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# EFFECT OF NITROGEN ADDITION ON THE FERRITE VOLUME FRACTION OF A DUPLEX STAINLESS STEEL

## *Efeito da Adição de Nitrogênio na Fração Volumétrica de Ferrita de um Aço Inoxidável Duplex*

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**Abstract**

Duplex stainless steels are Fe-Cr-Ni alloys with ferrite and austenite on the structure. It is of great importance that the ferrite volume fraction is near 50 %. With lower levels of ferrite, the steel presents poor mechanical properties, low resistance to intergranular corrosion and susceptibility to hot cracking. On the other hand, if the ferrite content is higher, the steel shows low toughness and poor resistance to intergranular corrosion and pitting, and possible problems with brittle cracks during cooling. Nitrogen is a strong austenitizing element, favors the formation of austenite and allows the phase balance by approximately 50%. Duplex stainless steel is applied in centrifugal pumps manufactured by Sulzer do Brasil for offshore oil platforms and this work done to understand the effect of nitrogen addition on the ferrite volume fraction of CD4MCu steel. Solution treatment was performed at temperatures of 1050ºC during 2 hours, followed by water-cooling. After casting, the two steels had a ferritic matrix with many precipitates and austenite in elongated or needle forms nucleated within the ferrite grain and in the ferrite grain boundaries. The precipitates inside the ferrite were small (less than 1 mm) in a spherical or rod forms. The precipitates found in the "as casted" samples were dissolved after solution treatment, proving the effectiveness of the thermal treatment. The nitrogen addition reduced the ferrite volume fraction from 77% to 52% after solution treatment, achieving the desired balance in the structure near 50% of ferrite and 50% of austenite, without precipitates.

**Keywords:** Duplex stainless steel, nitrogen, solution heat treatment.

**Resumo**

Aços inoxidáveis duplex são ligas Fe-Cr-Ni ligas contendo ferrita e austenita na sua microestrutura. É de grande importância que a fração volumétrica da ferrita esteja perto de 50%. Com os níveis mais baixos de ferrita, o aço apresenta propriedades mecânicas pobres, de baixa resistência à corrosão intergranular e suscetibilidade à fissuração a quente. Por outro lado, se o teor de ferrita é maior, o aço apresenta dureza baixa e baixa resistência à corrosão intergranular e por pites e possíveis fissuras frágeis com durante o resfriamento. O nitrogênio é um forte elemento austenitizante, favorece a formação de austenita e permite o equilíbrio de fases em cerca de 50%. Aço inoxidável duplex é aplicado em bombas centrífugas fabricadas pela Sulzer do Brasil para plataformas de petróleo offshore e este trabalho tem o objetivo de compreender o efeito da adição de nitrogênio na fração volumétrica de ferrita num aço inoxidável CD4MCu. Tratamento térmico de solubilização foi realizado a temperaturas de 1.050ºC durante duas horas, seguido por resfriamento em água. Após a fundição, os dois aços tinham uma matriz ferrítica com muitos precipitados e austenita em formas alongadas ou de agulha nucleadas dentro do grão e ferrita nos contornos de grão. Os precipitados dentro do ferrita eram pequenos (menos de 1 mm) e em uma forma esférica ou de bastões. Os precipitados encontrados nas amostras do material fundido foram dissolvidos após o tratamento com solubilização, comprovando a eficácia do tratamento térmico. A adição de nitrogênio reduziu a fração volumétrica de ferrita de 77% para 52% após o tratamento com solubilização, alcançando o equilíbrio desejado na microestrutura de quase 50% de ferrita e 50% de austenita, sem precipitados.

**Palavras-chave:** aços inoxidáveis duplex, nitrogênio, solubilização.

## INTRODUCTION

Duplex stainless steels are Fe-Cr-Ni alloys with ferrite and austenite on the structure. It is of great importance that the ferrite volume fraction is near 50 %. With lower levels of ferrite, the steel presents poor mechanical properties, low resistance to intergranular corrosion and susceptibility to hot cracking. On the other hand, if the ferrite content is higher, the steel shows low toughness and poor resistance to intergranular corrosion and pitting, and possible problems with brittle cracks during cooling.

The duplex stainless steel CD4MCu (25% Cr-5% Ni-2% Mo-3% Cu), nomenclature designated by the ACI (Alloy Casting Institute), was developed in the United States in the late of 1950 decade. However, due to the brittleness of casted parts, the chromium content was reduced to 22 – 23 % and the solution treatment followed by water-cooling was adopted to improve the ductility (Charles, 1991).

The need to improve weldability and corrosion resistance and the developing new process for stainless steel production, like AOD, VOD and VIM led to the second generation of duplex stainless steels, characterized by nitrogen addition. This new generation offers excellent resistance to pitting and galvanic corrosion, significantly better resistance to stress corrosion compared to austenitic stainless steels, good toughness (Ritoni, 2007) and yield stress two to three times higher than the AISI 304 or AISI 316 stainless steels (Lundin, 2005). Nitrogen is a strong austenitizing element witch favors the formation of this phase and allows the phase balance by approximately 50%.

The duplex stainless steels after casting have a ferritic matrix with austenite islands and several precipitates depending on the composition of the steel and the cooling history. These precipitated may be carbides, nitrides and intermetallic phases. The most important secondary phase is the intermetallic sigma (ó), due to its large volume fraction frequently observed and its bad influence on the mechanical properties and the corrosion resistance (Hall, 1966; Barbosa, 1976; Raynor, 1988). This phase is rich in chromium and molybdenum, depleting the matrix around them and reducing the corrosion resistance. As the level of sigma phase increases, the ferrite decreases, since the sigma is formed from the ferrite (Martins, 2006). The solution treatment is used to dissolve the secondary phases (carbides, nitrides and intermetallics) and to adjust the proportions of ferrite and austenite on the microstructure.

Duplex stainless steel is applied in centrifugal pumps manufactured by Sulzer do Brasil for offshore oil platforms and this work done to understand the effect of nitrogen addition on the ferrite volume fraction of this steel.

# EXPERIMENTAL PROCEDURES

The steels were melted in induction furnace under vacuum. The design of 25 mm diameter and 300 mm length casting samples was done in an AUTOCAD 2006 and modeled in 3D with Autodesk Inventor 10. The chemical composition was measured in an ARL spectrometer, model 3640, in Sulzer Brazil. Solution treatment was performed in a Brasimet furnace at 1050 ° C during 2 hours, followed by a rapid cooling in water. Optical microscopy was performed on a Zeiss MAT Axiovert 40 microscope equipped with the software Axio Vision 4.7.2. Electrolytical polishing was carried out in a Struers Electropoli-5 with oxalic acid 10%.

With the exception of CD4MCu as casted sample (due to very fine austenite needles), the ferrite volume fraction was obtained by 20 measurements for each steel by quantitative optical metallography (ASTM Standard E-562) and also by Feritscope Fischer MP30.

Scanning electron microscopy (SEM) was performed at the Federal University of São Carlos (UFSCar) with a LEO Stereoscan 440, with a resolution of 4.5 nm to 30 kV.

# RESULTS AND DISCUSSION

## CHEMICAL ANALYSIS

Chemical compositions of the steels used in present study, as well as the compositions required by ASTM Standard A890/A890M are illustrated in Table 1. It may be noted that the two steels have compositions within the ranges specified by the standard. In addition, the CD4MCu and CD4MCuN compositions are the same, except for the 0.18% nitrogen added in second one.

Using the Fe-Cr-Ni diagram at 1300 °C (Figure 1) it is observed that these steels solidify fully in the ferritic field. The green field indicates the band contained the duplex

**Table 1.** ***Chemical composition (mass %).***

| Steel | C | Cr | Ni | Mn | Si | Mo | S | P | Cu | N |
|---|---|---|---|---|---|---|---|---|---|---|
| **CD4MCu ASTM Standard** | 0.04 max | 24.5 – 26.5 | 4.75 – 6.00 | 1.00 max | 1.00 max | 1.75 – 2.25 | 0.04 max | 0.04 max | 2.75 – 3.25 | – |
| **CD4MCu This work** | 0.03 | 25.5 | 5.57 | 0.73 | 0.86 | 1.99 | 0.004 | 0.02 | 3.02 | 0.03 |
| **CD4MCu This work** | 0.04 max | 24.5 26.5 | 4.75 – 6.00 | 1.00 max | 1.00 max | 1.75 – 2.25 | 0.04 max | 0.04 max | 2.75 – 3.25 | 0.10 – 0.25 |
| **CD4MCuN This work** | 0.03 | 25.5 | 5.58 | 0.71 | 0.83 | 2.08 | 0.004 | 0.02 | 2.96 | 0.18 |

stainless steels. To use this diagram it was assumed that the real nickel content was the sum of Ni + Cu + Mn + N + C, because these other elements have the same austenitizing effect than nickel. In addition, the real chromium content was considered Cr + Mo, due to the same behavior as the tendency to form ferrite.

**Figure 1:** ***Location of the alloys studied on Fe-Cr-Ni diagram at 1300 ºC (adapted from Metals Handbook, vol.3 p.140-144, 1994).***

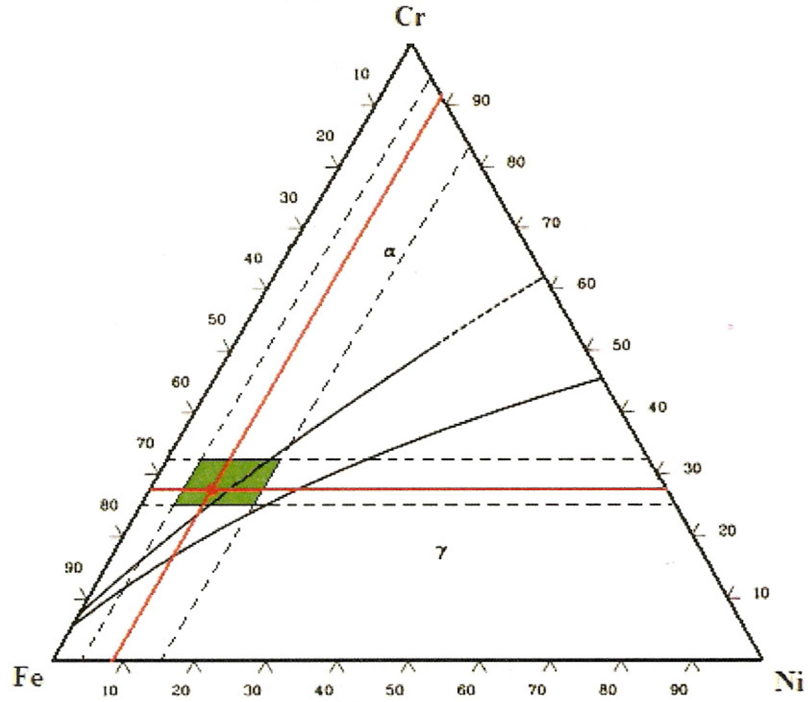



Figure 2a shows that at 1000 °C the microstructure consists of ferrite and austenite, indicating the formation of austenite from ferrite in the solid state. When temperature reaches 650°C sigma phase is also present (Figure 2b), since the sample is held for a long period in this temperature.

## MICROSTRUCTURAL ANALYSIS

Optical microscopy observations (Figure 3) showed that the "as casted" steels presented a ferritic matrix with many precipitates and austenite, in lathe and needle shapes, nucleated inside and on the ferrite grain boundaries. The CD4MCu showed a

**Figure 2.** ***Location of the alloys studied on Fe-Cr-Ni diagram at 1000 ºC (a) and 650 ºC (b) (adapted from Metals Handbook, vol.3 p.140-144, 1994).***

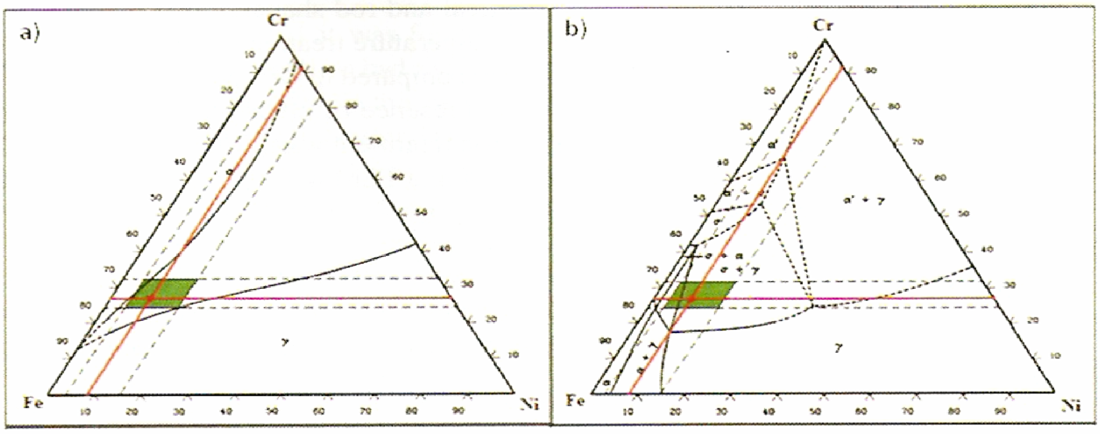
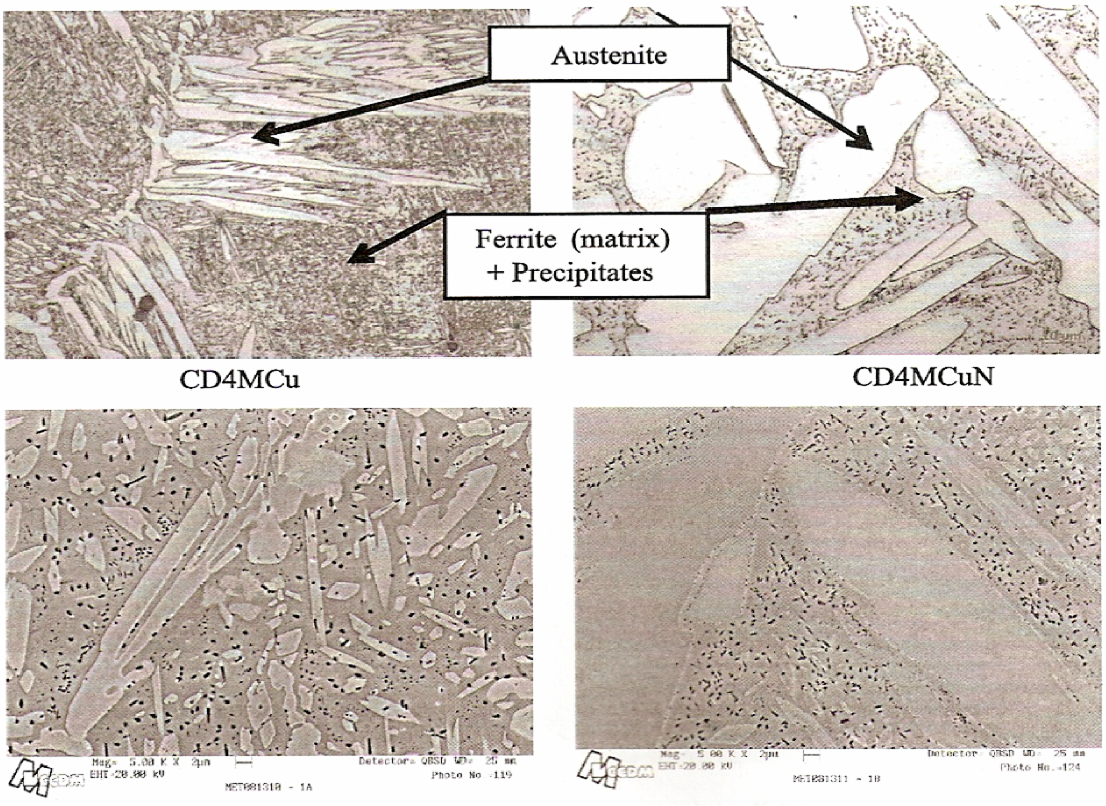



**Figure 3.** ***"As casted" structures of CD4MCu and CD4MCuN steels. Etching: Electrolytic /Oxalic acid at 10% in volume.***



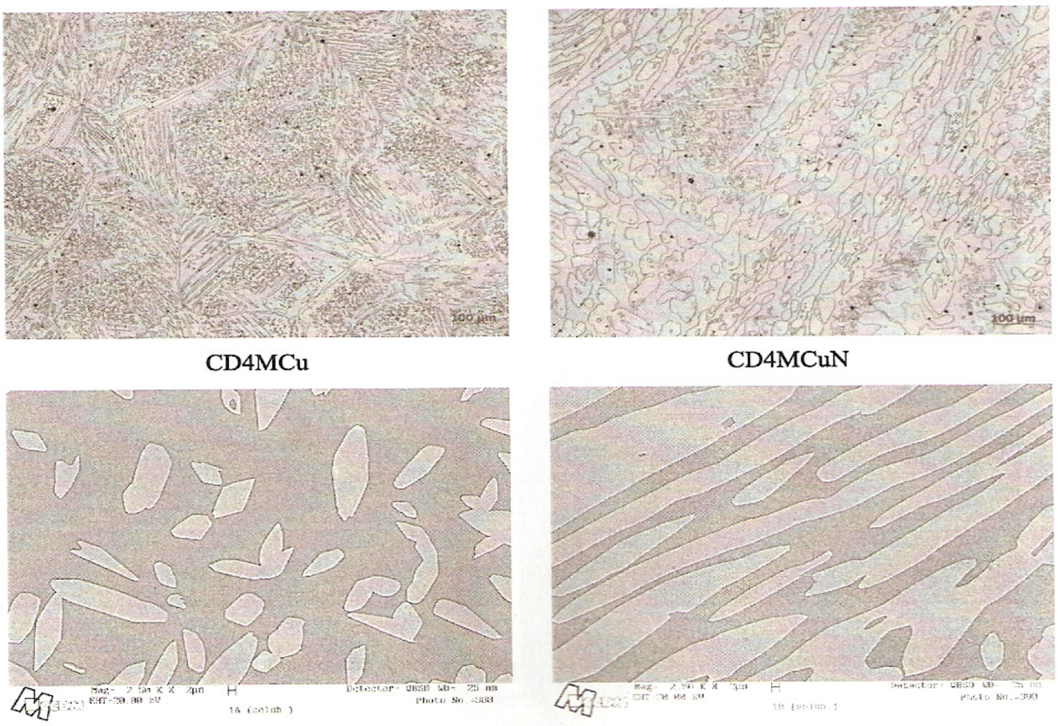
lower percentage of austenite in relation to CD4MCuN, which had already been determined by quantitative microscopy analysis. Through SEM observations it was observed the presence of small particles (less than 1mm in diameter) inside and at ferrite grain boundaries. The precipitates had spherical and rod shapes.

Comparing the two steels after solution temperature treatment it is easy to see that CD4MCuN steel had a lower content of ferrite compared to CD4MCu steel (Figure 4). SEM observations showed that there was no presence of other phases in addition to ferrite and austenite, indicating that the solution treatment was effective to dissolve the precipitates formed during the steels casting. RX and TEM will be carried out to identify the precipitates formed.

## FERRITE VOLUME FRACTION

Based on ASTM A800/A800M and Schoefer Diagram the ferrite volume fraction can be predicted (eq.01).

**Figure 4.** ***CD4MCu e CD4MCuN steels after solution treatment at 1050 °C followed by water-cooling. Etching: Electrolytic /Oxalic acid at 10% in volume.***



CD4MCu CD4MCuN

CD4MCu CD4MCuN

$$\frac{Cr_{eq}}{Ni_{eq}} = \frac{Cr(\%) + 1.5Si(\%) + 1.4Mo(\%) + Nb(\%) - 4.99}{Ni(\%) + 30C(\%) + 0.5Mn(\%) + 26(N - 0.02\%) + 2.77} \quad \text{(eq. 01)}$$

Using the Equation 01 it was found Creq/$Ni_{eq}$ = 2.49 for CD4MCu and 1.79 for CD4MCuN steel. As Creq/Nieq had a value above 2.2 for CD4MCu steel it was impossible to use the Schoefer Diagram. In this case, it is expected a ferrite content above 70%. For the CD4MCuN steel, the Schoefer Diagram predicts the ferrite content around 56%, in the range of 42 to 67%.

Table 2 show the ferrite volume fraction measured both by optical microscopy and by Feritscope. Note that there is not a significant variation in the results using the two techniques. Therefore, the values obtained with the in Feritscope can be assumed as reliable. In "as casted" samples the ferrite volume fraction was 38% lower in the steel with nitrogen in relation to the nitrogen free steel: 62 and 45%, respectively. After solution treatment, the ferrite volume fraction was 48% lower in the steel with nitrogen in relation to nitrogen free steel: 77 and 52 %, respectively. Therefore, with nitrogen addition and solution treatment at 1050°C it was possible to achieve the desired balance in the structure; 50% of ferrite and 50% of austenite, without precipitates. It is observed that in the CD4MCu steel, as predicted by Schoefer Diagram, the ferrite content was above 70% and in the CD4MCuN steel the ferrite content was 52%, showing that the use this diagram provides reliable values for ferrite volume fraction in these steels.

**Table 2.** ***Ferrite volume fraction measured by Quantitative Optical Microscopy (QOM) and by Feritscope (FT) and calculated from Schoefer Diagram.***

| Steel | Schoefer diagram | As casted | | Solub. at 1050 °C | |
|---|---|---|---|---|---|
| | | QOM | FT | QOM | FT |
| CD4MCu | >70 | - | 62 ± 1 | 79 ± 1 | 77 ± 3 |
| CD4MCuN | 56 | 44 ± 2 | 45 ± 1 | 51±2 | 52 ± 3 |

## CONCLUSIONS

For duplex steels with no nitrogen added (CD4MCu) and with the addition of 0.18% nitrogen (CD4MCuN) in the "as casted" condition and after solution treatment during 2 hours at 1050°C it was concluded that:

1 After casting, the two steels had a ferritic matrix with many precipitates and austenite in elongated or needle form nucleated within the ferrite grain and in the ferrite grain boundaries. The precipitates inside the ferrite were small (less than 1mm) in a spherical or rod forms.

2 The precipitates found in the "as casted" samples were dissolved after solution treatment, proving the effectiveness of the thermal treatment.
3 The nitrogen addition reduced the ferrite volume fraction from 77% to 52% after solution treatment, achieving the desired balance in the structure near 50% of ferrite and 50% of austenite, without precipitates.
4 The Schoefer Diagram can predict reliable values for ferrite volume fraction up to 70% in these steels after solution treatment.

## REFERENCES

American Society for Testing and Materials ASTM A800/A800M. Standard Practice for Steel Casting, Austenitic Alloy, Estimating Ferrite Content Thereof. Annual Book of ASTM Standards, vol. 01.02., U.S.A, 2001, p. 448-453.

American Society for Testing and Materials ASTM A890/A890M. Standard practice for castings, iron-chromium-nickel-molybdenum corrosion-resistant, duplex (Austenitic/ferritic) for general application. Annual Book of ASTM Standards, vol. 01.02., U.S.A, 1999, p. 576-579.

American Society for Testing and Materials ASTM E562. Standard Practice for Determining Volume Fraction by Systematic Manual point Count. Annual Book of ASTM Standards, vol. 01.02., 1998, p. 575-579.

Barbosa, C. A., Mori, F. Y., Souza, M. H. C., Falleiros, I. G. S.; *Formação de fase sigma em aço inoxidável austenítico-ferrítico.* Metalurgia ABM, nº. 227, v. 32, out. 1976, p. 669-73.

Charles J.; Bernhardsson, S. *Super duplex stainless steels: structure and properties.* In: DUPLEX STAINLESS STEELS'91 Proceedings. Ed: Charles, J.; Bernhardsson, S. Les Ulis, France, Les Editions de Physique, v.1, 1991, p. 3-48.

Hall, E. O., Algie, S. H.; The sigma phase. Metallurgical Review, v. 11, 1966, p. 61-88.

Lundin, C. D.; Russel, S. W.; *The development of qualification standards for cast duplex stainless steel.* Materials Joining Group – Materials Science and Engineering the University of Tennessee, Knoxville, 2005, 166 p. (This is volume 2 to 5 of the final report for The Department of Energy Grant # DE-FC07-00 ID13975 entitled "Behavior of Duplex Stainless Steel Castings").

Martins, Marcelo. *Caracterização microestrutural-mecânica e resistência à corrosão do aço inoxidável super duplex ASTM A890 / A890M Grau 6A.* São Carlos, Universidade de São Paulo, Interunidade EESC-IFSC – IQSC, 2006, 268 p. Tese (Doutorado).

Metals Handbook, vol. 3. Alloy Phase Diagrams. American Society for Metals, Metals Park – Ohio, U.S.A., 1994, p. 140-144.

Raynor, G. V., Rivlin, V. G.; *Phase equilibria in iron ternary alloys.* The Institute of Metals: London, 1988, p. 316-32.

Ritoni, E.; Martins, M.; Tenacidade ao impacto dos aços inoxidáveis duplex CD4MCu e CD4MCuN, 13º CONAF - Congresso de Fundição, de 25 a 28 de Setembro de 2007 - São Paulo - SP.

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