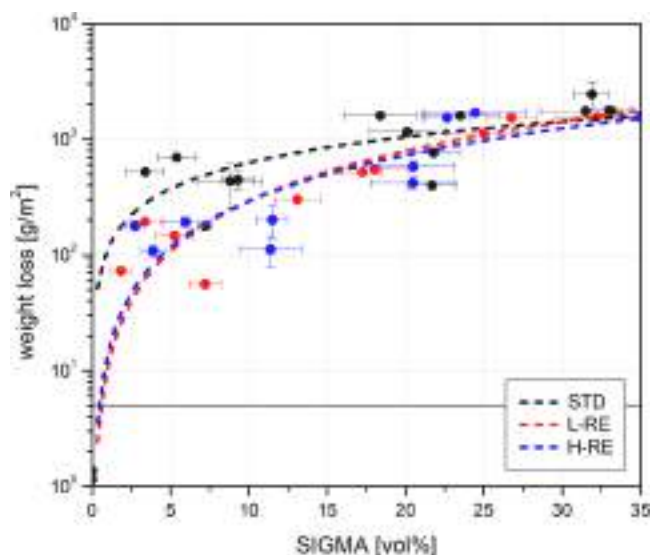


Fig. 14. Effect of σ -phase and rare earth on corrosion tests.

intermediate σ -phase fractions, the plastic deformation is particularly reduced. In this condition, the STD and H-RE casts show slightly higher ductility compared to the L-RE material, which appears less deformed. At higher levels of σ -phase content, fracture surfaces become flat, typical of a completely brittle fracture. In this case, the influence of rare earth additions does not produce any difference in behaviour, as the

embrittling effect of the σ -phase is dominant.

High-magnification SEM analyses of Fig. 13 further confirm these findings. In σ -phase free specimens, fracture occurs through micro void nucleation and coalescence, with numerous small dimples indicating ductile rupture. The nucleation of these voids generally occurs around non-metallic inclusions, which locally intensify stresses. As the σ -phase content increases, plastically deformed regions become progressively limited, while cleavage planes, slip bands, and microcracks become dominant, confirming a transition to brittle fracture. In several regions, distinct σ -phase imprints or exposed σ -phase particles can be observed on the fracture surface, identifiable by their morphology and verified via backscattered electron imaging and EDX analysis. These observations confirm the extreme alteration of fracture mechanisms induced by σ -phase precipitation.

A comparison between the different alloys does not reveal significant variations in the overall fracture morphology at the microscale. However, in the rare earth-containing samples, inclusions associated with rare earth elements are detected within the dimples, without significantly affecting the dominant fracture mechanisms.

3.3.4. Effect of σ -phase and rare earth on corrosion resistance

The results of the immersion corrosion tests, summarized in Fig. 14 as a function of the σ -phase content, clearly show the detrimental influence of this phase on corrosion resistance. The grey line represents the acceptance limit defined by the NORSOK M-630 standard [40]. A marked increase in weight loss is observed with increasing σ -phase fraction, ranging from a few grams per unit area in fully solubilized specimens to an asymptotic value of approximately 1500 g/m² for σ -phase contents above 30%, corresponding to the as-cast condition.

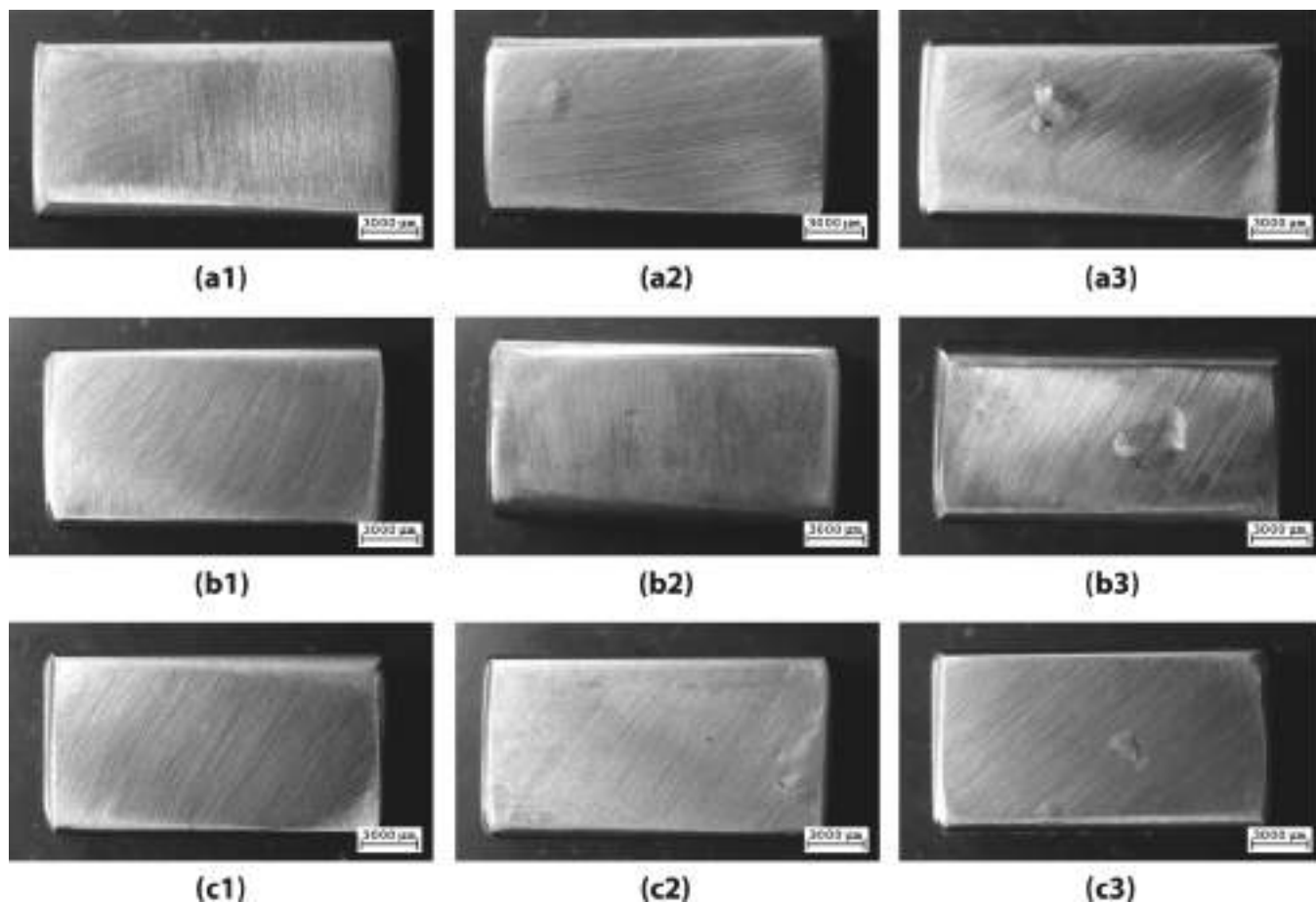


Fig. 15. Macro fractography of some corrosion samples representative of the different castings analysed: (a-) STD casting, (b-) L-RE casting, (c-) H-RE casting, (-1) 0% σ -phase, (-2) 10% σ -phase, (-3) 20% σ -phase.

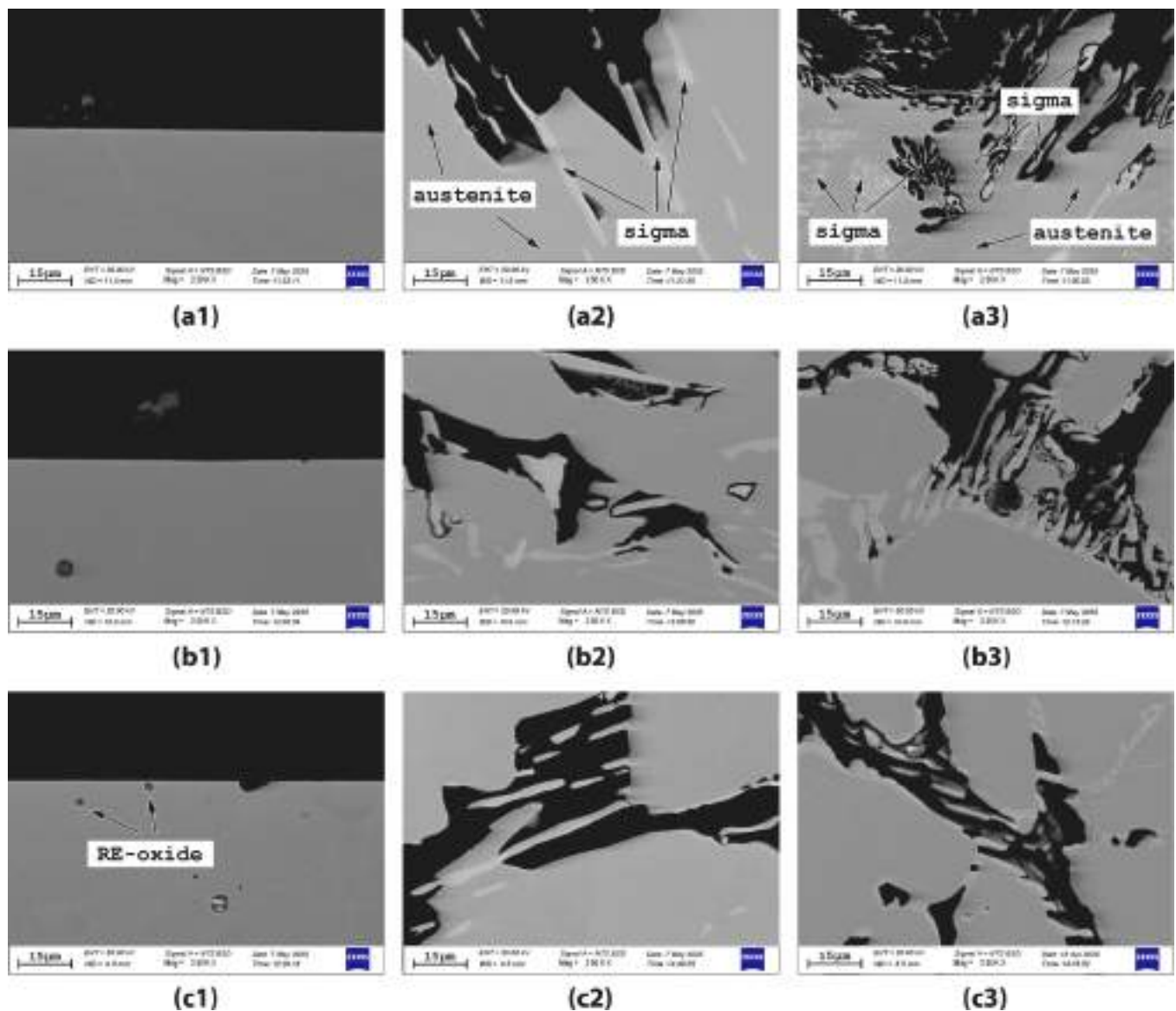


Fig. 16. SEM cross-section analysis of some corrosion samples representative of the different castings analysed: (a-) STD casting, (b-) L-RE casting, (c-) H-RE casting, (-1) 0% σ -phase, (-2) 10% σ -phase, (-3) 20% σ -phase.

This trend likely reflects a transition from localized corrosion mechanisms at low σ -phase levels to generalized corrosion as the amount of this phase increases.

The L-RE alloy exhibits improved corrosion resistance compared to the STD alloy at low σ -phase contents. For higher σ -phase fractions, however, the corrosion behaviour of all materials becomes comparable, as the overall response is dominated by the presence of σ -phase rather than alloying additions. These observations indicate that rare earth elements have a beneficial effect on the corrosion resistance of duplex stainless steels. This improvement is generally attributed to the modification of non-metallic inclusions and the resulting reduction in preferential sites for pit initiation, as well as to the formation of a more stable and protective passive film on the steel surface, which enhances resistance to localized corrosion phenomena [27,55].

The H-RE alloy, containing a higher amount of rare earth elements, shows a corrosion response nearly identical to that of the L-RE alloy. Unlike what was observed for the mechanical properties, increasing the RE content does not lead to a significant improvement in corrosion resistance.

Overall, acceptable corrosion performance, according to the

reference standard, is achieved only in the absence of σ -phase. Despite their longer duration, immersion tests prove to be an effective and straightforward method to reveal the presence of σ -phase in the material.

Macroscopic surface observations after immersion, shown in Fig. 15, confirm these findings. Fully solubilized samples exhibit no visible signs of corrosion, whereas samples containing σ -phase display localized swellings and surface depressions. Mechanical probing of these areas revealed extensive subsurface attack, suggesting that corrosion initiates from small pits formed where the passive film is locally disrupted by the σ -phase, subsequently propagating under the surface due to the locally increased aggressiveness of the electrolyte, consistent with the mechanisms of pitting and crevice corrosion [56].

At the macroscopic scale, no significant differences can be observed between the different alloys, indicating that the overall corrosion morphology is primarily governed by the presence and distribution of σ -phase. The effect of rare earth additions is therefore not directly evident from surface observations, although their influence on corrosion resistance is reflected in the quantitative results.

A more detailed analysis was performed by SEM in backscattered

electron mode on polished cross-sections, as shown in Fig. 16. These images confirm the absence of corrosion in fully solubilized specimens and highlight the cathodic nature of σ -phase, which is enriched in chromium and molybdenum. Corrosion preferentially develops in the adjacent ferritic regions acting as anodic zones. As a result, localized dissolution of the ferrite can lead to the detachment of non-corroded material fragments. Moreover, as illustrated in Fig. 16(c1), rare earth oxide inclusions located near the surface do not appear to initiate pits or other localized attack. Among the different alloys, no significant variation in corrosion mechanisms is observed at the microscale. SEM observations therefore suggest that, although the addition of rare earth elements does not alter the fundamental corrosion mechanism, their beneficial influence on overall corrosion resistance is clearly reflected in the weight loss measurements.

4. Conclusions

This study examined the microstructural evolution, mechanical behaviour and corrosion resistance of the SAF 2507 (X2CrNiMoN25–7–4) super duplex stainless steel, with particular attention to the effects of heat-treatment parameters and rare earth additions. Beyond confirming the influence of σ -phase precipitation, the study provides practical guidelines for optimizing both heat treatment and rare earth additions in industrially produced cast components. Moreover, the results provide practical instruments for optimizing phase balance and performance in industrial applications.

The main findings are summarized below:

- chemical analysis confirmed the successful production of the target SAF 2507 composition in all investigated alloys, with PREN values exceeding 40;
- σ -phase gradually solubilizes as the temperature and holding time increase; the introduction of rare earth elements significantly enhances phase stability by promoting austenite formation and effectively reducing σ -phase precipitation, particularly at lower temperatures;
- hardness increases with σ -phase content but remains within the standard limits; σ -phase significantly reduces tensile strength and ductility, while rare earth additions consistently improve the mechanical response, leading to higher strength and enhanced ductility compared to the standard alloy;
- corrosion resistance worsens in the presence of σ -phase, while rare earth elements markedly improve corrosion performance, especially at low σ -phase fractions, by enhancing microstructural homogeneity and stability; only fully solution-treated specimens meet the required corrosion performance.

Among the investigated compositions, the H-RE alloy exhibited the best overall balance between microstructural stability, mechanical properties and corrosion resistance, indicating that the higher rare earth addition adopted in this study represents the most effective alloying condition among those investigated.

Overall, the results clearly demonstrate that the combined optimization of solution heat treatment and rare earth additions represent an effective alloying strategy to enhance both microstructural stability and service performance of super duplex stainless steels, particularly under conditions prone to σ -phase formation.

These observations highlight the potential of tailored alloying strategies to fine-tune the behaviour of super duplex stainless steels and provide practical processing guidelines for industrial castings requiring high mechanical performance and corrosion resistance. Future work should systematically investigate thickness-dependent microstructural evolution to enable reliable upscaling to industrial components.

CRediT authorship contribution statement

Francesco Sordetti: Writing – review & editing, Writing – original draft, Validation, Methodology, Formal analysis, Conceptualization. **Niki Picco:** Writing – review & editing, Investigation. **Michele Magnan:** Investigation. **Elia Marin:** Writing – review & editing, Investigation. **Claudio Maranzana:** Resources. **Alex Lanzutti:** Writing – review & editing, Supervision.

Declaration of Generative AI and AI-assisted technologies in the writing process

No generative AI or AI-assisted technologies were used in the preparation of this manuscript.

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Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Data availability

The data that has been used is confidential.

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