Mechanical and Microstructural Characterization of a New Corrosion Resistant Stainless Steel

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Abstract. The paper investigates the manner in which the chemical composition and delivery status of a new type of stainless steel, highly alloyed with Ni and Cr, affect mechanical properties, microstructure and corrosion resistance. The results obtained during the mechanical test (tensile, compression, Charpy test and micro-hardness) have revealed promising values. During the corrosion test, the preferential attack of the reagent (Aqua regia) located on the grain boundaries, inclusions or polyhedral precipitates have been observed. On the corroded surfaces, some localized pitting effects on grain boundaries have been revealed. The analyses of the parameter values recorded during the corrosion test revealed that the corrosion current density had a low value, comparable to that of other specific types of stainless steels. The actual I_{corr} (1.089 µA/cm^2) value measured for the experimental alloy proves good resistance to corrosion in 3% NaCl saline solution. The estimated rate of corrosion presented acceptable values (0.011 mm/year).

1. Introduction
Austenitic microstructure refractory alloys, class X10NiCrAlTi 32-20, containing 32% Cr and 20% Ni, are currently used for the manufacture of components integrated in industrial equipment and plants operating in corrosive environments at high temperatures.

The main requirements imposed on these alloys are related to their microstructural stability at high temperatures (creep resistance) and corrosion resistance [1].

There are currently known grades of similar refractory stainless steel (X 10 NiCrAlTi 32 20*/X 5 NiCrAlTi 31 20**/X 10 NiCrAlTi 32 20 H***) - manufactured by specialized companies - serviceable in the best conditions up to temperatures of 500°C in humid corrosive environments. Similar alloys with high resistance to high stress, high temperatures and corrosive environments are manufactured on the specialized market under different trade names (Dicaloy, A286) used for turbine rotors, engines or chemical reactors components [2].

EN 14532-2 provides X10NiCrAlTi 32-21 and X0NiCrAlTi 32-21 (RK) as serviceable in the 600 - 1000^{o}C temperature range for up to 300000 hours of operation. Unfortunately, super-austenitic steels do not behave well at temperatures above 680^{o}C, and nickel based super alloys (Inco 617, INCOLOY 800, 800T, 8000HT, Waspaloy) [3-7] are required for such applications.

The Asian market can be considered the main competitor in the special steels market at global level. Some of the most famous manufacturers of special steels and super alloys are: SPECIAL Metals Corporation - USA**;** Bibus Metal - Switzerland**;** Santok Steel - India**;** Piyush Steel - India**;** Tools&Die

Steels - China**;** Aubert Duval-France. The first paragraph after a heading is not indented (Bodytext style).

According to the Romanian National Institute of Statistics, the total annual steel consumption in Romania (an accurate indicator of the GDP evolution) in 2017 amounted to approx. 3.4 million tons, of which, the special alloys required amounted to approx. 40,000 t/year, quantity fully imported.

The X10NiCrAlTi 32-20 refractory alloy manufactured in Romania is classified as stainless steel due to the very high Ni content (32.0 - 38.0%), although its chemical composition is very close to the one of a super alloy (Ni-based), taking from it not only the advantages (corrosion resistance, high working temperature etc.), but also the disadvantages, of which the most important are the low technological properties, thus creating great problems for obtaining desired quality parts.

The high content of Cr (19 - 23%) also creates great problems during production and casting, requiring smart solutions for placing coolers in zones with high contractions and sections to ensure a low level of impurities (by refining and micro-alloying with the Ti, Al, Ce stabilizing elements).

Since the main problem in the processing of this alloy is the loss of microstructural stability and the hot cracking [9, 10], elements such as Ti, Al and lanthanides (Ce) are added to the chemical composition in order to finish the granulation and limit the effects of precipitation of chromium carbides, causing the alloy to become brittle at high temperatures.

The aggregate content of the micro alloying elements should be less than 0.8% (Al + Ti + Ce) in order not to generate additional hardening effects and to maintain the tenacity of the metal matrix.

The aim of the paper is to present the results for the execution and testing of a new grade of refractory austenitic steel, highly alloyed with 32% Cr and 20% Ni and stabilized with titanium, in order to obtain parts which can be used in various niche fields in the industry. The development of the production technology combined with the casting technology for this steel grade will bring economic benefits and prestige to the manufacturer, IMA METAV, one of the few SMEs in Romania whose activity is the manufacture of castings made of special alloys.

2. Materials

The experimental X10NiCrAlTi 32-20 refractory stainless steel were obtained in the RAV plant of IMA METAV, Bucharest.

The chemical composition of the new austenitic refractory stainless steel was determined by optical emission spectrometry using the SpectromaXxM spectrometer and the Fe-30-M (Cr-Cr/Ni-steel – M) program.

For inter-comparison, the chemical composition analysis was conducted by IMA-METAV as well, using the Fe-30 program, and the results are summarized in Table 1.

Table 1. Chemical composition of X10NiCrAlTi 32-20, wt. %.

C	Si	Mn	Cr	Ni	Mo	Al	Cu	Ti	P	S
UPB										
0.104	1.09	0.42	19.98	32.28	0.453	0.432	0.160	0.175	0.014	0.0011
IMA METAV										
0.094	1.22	0.689	19.0	31.69	0.435	0.46	0.191	0.151	0.018	0.012

3. Testing methods

3.1. Mechanical tests

The tensile tests were carried out using the ”W+b” Walter+Bai AG traction/compression testing machine, using specimens taken from the cast melts, processed by milling (Figure 1).

The results of the tensile test performed on a batch of 3 identical specimens are shown in Figure 2 and Table 2.

The elasticity modulus was determined by linear regression E = 104608.98±3946.2 Mpa.

Figure 1. Continuous tensile test specimen, dimensions: 9.54x3.99 mm and Lc=105 mm, before and after fracture.

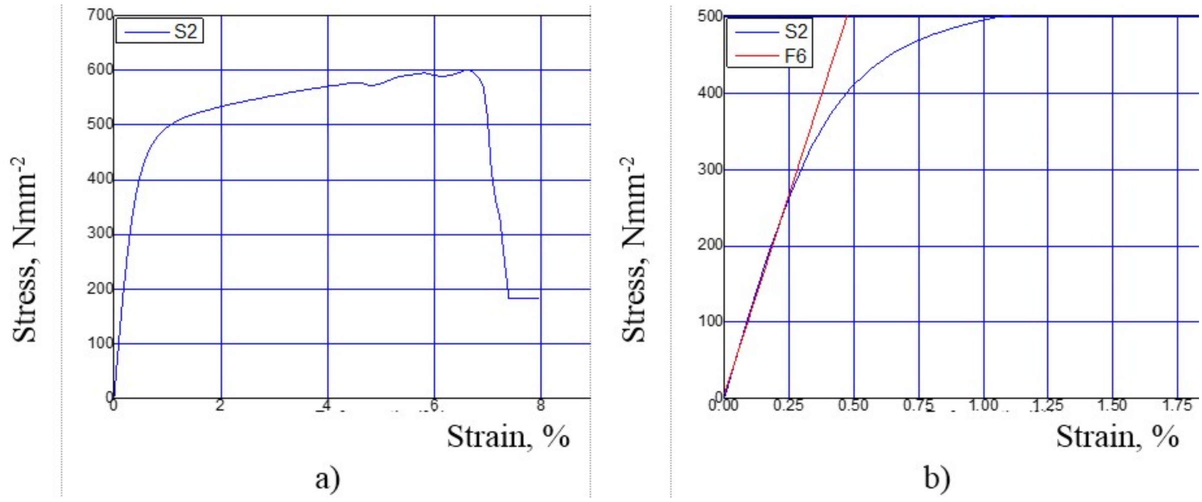


Figure 2. The tensile stress-strain diagrams: (a) global diagram; (b) proportionality zone for 0.25% proportional deformation.

Table 2. The average values of mechanical characteristics for experimental refractory stainless steel.

Material	σ_e [MPa]	$\sigma_{0.2}$ [MPa]	σ_{max} [MPa]
X10NiCrAlTi 32-20	260	450	601

The compression test results are presented in Figure 3.

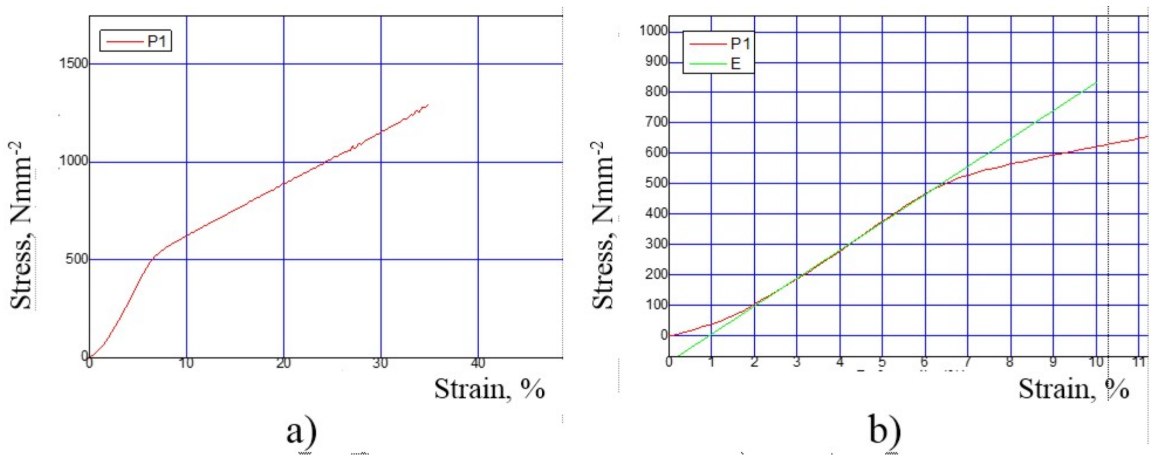
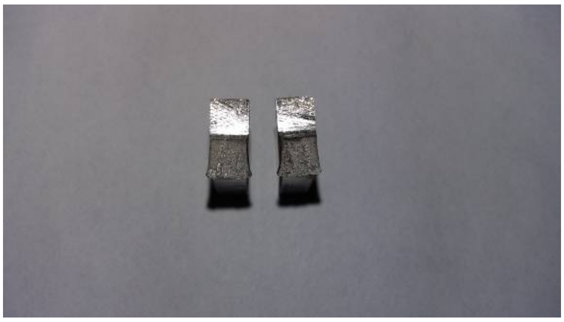
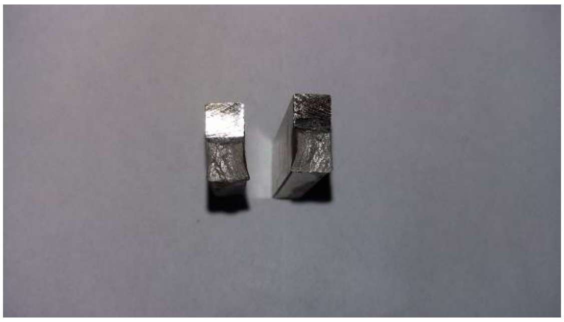


Figure 3. Stress-strain diagrams for the compression test: (a) Stress-strain diagram; (b) Determination of the elastic limits value: 498MPa with 6.34% deformation.

The impact tensile test was conducted at ambient temperature (23 ºC. 45% humidity), using the W+b (Walter+Bai AG) testing machine. Four identical specimens, with small cross-section, were tested, and the results are shown in Figure 4 and Table 3, indicating the mixed-mode fracture (ductile/brittle) and the existence of sliding planes.



Test 1



Test 2

Test 3

Test 4

Figure 4. Macroscopic appearance of impact fracture surfaces.

Table 3. Absorbed energy values during the impact test.

Sample	**1**	**2**	**3**	**4**	**Average value**
Absorbed energy, J	14.4	11.1	8.9	9.9	11

3.2. Corrosion resistance assessment of stainless steel

The corrosion resistance was determined using *the linear polarization technique,* consisting of the following steps: measurement of open circuit potential (E_{OC}) over 6 hours; plotting the potential-dynamic polarization curves from -1 V (vs OCP) to +1 V (vs SCE), at a 1 mV/s scan rate. The corrosion resistance evaluation tests were conducted using a potentiostat / galvanostat (PARSTAT 4000 model, manufactured by Princeton Applied Research, USA), and the potential dynamic curves were acquired using the Versa Studio v.2.50.3 software.

The tests were conducted using an electrochemical cell (Figure 5) consisting of a calomel saturated electrode (CSE) - a reference electrode, a platinum electrode - a recording electrode and a working electrode, represented by the stainless steel samples investigated.

The surface of the samples was prepared before the tests were carried out by: grinding using 400- to 1000-grit metallographic papers, polishing with a particle suspension of Al_2O_3 with an average diameter of 1 μm. In order to ensure the electrical contact, the surface of the samples was coated with an epoxy resin and the surface exposed to corrosion was of approximately 1 cm^2.

Figure 5. Electrochemical cell used in corrosion tests.

The tests were conducted in 3.5% NaCl saline solution at 25 °C. Before the tests, the samples were immersed in electrolyte until the open circuit potential (OCP) stabilized. The open circuit potential variation (E_{oc}) of the stainless steel is shown in Figure 6, and the potential dynamic curve is shown in Figure 7. The polarisation resistance, used to characterise the corrosion resistance, was calculated using the parameters determined by the Tafel technique. The main parameters of the electrochemical corrosion process are presented in Table 4.

Table 4. The main parameters of the corrosion process.

Material	E_{oc} (mV)	E_{cor} (mV)	i_{cor} (μA/cm^2)	β_c (mV)	β_a (mV)	Rp (kΩxcm^2)	CR (mm/year)
Stainless steel	-179	-369	1.089	103.13	1333	38.21	0,011

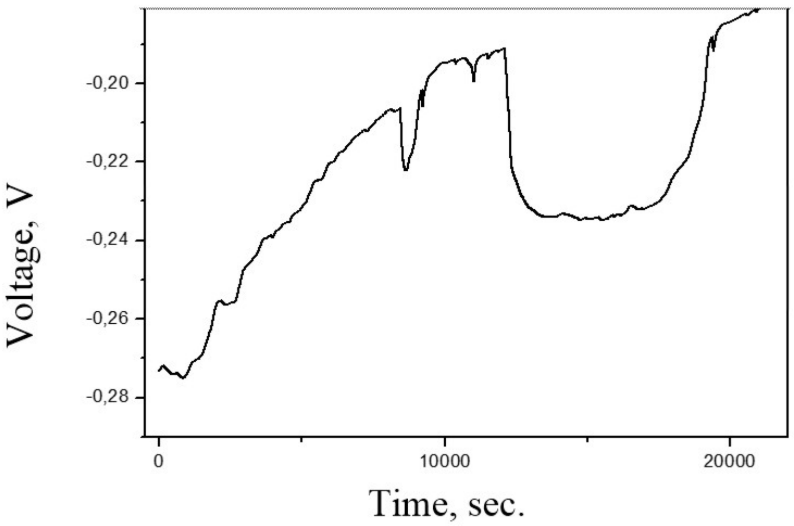


Figure 6. The evolution of the open circuit potential (E_{oc}).

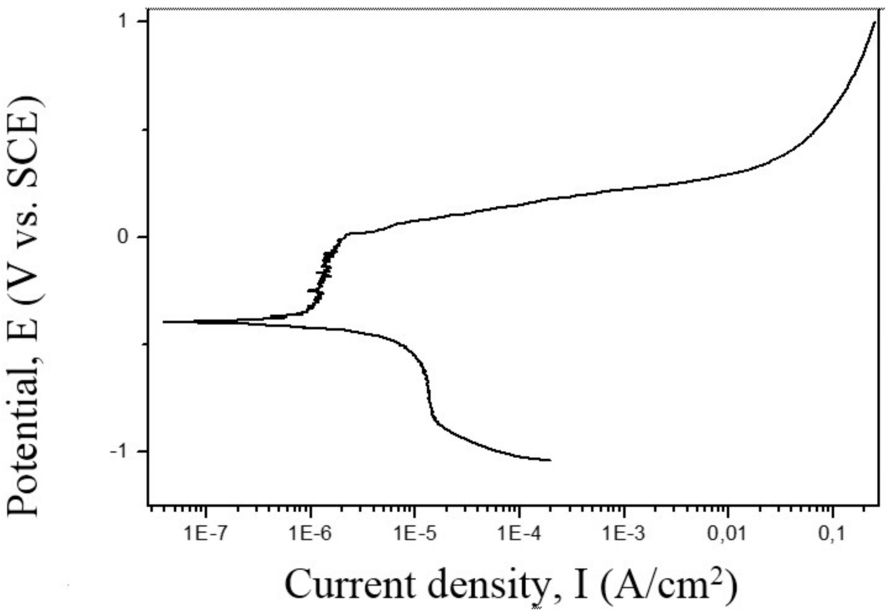


Figure 7. The potential dynamic curve of experimental stainless steel.

The analysis of recorded and calculated parameters reveals that the corrosion current density is low and close to other types of stainless steel. This i_{cor} (1.089 µA/cm^2) value of the material being investigated gives it good resistance to corrosion in 3% NaCl saline solution.

Furthermore, in terms of corrosion rate, there can be seen that it has acceptable values (0.011 mm/year), but account must be taken of the operating mode and the application.

The variation of the potential in open circuit reveals its evolution to more electro-positive potentials (passivation), but with periods when the potential decreases strongly (the protective oxide layer on the surface deteriorates), followed by re-passivation.

The shape of the potential dynamic curve reveals in the cathodic curve a passivation trend between - 300 mV and 0 V with a small variation in the density of the corrosion current followed by a decrease in the current density, which indicates sensitivity to pitting.

3.3. Metallographic analysis

The samples selected for the metallographic analysis were sanded using abrasive paper (600-1000 grain size) and then polished with fine Al_2O_3 abrasive powder, 1.0 to 0.25µm grain size.

Sample surfaces were ultrasonically degreased for 30 minutes in ethanol then chemically attacked with metallographic reagent (Aqua regia) and subjected to metallographic analysis (Figure 8).

The microstructural aspects highlighted by metallographic analysis indicate the dendritic microstructure, with pitting effects, as a result of the preferential attack of the chemical reagent on the grain boundaries.

There can also be noted the intra-granular separation of polyhedral inclusions and precipitations.

The fracture surfaces reveal the presence of polygonal inclusions and sliding or flattening planes, alternating with cup-type ductile fracture zones.

The metal matrix micro hardness was measured using a Shimadzu HMV 2T micro hardness tester, in longitudinal section (198 HV_1) and in cross section (194 HV_1).

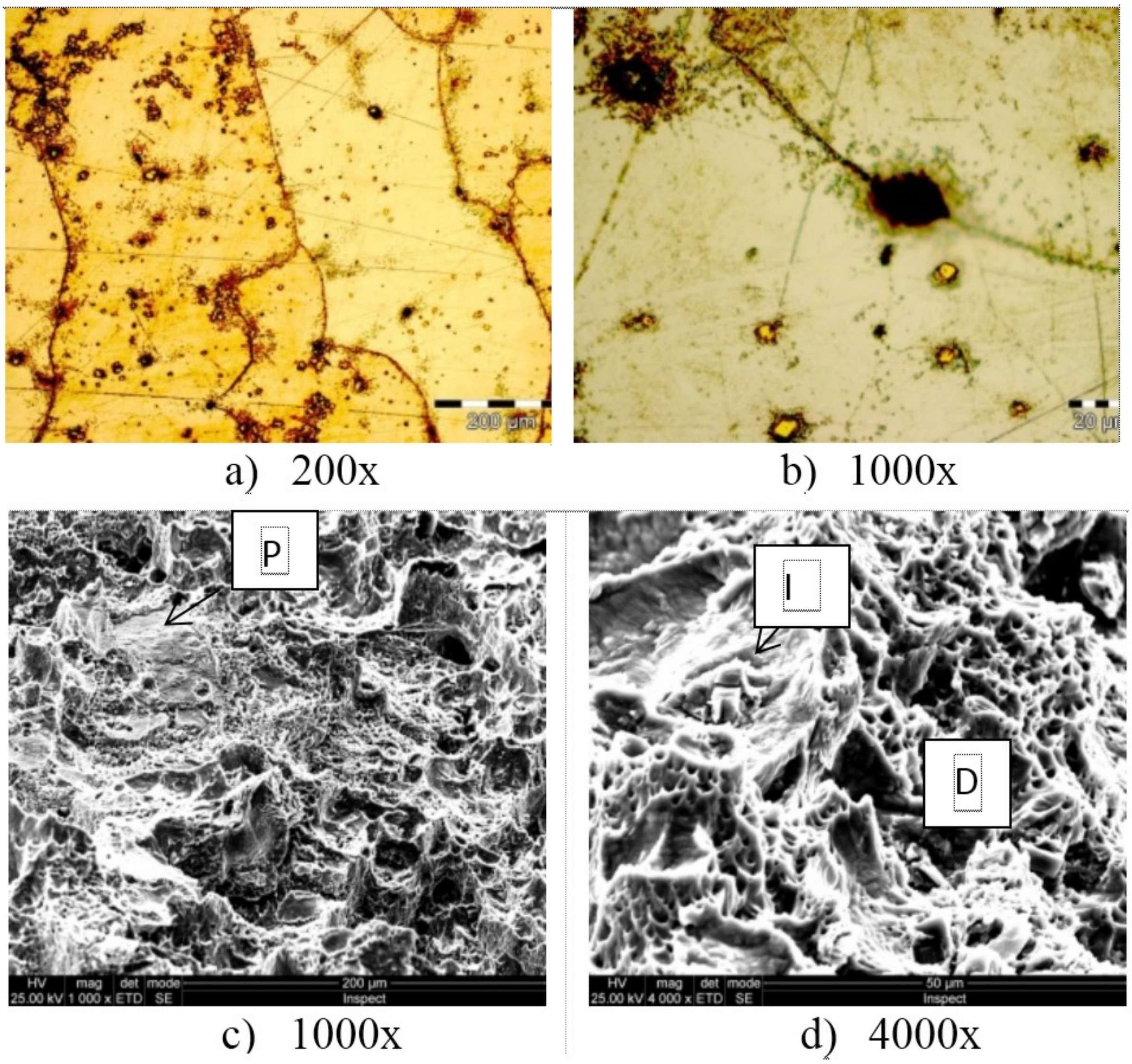


Figure 8. Microstructural aspects of experimental refractory stainless steel; (a), (b) dendritic microstructure and precipitation of inter-metallic compounds (optical micrograph); (c), (d) Fracture surfaces: flattening and sliding planes (P) alternating with cup-type ductile fracture zones (D) and polygonal inclusions (I) (SEM micrograph).

4. Conclusions

The microstructural results are in good agreement with the impact fracture behaviour, the values obtained being inferior to a steel of the same alloying class, but in laminated state.

The hardness values determined by the Vickers method fall within the usual limits for the steel class of the analysed experimental material (200HV), with no significant differences between the values determined in cross section or longitudinally, attesting the homogeneity of the metal matrix.

The compression test behaviour of the analysed alloy is satisfactory, the value of the longitudinal elasticity coefficient being of maximum 9855.99 ± 37.17MPa and the value of the elastic limit being 498MPa. The fracture energy values fall within the margin of medium resistance steels.

The analysis of the results obtained in the corrosion tests reveals that the density of the corrosion current has a low value, close to the one of other types of stainless steel (i_{corr} = 1.089 µA/cm^2), giving it good corrosion resistance in 3% NaCl saline solution. In terms of corrosion rate, the experimental steel features acceptable values (0.011 mm/year).

5. References

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Acknowledgments
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