

THE INFLUENCE OF HEAT TREATMENT ON STRUCTURAL AND MECHANICAL PROPERTIES OF THE NICKEL-BASED ALLOY BC1

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Abstract. *The superalloy BC1 (trademark of HAYNES International, Inc.) is an alloy used in the production processes of organic acids at high temperature, refining industry and a wide variety of chemical applications using hydrochloric and sulfuric acids. The HYBRID-BC1 is an alloy composed essentially of 62% of nickel, 22% of molybdenum and 15% of chromium. Its matrix is austenitic and its structure is face-centered cubic. The aim of this work is to study the influence of heat treatment on the structural and mechanical properties of the nickel based alloy. Indeed, four temperatures were chosen 700°C, 800°C, 900°C and 1000°C for a treatment time of 3 hours. The final hardness of the alloys treated at 700°C, 800°C, 900°C and 1000°C is equal respectively to 47.25 HRF, 47 HRF, 47 HRF and 47.5 HRF. The images obtained by optical microscopy after the iso-thermal treatments showed the presence of carbides at the joints and inside the grains in several morphologies, discontinuous transformations and eutectic precipitates. The X-ray diffraction spectra done during over aging consist of peaks of the austenite phase and precipitates.*

Keywords: *Nickel-based alloy, thermal treatments, hardness, optical microscopy, X-ray diffraction.*

1. INTRODUCTION

The large family of nickel-based alloys has been empirically developed over the last 60 years from a matrix consisting of nickel-chromium [1]. These austenitic alloys have a face-centered cubic structure which improved mechanical properties at high temperatures compared to alloys body-centered cubic structure [1].

The family B contains nickel-chromium based alloys characterized by good resistance to oxidizing environments [2]. The alloys of the family C are Nickel-Chromium-Molybdenum based alloy that combine a good resistance to reducing and oxidizing environments [3]. According to the manufacturer, the superalloy HYBRID-BC1 is an alloy used in applications even in the presence of various oxidizing impurities that neither the alloys of the family B and C can support.

The addition of aluminum protects the alloy against corrosion at high temperature by forming a layer of oxide Al₂O₃ [4]; a protective layer Cr₂O₃ is also formed due to the presence

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of chromium [5]. The role of Silicone added in small proportion is to maintain these oxide layers [4]. Molybdenum is a refractory element [6] and which can also drastically degrades resistance to corrosion at high temperature for Nickel-based superalloys [4].

In industrial application, structural changes occurs which can be beneficial or not. For example, carbon tends to form carbides [5] and their precipitation in the grain boundaries depletes zones close to grain boundaries of chromium which leads to corrosion [7]. While the precipitation of phase γ' increases the hardness [8].

The objective of this work is to treat the alloy BC1 thermally at 4 different temperatures 700 °C, 800 °C, 900 °C and 1000 °C for 3 hours. Indeed, we followed the progression of structural and mechanical properties.

2. MATERIALS AND METHODS

2.1. PREPARATION OF ALLOYS

A plate is supplied by the HAYNES International, Inc company. The samples, obtained by sawing, have a square shape of dimensions 20 mm \times 19.5 mm and thickness of to 3 mm. The composition of the alloy BC1 is given in the table below:

Table 1. Chemical composition of the alloy BC1

Ni**	Mo	Cr	Al	Mn	Fe	C	Si
62	22	15	0.5 *	0.25	2*	0.01 *	0.08 *

*Maximum Percentage, **: Balance.

Nickel-based superalloys have a face-centered cubic structure [1], due to the presence of high proportion of nickel which has the role of stabilizer of this structure [9]. According to the ternary diagrams [10], with 62% nickel, 22% molybdenum and 15% chromium, we notice that the matrix is austenitic. We also note the existence of phases P and σ which are undesirable intermetallic compounds. At the temperature 600 °C, the phase P is present in the matrix, at 800°C the phase μ is formed and at 1250 °C the phase P reappears. We observe also that by increasing the temperature and the concentration of nickel the austenitic domain widens while chromium tends to favor crystallization of alpha phase [5].

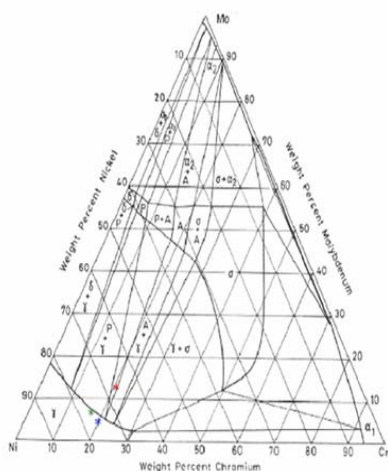


Figure 1. Phase diagram Ni-Cr-Mo at 600°C.

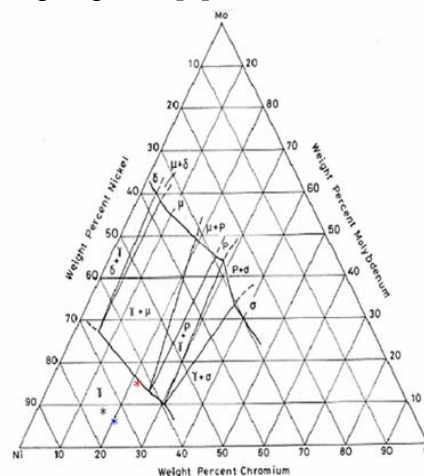


Figure 1. Phase diagram Ni-Cr-Mo at 850°C.

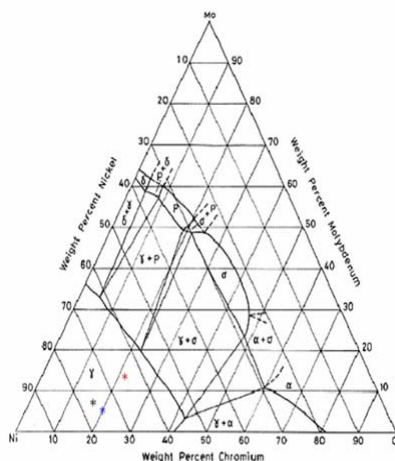


Figure 2. Phase diagram Ni-Cr-Mo at 1000°C.

2.2. HARDNESS

The ROCKWELL F hardness tests are realized by a universal durometer, the indenter used is a steel sphere with a 1/16-inch-diameter (1.588 mm) under a load of 60 Kgf. Each measurement is the average of 5 marks well distributed on the flat section. These sections are obtained by polishing and finishing using abrasives more and finer turning around a fixed axis with water lubrication to avoid overheating which could cause changes in structure.

2.3. X-RAY DIFFRACTION

The X-ray diffraction spectra of the four samples during aging and over-aging are obtained at room temperature using D2 PHASER diffractometer, Bragg-Brentano geometry, radiation type Cu $K\alpha = 1.5406 \text{ \AA}$ and the scanning interval is 15 to 100 ° with a step of 0.01 (2 θ).

2.4. OPTICAL MICROSCOPY

After heat treatments, precipitates are formed from the saturated matrix [11] and in order to detect changes in structure, we used optical microscopy. In general, Micrographic observation requires physical polishing and chemical etching. In the case of nickel-based alloys, chemical etching is performed by aqua regia used immediately after preparation. The etching solution reveal grain boundaries and outline carbides, consisting of HCl and HNO₃ of with a proportion of 3: 1 and immersion time between 5 and 60 seconds [12].

3. RESULTS AND DISCUSSION

3.1. THE STUDY OF THE ALLOY BC1 TREATED AT 900 °C

3.1.1. Hardness measurement

According to Fig. 4, hardness remains almost constant in the first 40 minutes then it increases rapidly with an almost linear manner to reach a maximum value of 53 HRF after 100 minutes. It decreases slowly to reach a final hardness of 47.5 HRF after almost 23 days. The hardness curve in Fig. 4 shows that the aging kinetic is fast unlike overaging where the kinetic is slow.

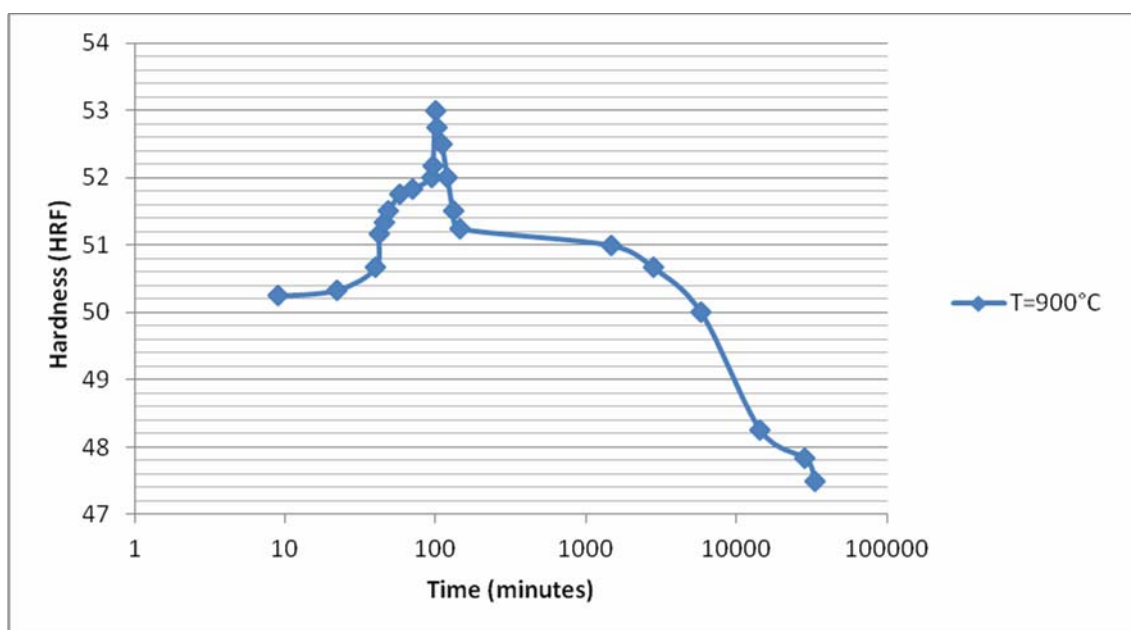


Figure 3. Evolution of hardness in HRF of piece treated at 900°C in function of time.

3.1.2. Optical Microscopy

The figures show that the precipitation is intergranular and intragranular with different morphologies. Fig. 5 shows the appearance of granular carbides after 11 days which are distributed randomly in the matrix which represent the source of carbon during the heat treatment [2]. Fig. 6 shows after 11 days the appearance of precipitates of different morphology which are eutectic precipitates γ - γ' [13], the size and the proportion of γ' influence significantly on the properties of the nickel-based alloys at high temperatures [14]. Fig. 7 shows the precipitation of carbides at grain boundaries γ/γ after 11 days from quench which constitutes privileged sites for precipitation [15]. The grain boundaries have a high interfacial energy [16] and they are considered as preferential site for precipitation. They form a continuous "film" on grain boundaries that leads to a degradation of mechanical properties [3].

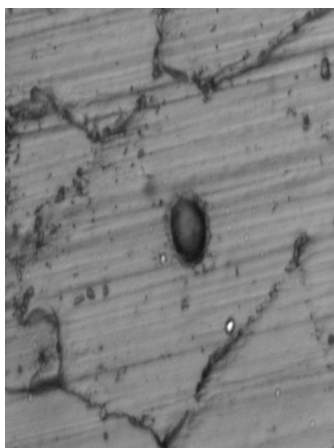


Figure 4. Visualization of the structure of the BC1 alloy treated at 900°C, attacked with aqua regia, after 11 days from quench.

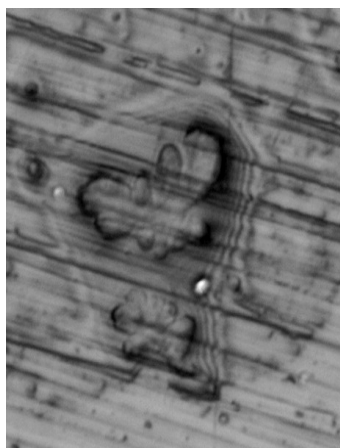


Figure 5. Visualization of the structure of the BC1 alloy treated at 900°C, attacked with aqua regia, after 11 days from quench.

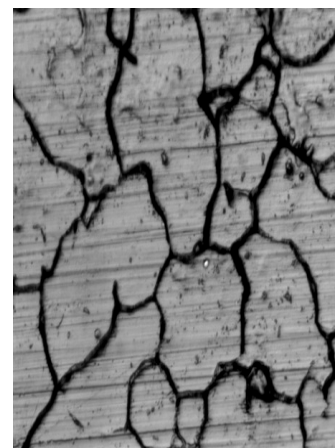


Figure 6. Visualization of the structure of the BC1 alloy treated at 900°C, attacked with aqua regia, after 11 days from quench.

3.1.3. X-Ray Diffraction

In figure 8, we notice in the diffractogram that the treated alloy structure remains face-centered cubic characterized by planes (111), (200), (220) and (311). We also note that peaks consisting of singlets during aging at the positions (b), (c) and (d) become in over aging doublets because of the formation of precipitates.

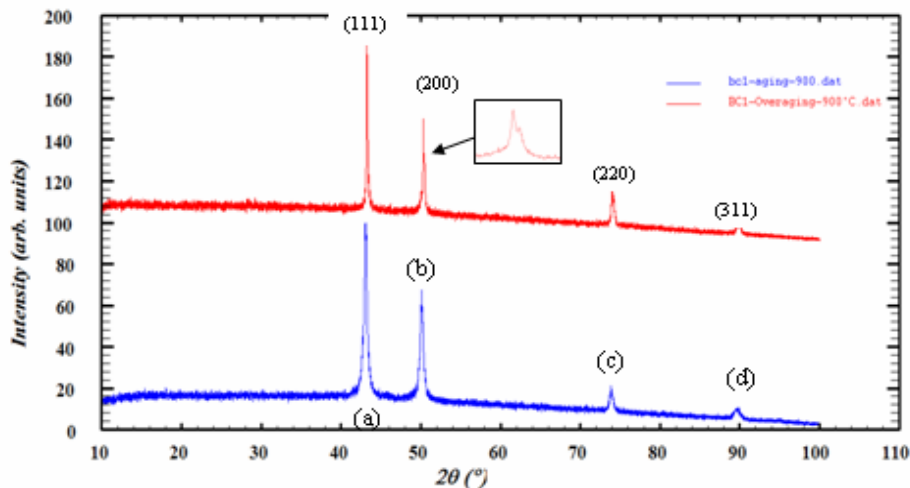


Figure 7. X-ray diffraction spectra of the alloy BC1 during aging and over-aging treated at 900°C.

According to Table 2, during over aging, the alloy is more stable because the intensity of peaks increased compared to aging and that influences badly on mechanical properties and making them deteriorated [17].

Table 2. Peak intensity of aging and over aging spectra of the piece treated at 900°C.

POSITIONS (2 θ)	PEAK INTENSITY	
	AGING (%)	OVER AGING (%)
42	49	73
89	81	83
46	71	13
28	5	13

3.2. THE STUDY OF THE INFLUENCE OF THE THERMAL TREATMENT

3.2.1. Hardness measurement

Fig. 9 shows the evolution of hardness of the alloy treated at 700 °C, 800 °C, 900 °C and 1000 °C versus time. We find that the phenomena of aging and over aging are similar for the four temperatures, indeed for:

- The temperature 700°C, hardness begins with a rapid augmentation from 49 HRF to 52.75 HRF in 151 minutes, this phase of preliminary hardening is almost linear, followed by a slow hardening to reach a maximum value of 53 HRF after 26 hours. Thereafter, there is a remarkable decrease in hardness which stabilizes at 47.25 HRF after 26 days.
- The temperature 800°C, we observe that hardness is stable for 16 minutes followed by a rather important hardening in terms of amplitude from 50.67 HRF to 52.50 HRF in 94 minutes. After, it decreases slightly during over aging before stabilizing at 47 HRF after 26 days.
- For temperature 1000°C, the aging phase is reached quickly just after 132 minutes with a hardness of 51 HRF. Then the hardness decreases slowly to reach a value of 47 HRF in 21 days.

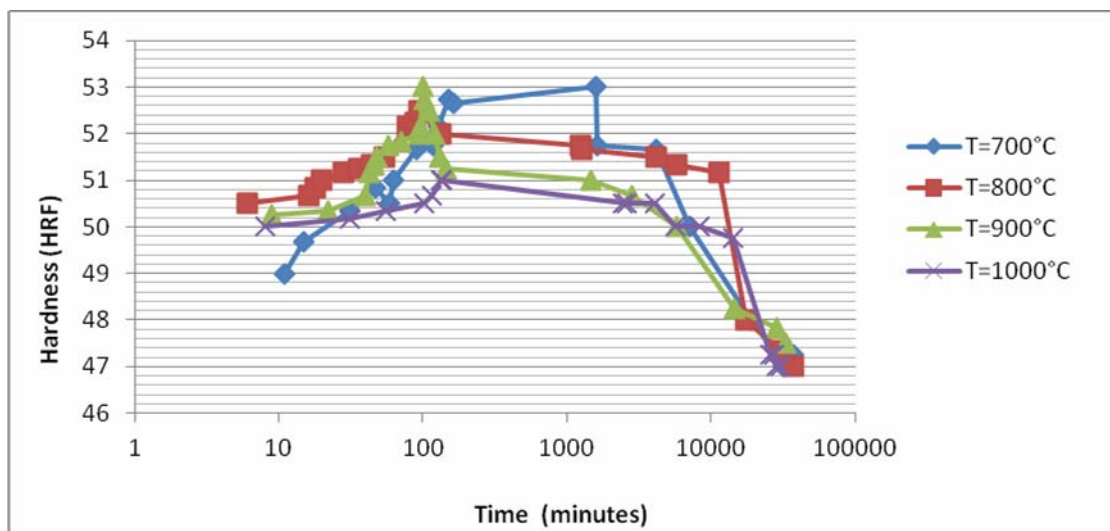


Figure 8.The evolution of the hardness of the piece treated at 700°C, 800°C, 900°C and 1000°C in function of time.

3.2.2. Optical Microscopy

The emplacement, the morphology and the composition of carbides influence the alloy properties [18]. The figures 10-12 show intragranular precipitation of primary granular carbides. According to these figures, we also see the movement of carbides fronts which are intimately linked to the hardness of the alloy. In figure 11, we notice the coalescence phenomenon that leads to increasing the size of carbides.

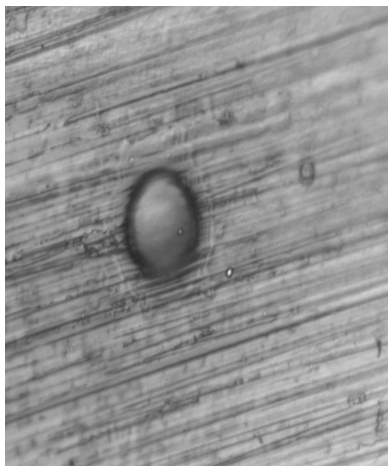


Figure 9. Visualization of the structure of the BC1 alloy treated at 700°C, attacked with aqua regia, after 13 days from quench.

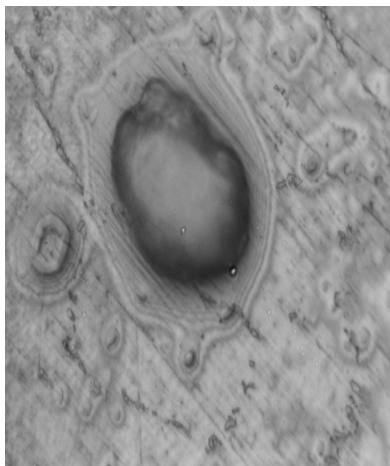


Figure 10. Visualization of the structure of the BC1 alloy treated at 800°C, attacked with aqua regia, after 15 days from quench.

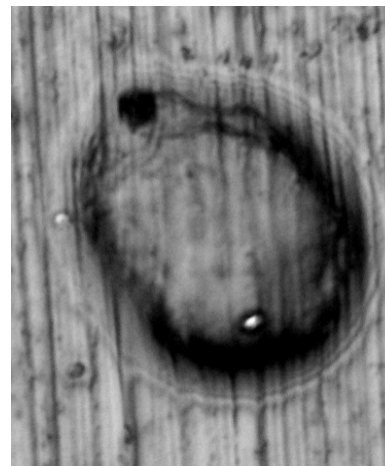


Figure 11. Visualization of the structure of the BC1 alloy treated at 1000°C, attacked with aqua regia, after 11 days from quench.

The figures 13-15 show intergranular precipitation of carbides in form of continuous “film” formed as a result of the decomposition of primary carbides and they tend to precipitate at grain boundaries [19].

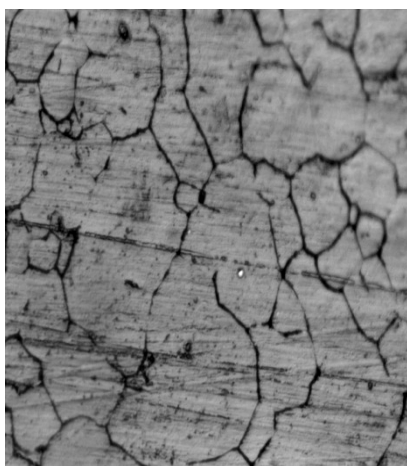


Figure 12. Visualization of the structure of the BC1 alloy treated at 700°C, attacked with aqua regia, after 13 days from quench.

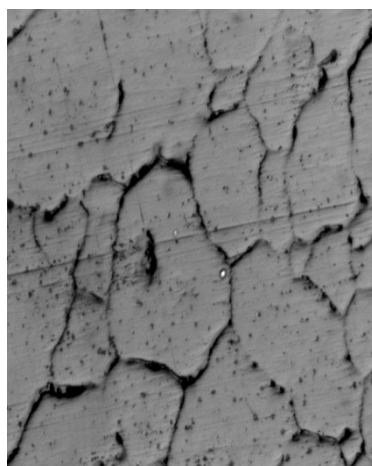


Figure 13. Visualization of the structure of the BC1 alloy treated at 800°C, attacked with aqua regia, after 13 days from quench.

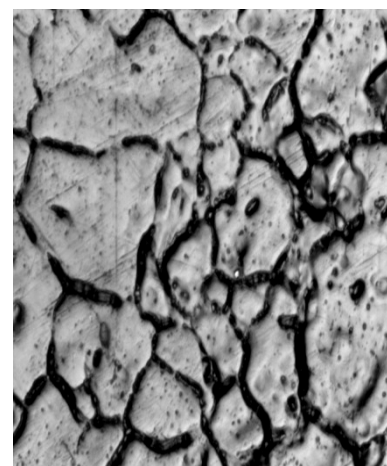


Figure 14. Visualization of the structure of the BC1 alloy treated at 1000°C, attacked with aqua regia, after 13 days from quench.

In figures 16 and 17, it can observe a dispersion of fine particles precipitated in the matrix during aging of the alloys treated at 700 °C and 1000 °C which are acting as a barrier to dislocation motions and leads to an increase in hardness [20].

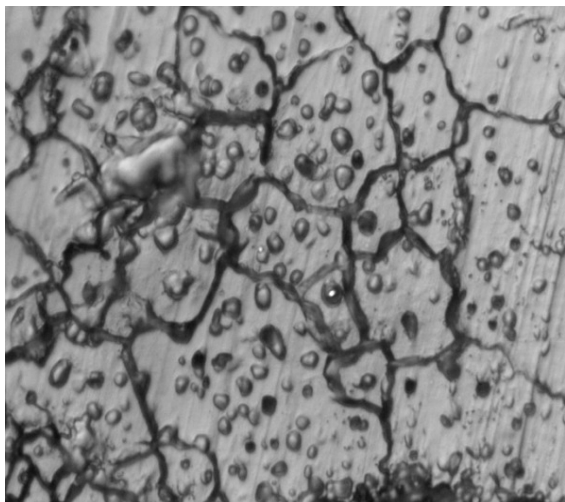


Figure 15. Visualization of the structure of the BC1 alloy treated at 700°C, attacked with aqua regia, after 13 days from quench.

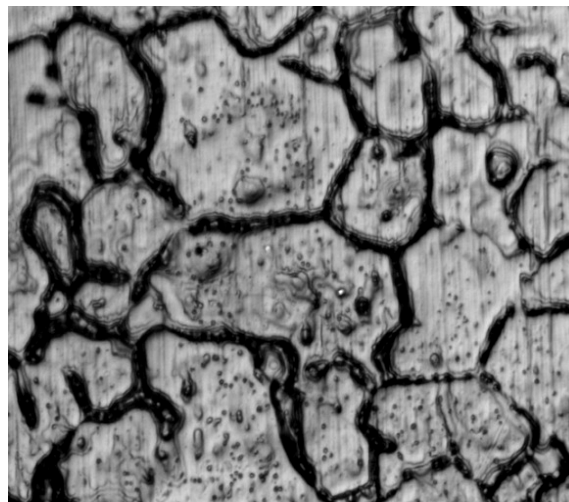


Figure 16. Visualization of the structure of the BC1 alloy treated at 1000°C, attacked with aqua regia, after 13 days from quench.

Figures 18 and 19 show a discontinuous transformation of alloy Hybrid-BC1 treated at 700°C and 800 °C. In Figure 20, the matrix of the alloy treated at 900 °C during over aging is almost covered by precipitates which prove the decrease of hardness [5].

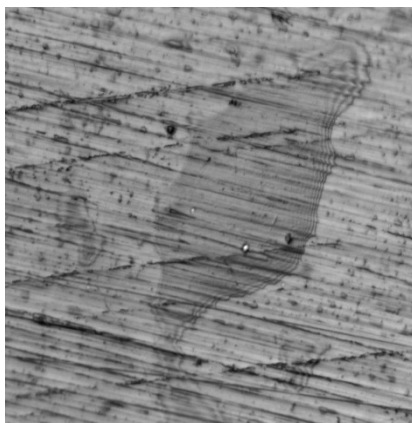


Figure 17. Visualization of the structure of the BC1 alloy treated at 700°C, attacked with aqua regia, after 13 days from quench.

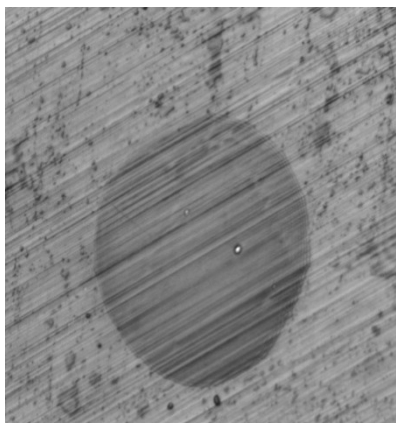


Figure 18. Visualization of the structure of the BC1 alloy treated at 800°C, attacked with aqua regia, after 15 days from quench.

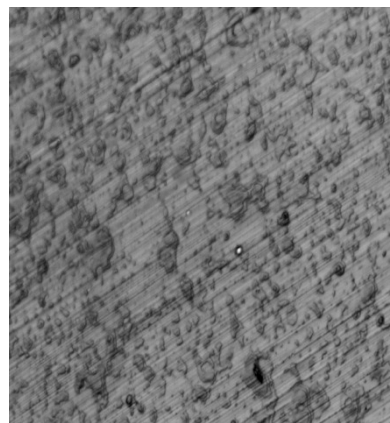


Figure 19. Visualization of the structure of the BC1 alloy treated at 1000°C, attacked with aqua regia, after 13 days from quench.

In the figures below we notice the existence of morphology of secondary carbides. Figures 21-23 show the presence of square and blocky carbides. In figure 24, we observe carbides localized at the grain boundaries where the diffusion is greater compared

to the crystal lattice [21] which have a globular form at grain boundaries in the case of water quench and in a lamellar form in a cooling air [22].

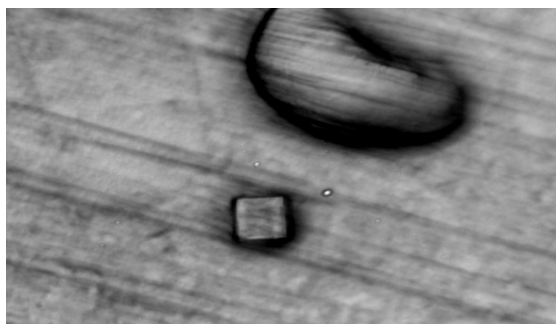


Figure 20. Visualization of the structure of the BC1 alloy treated at 700°C, attacked with aqua regia, after 13 Days from quench.

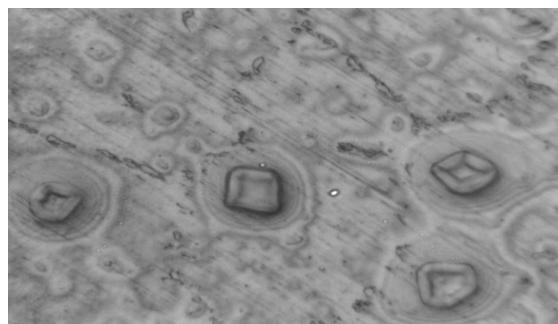


Figure 21. Visualization of the structure of the BC1 alloy treated at 700°C, attacked with aqua regia, after 15 Days from quench.

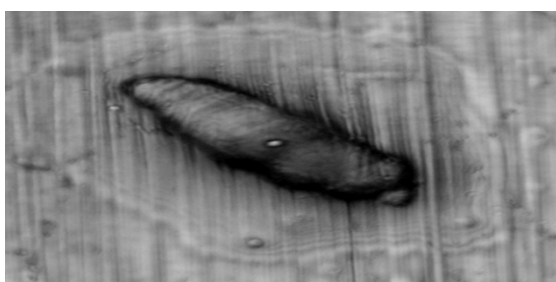


Figure 22. Visualization of the structure of the BC1 alloy treated at 1000°C, attacked with aqua regia, after 13 Days from quench.

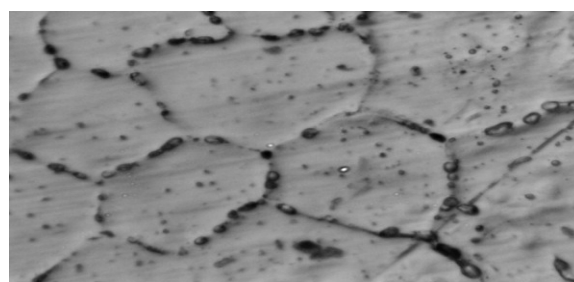


Figure 23. Visualization of the structure of the BC1 alloy treated at 1000°C, attacked with aqua regia, after 14 Days from quench.

3.2.3. X-Ray Diffraction

Figure 25 show that the peak of the spectra at positions (a), (b), (c) and (d) consist of doublets relative to nickel-based alloy and precipitates. The peaks of the spectra of the alloy treated at four temperatures have same positions therefore the structure remains monophasic austenitic. The appearance of a new peak at position (e) $2\theta \approx 94,58^\circ$ in diffractogram of the piece treated at 1000°C due to the formation of precipitates.

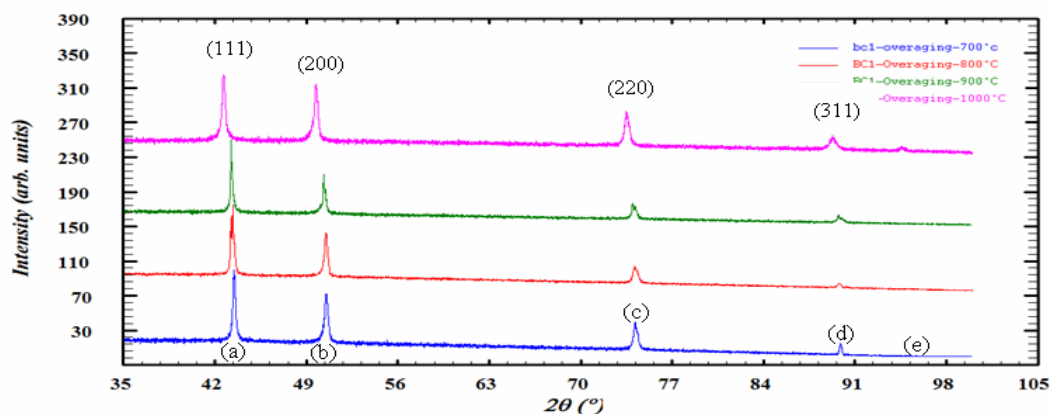


Figure 24. X-ray diffraction spectra of the alloy BC1 treated at 700 °C, 800 °C, 900 °C and 1000 °C during overaging.

According to Table 3, during over aging peak intensity of the alloy increased with time. This is explained by the fact that the alloy tends to a more stable structure.

Table.3. Peak intensity of aging and over aging spectra of the piece treated at 700°C , 800°C, 900°C and 1000°C

POSITIONS (2θ)	T=700°C		T=800°C		T=900°C		T=1000°C	
	AGING (%)	OVERAGING (%)	AGING (%)	OVERAGING (%)	AGING (%)	OVERAGING (%)	AGING (%)	OVERAGING (%)
42	79	79	79	79	81	83	76	76
49	51	54	53	71	46	71	58	65
73	24	30	21	27	13	28	20	39
89	9	13	5	8	5	13	8	13

3.2.4. Lattice parameter

To calculate the lattice parameter a , for each treatment temperature, we used the interplanar spacing determined from diffractograms obtained experimentally, and using the following relation:

$$d = a / \sqrt{(h^2 + k^2 + l^2)}$$

with d = interplanar spacing;

a = lattice constant ;

h, k, l = Family of reticular planes.

Table 4. Crystallographic parameters of the thealloyBC1 treated at 700°C , 800°C, 900°C and 1000°C

T=700°C			T=800°C			T=900°C			T=1000°C		
$d_{hkl}(\text{Å})$	hkl	$a(\text{Å})$	$d_{hkl}(\text{Å})$	hkl	$a(\text{Å})$	$d_{hkl}(\text{Å})$	hkl	$a(\text{Å})$	$d_{hkl}(\text{Å})$	hkl	$a(\text{Å})$
1.36	111	2.04	1.37	111	2.055	1.36	111	2.04	1.37	111	2.055
1.18	200	2.36	1.18	200	2.36	1.18	200	2.36	1.19	200	2.38
0.83	220	3.32	0.83	220	3.32	0.83	220	3.32	0.84	220	3.36
0.71	311	3.905	0.71	311	3.905	0.71	311	3.91	0.71	311	3.905

Nickel-based alloys have been developed to maintain the face-centered cubic structure, during their utilization .We deduced from the table 4. that the lattice parameters are almost equal with an average of 2.9 Å for each temperature treatment. Therefore the structure of the alloy BC1 alloy is face-centered cubic (CFC). whatever the temperature of the treatment.

CONCLUSIONS

In this work we treated for 3 hours the alloy BC1 at 4 different temperatures 700 °C, 800 °C, 900 °C and 1000 °C.

The heat treatments performed don't have a big influence on the final mechanical properties of the alloy BC1: the hardness of the alloy treated at 700 °C is 47.25 HRF. for the treatment at 800 °C and 900 °C the alloy has hardness of 47 HRF and for the alloy treated at 1000°C it is of 47.5 HRF.

The nickel-based alloy is developed mainly in order to resist to corrosion at high temperature in corrosive environments. However, the iso-thermal treatments lead to intergranular and intragranular precipitation of different morphologies of chromium carbides and deplete zones near to grain boundaries of chromium which leads to corrosion because its anticorrosive power is through the creation of an oxide layer of chromium. It has also been found the presence of the phase γ' which increases the hardness; however it influences negatively on the ductility of the alloy.

The X-ray diffraction spectra obtained after the treatment revealed that the structure remains austenitic. the presence of peaks at different temperatures and the appearance of a new peak for samples treated at 1000 °C of precipitates. The alloy BC1 crystallizes in a cubic faces centered structure with lattice parameter equal to a $\approx 2.9 \text{ \AA}$ whatever the temperature of the treatment.

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