

# Carbonitreção a plasma em gaiola catódica da superliga Co-Cr-Fe em baixas temperaturas

## Plasma Carbonitriding of the Co-Cr-Fe Superalloy in a Cathodic Cage using Low Temperatures

Eliane Correia Nascimento Souza<sup>1</sup>, Adonias Ribeiro Franco Júnior<sup>1</sup>, Antônio César Bozzi<sup>2</sup>

### RESUMO

Neste estudo, utilizou-se o tratamento de carbonitreção a plasma em uma superliga do sistema Co-Cr-Fe com o objetivo de verificar a possibilidade de formação de fase S em baixas temperaturas. Os tratamentos de carbonitreção foram realizados em uma atmosfera gasosa composta por 73% de H<sub>2</sub>, 25% de N<sub>2</sub> e 2% de CH<sub>4</sub> com temperaturas de 460°C e 500°C por um período de 1 hora. Durante os tratamentos as amostras permaneceram sob uma gaiola catódica feita com a liga AISI 304L. Após o tratamento termoquímico as amostras foram avaliadas com relação a microestrutura superficial por Microscopia Eletrônica de Varredura (MEV), foi feita a identificação qualitativa das fases por Difração de Raios-X e realizado o ensaio de microdureza aplicando-se uma carga de 50 g. Os resultados mostraram que no tratamento realizado a 460°C foi possível a formação da fase S. No entanto, foi constatada a presença dos precipitados de Fe<sub>3</sub>C e Fe<sub>3</sub>N na camada modificada. No tratamento realizado a 500°C a camada formada na superfície da superliga foi constituída basicamente por Fe<sub>3</sub>C apresentando um significativo aumento na dureza superficial.

**Palavras-chave:** Carbonitreção, Fase S, Superliga de Cobalto.

### ABSTRACT

In this study, the treatment of plasma carbonitriding was used on a superalloy of the Co-Cr-Fe system in order to verify the possibility of an S-phase formation at low temperatures. The carbonitriding treatments were performed in an AISI 304L steel cathodic cage using a gas composed of 73% H<sub>2</sub>, 25% N<sub>2</sub> and 2% CH<sub>4</sub> at temperatures of 460°C and 500°C over a period of 1 hour. After the thermochemical treatment, the samples were evaluated in relation to the superficial microstructure the samples were evaluated in relation to the surface microstructure by Scanning Electron Microscopy (SEM), qualitative identification of the phases by X-ray diffraction (XRD), and mechanical properties through a microhardness test by applying a 50g load. The results showed that, in the treatment carried out at 460°C it was possible to form the S-phase. However, Fe<sub>3</sub>C and Fe<sub>3</sub>N precipitates were detected in the modified layer. In the treatment carried out at 500°C, the layer formed on the superalloy surface is essentially consisted by Fe<sub>3</sub>C, showing a significative increasing on the surface resistance.

**Keywords:** Carbonitriding, S-phase, Cobalt Superalloy.

<sup>1</sup>Instituto Federal do Espírito Santo – Vitória (ES) - Brasil

<sup>2</sup>Universidade Federal do Espírito Santo – Vitória (ES) – Brasil

**Autor correspondente:** Eliane Correia Nascimento Souza - Instituto Federal do Espírito Santo – Avenida Vitória, 1729, Jucutuquara – CEP 29040-780 – Vitória (ES) – Brasil

Email: elianecns23@gmail.com

**Recebido:** 31/01/2017 **Aprovado:** 07/06/2017

## INTRODUCTION

Superalloys are materials that exhibit high mechanical strength and resistance corrosion, as well as good metallurgical stability and resistance to surface degradation at elevated temperatures. These materials are consist of nickel, iron-nickel or cobalt-based alloys, most of which are used at temperatures above 540°C (1000°F)<sup>(2,3)</sup>.

Among the superalloys, the cobalt-based alloys generally have good corrosion wear resistance properties. These alloys (Co-Cr) may contain different binding elements in their composition, such as tungsten, molybdenum, chromium and carbon, among others. The high chromium content in these alloys is responsible for the high resistance to corrosion, besides contributing to the increasing of mechanical resistance by the formation of solid solution and carbides<sup>(4,5)</sup>. Some cobalt-based alloys, due to its high resistance to corrosion, are also used as biocompatible material<sup>(4)</sup>.

In 2010, studies done by Dong et al.<sup>(1)</sup> have shown that by using low treatment temperatures, it is possible to form a hardened surface layer, known as S-phase, which improves corrosion wear resistance in cobalt-based alloys. The use of temperatures above 500°C may improve a precipitation of secondary phases as chromium nitrides, CrN e Cr<sub>2</sub>N, which increase the alloy surface resistance; however, they cause a located decrease on the resistance to corrosion by the solid solution chromium reduction.

Generally, the use of thermochemical treatments in cobalt-based alloys has the objective of forming the S-phase in order to increase corrosion wear resistance. The S-phase, a solid solution supersaturated of N and/or C throughout the FCC structure interstices (face centred cubic), was first identified by Bell and Zhang in 1985<sup>(6)</sup> after the thermochemical treatment of austenitic stainless steel by plasma nitriding. Since then, the S-phase formation in austenitic stainless steels has been extensively studied and reported<sup>(7)</sup>. For many years, it was considered that the S-phase could only be formed in alloys with completely FCC structure. This fact may explain, in part, the almost two decade of delay in the development of S-phase surface engineering in Co-Cr alloys related to researches of S-phase formation in stainless steels and Ni-Cr alloys<sup>(1)</sup>.

Unlike austenitic stainless steels, the cobalt alloys, at room temperature, have a mixed crystalline structure, Because the kinetic of the FCC structure transformation to a hexagonal close packed (HCP) structure is very slow, cobalt alloys slow structures of stable hexagonal close packed phases (Co-ε) and metastable face-centered cubic phases (Co-α)<sup>(1)</sup>. According to Li et al.<sup>(7)</sup> and Chen et al.<sup>(8)</sup>, although the initial structure of Co-Cr alloys does not meet the requirement of a completely FCC structure, S-phase formation is possible, because the stabilizing elements of the FCC structure, such as N and C, when introduced into the surface of Co-Cr alloys, can transform part of the HCP phase structure into FCC structure, and then, it forms the S-phase. Several studies have been conducted in order to understand the formation of the S-phase in Co-Cr alloys, and great scientific advances have been

obtained. However, the S-phase formation mechanism in cobalt alloys has not yet been completely enlightened<sup>(8)</sup>.

The most cited cobalt alloys in texts or studies of thermochemical treatments belong to the Co-Cr-Mo class. The superalloy used in this study has a high iron content, has a nominal chemical composition very close to the commercial cobalt alloy (Stellite 250) reported in texts as an alloy resistant to heat, impact and corrosion<sup>(9,10)</sup>. The goal of this study when using the Co-Cr-Fe superalloy is to verify the possibility of an S-phase formation at low temperatures of plasma carbonitriding.

## MATERIALS AND METHODS

The Co-Cr-Fe alloy was received in a casting state. Its chemical composition was analyzed by plasma and atomic absorption spectrometry. The carbon content analysis was done at an elemental carbon analyzer. Before plasma carbonitriding, the samples were submitted to metallographic sanding techniques and then, polished with 0,3 μm alumina paste granulometry. They were then immersed in an ethyl alcohol bath in an ultrasonic device over a period of 5 minutes.

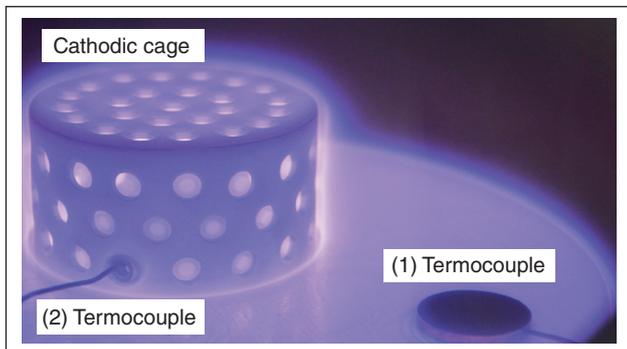
The carbonitriding treatments were performed in a plasma reactor (SDS model, Thor NP 5000). The total gas flow used in the experiments was 400 sccm (standard cubic centimeters per minute) with a gas atmosphere consisting of 73% H<sub>2</sub>, 25% N<sub>2</sub> and 2% CH<sub>4</sub>. During the treatments, the working pressure remained at 2.5 Torr. It was used two treatment temperatures, 460°C and 500°C, over a period of 1 hour in order to verify the possibility of the S-phase formation. Three samples were used in each treatment condition.

The cathodic cage used in the carbonitriding treatment was made with stainless steel AISI 304L in a cylindrical shape with the dimensions of 112 mm in diameter, a height of 25 mm and a thickness of 0.8 mm. The cage structure shows holes 8 mm in diameter and a 9.2 mm distance between the centers of holes. The purpose of the cathodic cage was to minimize certain types of defects that can occur with the use of a continuous current, such as: opening of arches, edge effect and hollow cathode effect.

After the cleaning process, the samples and the cage were inserted into the treatment chamber. In this system, the cage is positioned on the samples and acts as a cathode. The plasma is formed on the cage and not directly on the sample surface, which remain on an insulated surface. Before starting the treatment, the cathodic cage was submitted to a hydrogen-induced sputtering process (200 sccm). Collisions of H<sub>2</sub> ions on the cage surface promote the final surface cleaning. The process lasted 30 minutes under a 1 Torr pressure and an average temperature of 127°C. After this procedure, the N<sub>2</sub> and CH<sub>4</sub> flow was introduced into the reactor, and the pressure and working temperature were gradually increased until reaching the chosen treatment parameters.

The samples heating until the working temperature was performed exclusively by the ions bombardment on the surface

of the cathodic cage and the cathode. The temperature adjustment was obtained by gradually increasing on the source pulse frequency, increasing the on-pulse time ( $T_{on}$ ). Two thermocouples were used on the temperature monitoring. This way, it can be possible to monitor both the temperatures inside and outside the cage simultaneously. With this method, one of the thermocouples was introduced into the cathodic cage (thermocouple 1) and the other at a distance of about 100 mm from the cage structure (thermocouple 2). Figure 1 shows the cathodic cage and the thermocouples use during the plasma carbonitriding treatment.



**Figure 1:** Visual aspect of the cathodic cage during carbonitriding.

After the carbonitriding treatment, the samples were evaluated in relation to the surface microstructure by Scanning Electron Microscopy (SEM), qualitative identification of the phases by X-ray diffraction (XRD), and mechanical properties through a microhardness test by applying a 50g load.

## RESULTS AND DISCUSSION

The chemical composition of the Co-Cr-Fe superalloy is shown in Table 1.

**Table 1:** Chemical composition (wt%) of the Co-Cr-Fe superalloy.

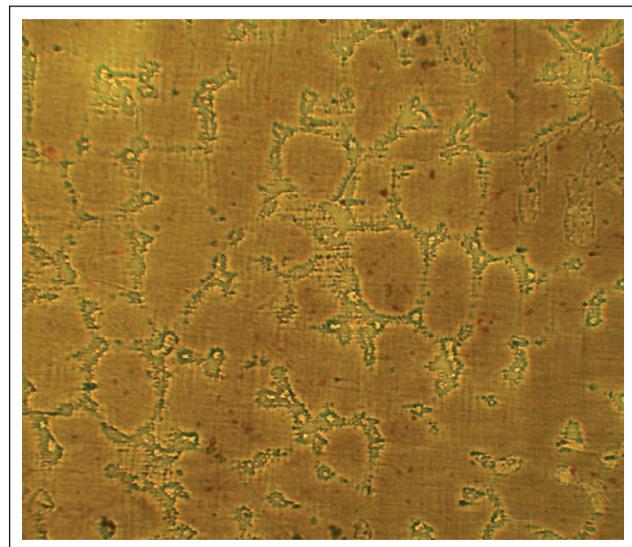
Co	Cr	Fe	C	Si	Mo
47.7	29.8	19.1	0.2	0.9	0.3

Figure 2 shows the Co-Cr-Fe alloy microstructure in the casting state, which consists of a matrix with precipitates located in the grain boundaries and interdendritic zones. These characteristics are consistent with those reported in texts about cobalt alloys produced by casting<sup>(11,12,13, 14)</sup>.

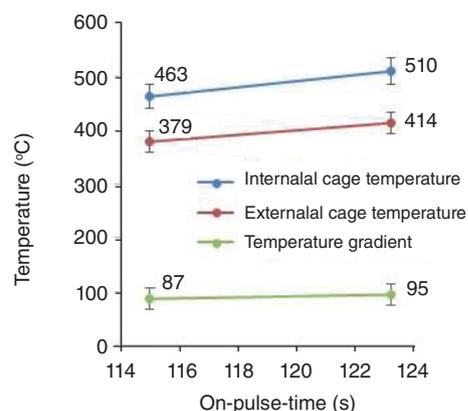
Execution data analyzes for plasma carbonitriding treatments gave average values related to the on-pulse time ( $T_{on}$ ) and to the temperatures inside and outside the cage. Figure 3 shows the effects of the on-pulse time ( $T_{on}$ ) increase on temperature gradient. Carbonitriding performed at 460°C, the temperature is about 18% higher inside the cage in relation to the external temperature. This result is close to the one recorded in carbonitriding at 500°C, which showed the temperature 19% higher inside the cathodic cage than outside.

It should be noted that the on-pulse time ( $T_{on}$ ) is affected by the power supply. On this condition, the longer the on-pulse time ( $T_{on}$ ) is, the greater will be the quantity of power supplied to the system. In this state, the ions bombardment on the surface of the cage is intensified, resulting in an increase in the temperature of the cathode, thereby increasing the temperature gradient, which, at 500°C, is close to 100°C.

Figure 4 shows that the Co-Cr-Fe alloy has a mixed crystalline structure, which is verified the presence of diffraction peaks related to the FCC (Co- $\alpha$ ) structure phase and HCP (Co- $\epsilon$ ) structure phase peaks. This result indicated that the transformation from a phase (FCC) to  $\epsilon$  phase (HCP) occurred in a manner that partially resulted in the FCC phase being metastable at room temperature<sup>(2)</sup>. To get a FCC and HCP phases volumetric fraction semi-quantitative estimate of the untreated sample, it was used Eq. 1 employed in Balagna et al. studies<sup>(15)</sup>. The obtained results indicated that the  $\epsilon$  (HCP) phase



**Figure 2:** Co-Cr-Fe alloy optical micrograph in the casting state. It was used 10g  $\text{CuSO}_4$ , 50 ml HCl and 50 ml of  $\text{H}_2\text{O}$  as metallographic reagent solution.



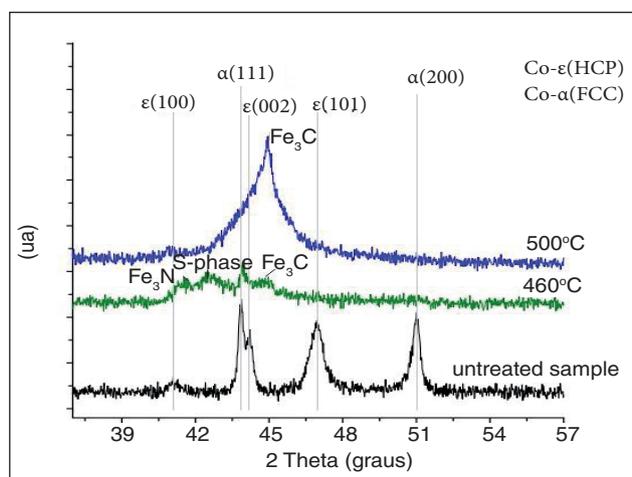
**Figure 3:** Effects of the increased on-pulse time ( $T_{on}$ ) in relation to the average internal and external temperatures of the cathodic cage.

volumetric fraction is equal to 51.8% and the  $\alpha$  phase (FCC) to 48.2%.

$$f_{\text{phaseW}}(\%) = \frac{\sum I_{\text{peaksW}}}{\sum I_{\text{peaks total}}} (\times 100) \quad (1)$$

Where: W = phase considered ( $\alpha$  or  $\epsilon$ );  $\sum I$  (W Peaks) = sum of peak intensities (I) belonging to the phase considered and  $\sum I$  (Total of peaks) = sum of the intensities of all the peaks in the diffractogram ( $\alpha + \epsilon$ ).

After plasma carbonitriding treatment at 460°C, X-ray diffraction analysis (Fig. 4) indicated the formation of an S-phase. However, the modified layer also showed carbides and nitrides of  $\text{Fe}_3\text{C}$  and  $\text{Fe}_3\text{N}$ . This result proved which part of the S-phase underwent decomposition and formed new phases.



**Figure 4:** X-ray spectra diffraction (XRD) of the untreated sample and of the samples subjected to carbonitriding treatment at temperatures of 460 and 500 °C.

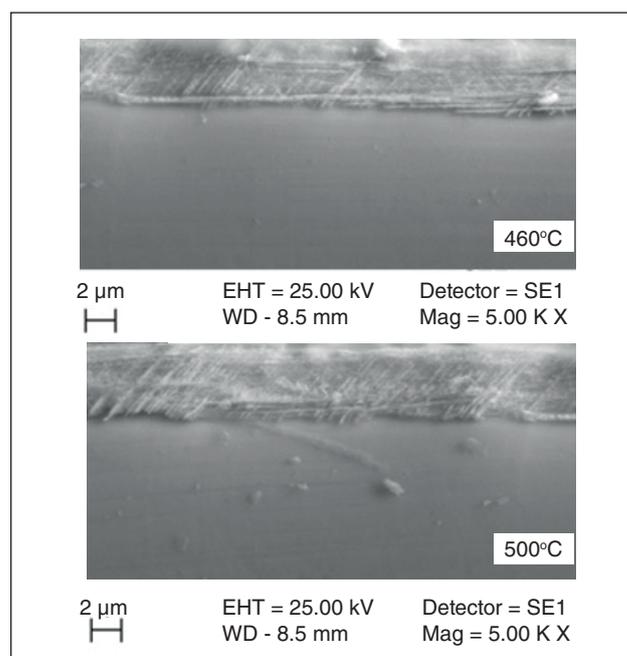
The S-phase peak present in the carbonitrided sample at 460°C is in the diffractogram displaced to the left in relation to the phase peak with the FCC structure of the substrate. This displacement occurred due to the presence of more N and/or C atoms interstitially diffused in the FCC structure, which generated a higher degree of the crystalline lattice expansion and, therefore, a greater displacement of the S-phase peak to a lower angle in relation to the  $\alpha$  phase peak (16,8).

In the treatment carried out at 550°C, the diffraction peaks were essentially of  $\text{Fe}_3\text{C}$ , which indicates that the rise in temperature favored the S-phase decomposition and the secondary phases formation. According to Dong<sup>(1)</sup>, the incubation time for S-phase decomposition decreases by increasing temperature as well as with the type and amount of diffused interstitial elements and with the presence of binding elements.

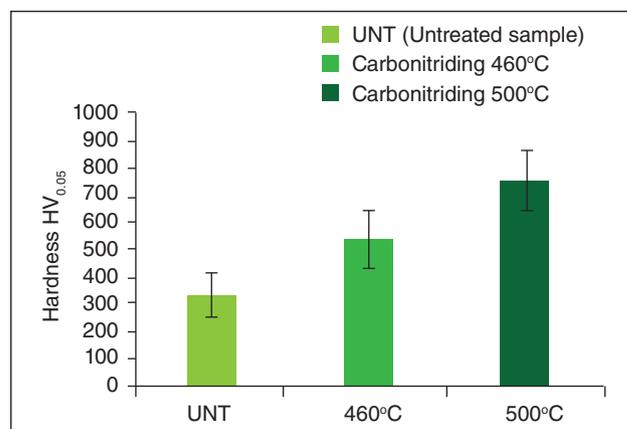
Figure 5 shows the scanning electron microscopy images of the modified layers formed on the surface of the Co-Cr-Fe alloy after the plasma carbonitriding process. It can be seen that in the treatment carried out at 460°C, the amount of precipitates with

needle shapes is lower when compared to the sample treated at 500°C. According to X-ray diffraction results (Fig. 4), the modified layer formed at 460°C consists of S-phase,  $\text{Fe}_3\text{C}$  and  $\text{Fe}_3\text{N}$ , while the layer formed at 500°C is basically composed by  $\text{Fe}_3\text{C}$ .

The surfaces microhardness values before and after the plasma carbonitriding treatment are shown in Fig. 6. It is noticed that the surface hardness of the carbonitrided samples was higher in relation to the untreated sample. The hardness value increased by increasing the carbonitriding temperature. This hardening is due to the combined effect of FCC structure supersaturation crosslinking by the interstitials (N and C) and to the formation of  $\text{Fe}_3\text{C}$  and  $\text{Fe}_3\text{N}$  precipitates<sup>(17)</sup>. At the highest carbonitriding temperature (500°C), the layer is essentially formed by  $\text{Fe}_3\text{C}$ , a phase with an orthorhombic structure of high hardness.



**Figure 5:** Modified layers on the superalloy surface after 1 hour of carbonitriding at different temperatures. Image obtained by scanning electron microscopy - electrolytic attack with nitric acid solution (10%).



**Figure 6:** Surface microhardness in samples of the Co-Cr-Fe alloy without treatment, after 1 hour of plasma carbonitriding treatment.

## CONCLUSIONS

The analysis results were satisfactory for the intended purpose and the following indicatives can be evidenced:

- With the cathodic cage utilization, the internal temperature was greater than the external temperature. As the temperature of carbonitriding increased, the temperature gradient within the area of the cathodic cage increased as well.
- The treatment conditions used, showed the possibility of S-phase formation by plasma carbonitriding in low temperatures and in short treatment time. However, the S-phase was only obtained at the lower temperature treatment (460°C), and the modified layer also presented carbide and nitride (Fe<sub>3</sub>C and Fe<sub>3</sub>N types). This result shows the need of using lower temperature in order to avoid the S-phase decomposition and precipitation of secondary phases.
- Carbonitrided samples presented greater surface hardness in relation to the sample with no treatment. The surface hardness of the samples was increased by increasing the temperature of carbonitriding.

## ACKNOWLEDGMENTS

I would like to thank CAPES for the master scholarship and opportunity to make this possible.

## REFERENCES

1. DONG, H., S-phase surface engineering of Fe–Cr, Co–Cr and Ni–Cr alloys, *International Materials Reviews*, v. 55, n. 2, pp. 65-98, Mar. 2010. <https://doi.org/10.1179/095066009X12572530170589>
2. DAVIS, J.R., *ASM Specialty Handbook: nickel, cobalt, and their alloys*. USA: ASM International, 2000.
3. DONACHIE, M. J.; DONACHIE, S. J. *Superalloys a technical guide*. 2° ed. USA: ASM International, 2002. p. 8-9.
4. SIBLEY, S. F. et al. Cobalt-Base Alloys, In: *ASM Handbook: Properties and selection - nonferrous alloys and special-purpose materials*, v. 2, USA: ASM International, pp.1407, 1992.
5. CROOK, P. Haynes International. Inc. Cobalt and Cobalt Alloys, In: *ASM Handbook: Properties and selection - nonferrous alloys and special-purpose materials*, v. 2, USA: ASM International, pp. 1404-1407, 1992.
6. ZHANG, Z. L.; BELL, T., Structure and corrosion resistance of plasma nitrided stainless steel, *Surface Engineering*, v. 1, n. 2, pp. 131-136, 1985. <https://doi.org/10.1179/sur.1985.1.2.131>
7. LI, X. Y. et al., Microstructural characterisation of a plasma carburised low carbon Co–Cr alloy, *Surface Engineering*, v. 23, n.1, pp.45-51, Jan. 2007. <https://doi.org/10.1179/174329407X161564>
8. CHEN, J.; LI, X. Y.; DONG, H., Formation and characterisations of S phase in plasma carburised high carbon Stellite 21 CoCr alloy, *Surface Engineering*, v. 26, n. 4, pp. 233-241, May. 2010.
9. STELLITE, C. D. P. K. <http://stellite.com/ProductsServices/HardfacingAlloys/WeldingRod/tabid/299/Default.aspx>, Access in June 10th, 2015.
10. DEAL, A. et al. Tensile property investigation os cast and wrought Co-Cr-Fe. *Microsc microanal*, v. 13, n. Suppl 2, 2007.
11. BALAGNA, C.; SPRIANO, S.; FAGA, M. G., Characterization of Co–Cr–Mo alloys after a thermal treatment for high wear resistance, *Materials Science and Engineering*, v. 32, n. 7, pp. 1868-1877, Oct. 2012. <https://doi.org/10.1016/j.msec.2012.05.003>
12. LIU, R. et al., Surface modification of a medical grade Co-Cr-Mo alloy by low-temperature plasma surface alloying with nitrogen and carbon, *Surface & Coatings Technology*, v. 232, pp. 906-911, Oct. 2013. <https://doi.org/10.1016/j.surfcoat.2013.06.122>
13. CHRISTIANSEN, T., SOMERS, M.A.J., On the crystallography structure of S-phase, *Scripta Materialia*, v. 50, pp. 35-37, 2004. <https://doi.org/10.1016/j.scriptamat.2003.09.042>