The Effect of Final Heat Treatment and Chemical Composition

on Sensitiztation, Strength and Thermal Stability of Alloy 625

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ABSTRACT

Time-Temperature-Sensitization diagrams have been established for a low-carbon version of alloy 625 (UNS N06625). Sensitization in terms of a 50 μm (2 mils) intergranular penetration criterion starts after about 3 h aging time at 750°C (soft annealed condition) or after less than 1 h aging time at 800°C (solution annealed condition) when tested according to ASTM-G 28 method A. Grain boundary precipitation of carbides occurs during aging of both the soft annealed and the solution annealed material, but the soft annealed material exhibits a more pronounced general precipitation of $Ni_3(Nb,Mo)$ phase giving rise to more distinct loss of ductility. Sensitization of alloy 625 may be retarded by lowering its iron content.

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INTRODUCTION

Alloy 625 (UNS N06625) is a widely used nickel-chromium-molybdenum alloy in various industries. Specified according to ASTM-B 443 [1] with a maximum carbon content of 0.1 wt % the alloy is available on the market in two versions: a low carbon version (less than 0.025 wt % carbon) for wet corrosion applications and normally used in the soft annealed condition (grade 1), and a high carbon version (about 0.045 wt % carbon) which is used for high temperature application in the solution annealed condition (grade 2). Typically soft annealing is done at 980°C and solution annealing at 1120°C. However, both versions of the alloy exhibit structural instability if they are exposed to the temperature range of 600 to 900°C. Structural instability also causes loss of ductility [2] and sensitization [3], both occurring most rapidly in the temperature range around 800°C. It has been found that solution annealing causes a noticeable shift of ductility loss to longer times compared to soft annealing [2] as shown in Fig. 1 whereas the effect of solution annealing on sensitization is not known so far. Therefore the primary aim of the work reported in this paper was to study the influence of final annealing on the Time-Temperature-Sensitization behavior of a low-carbon version of alloy 625.

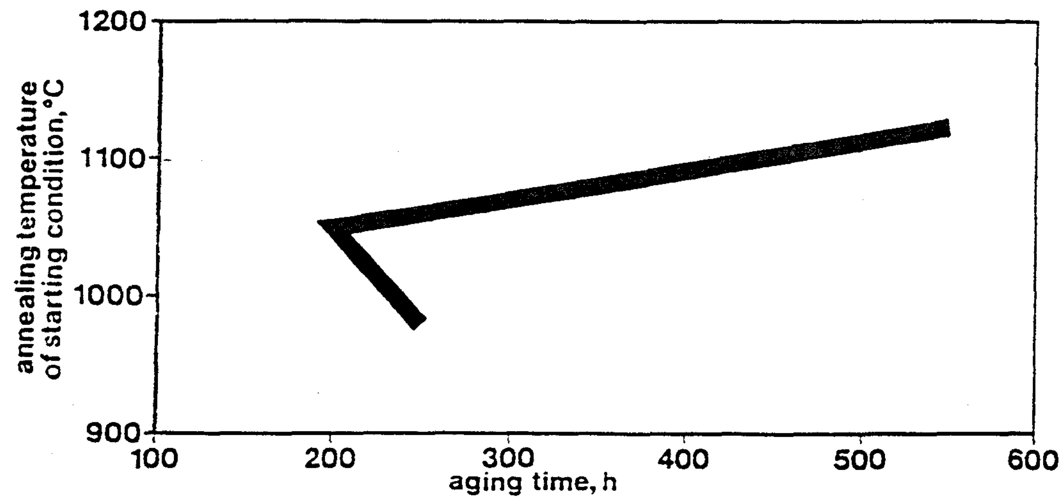


Figure 1: Minimum aging time required in an intermediate temperature range (around 800°C) in order to obtain a reduced Charpy-notch-impact energy of 50 J/cm² depending on final annealing temperature according to tests at room temperature on ISO-V-notch samples [1]

MATERIALS INVESTIGATED AND EXPERIMENTAL METHOD

The chemical composition of the alloy 625 heat investigated is shown in Table 1. The material used to study the sensitization behavior was now alloyed with 4.1 wt. % iron in comparison to the previous investigation [3] where a lower iron-containing alloy of 2 wt. % iron was used. Iron in alloy 625 is known to accelerate loss of ductility during aging [4], so an effect on sensitization may be expected as well.

TABLE 1
CHEMICAL COMPOSITION OF ALLOY 625 INVESTIGATED (WT %)

Ni	Cr	Mo	Fe	Cu	W	Mn	Si	Ti	Al	Cb	N	C	P	S
60.2	22.2	9.2	4.1	0.06	0.06	0.12	0.08	0.17	0.16	3.5	0.04	0.02	0.007	0.002

The alloy of Table 1 was hot rolled to plate of 5 mm thickness and subjected to either a solution anneal of 15 min at 1120°C or a soft or stabilizing anneal of 15 min at 980°C followed by a water quench. Subsequently samples of 5 x 20 x 30 mm size were cut from the plates to be annealed at 600, 700, 800 and 900°C for 1, 10 and 100 h. After annealing the samples were surface finished using 80 grit abrasive paper, cleaned, degreased, dried and weighed to the nearest 0.1 mg. After a 120 h immersion in boiling 42 g/l ferric sulfate / 50 % sulfuric acid solution according to ASTM-G 28 A [5], they were rinsed in water and acetone, dried and weighed for the corrosion rate calculation. According to the former definition in German standard SEP 1877/79 method II [6] the samples were determined to be free from intergranular attack if the depth of intergranular penetration (IP) did not exceed 50 μm (2 mils). The microstructure was analyzed using optical metallography. Brinell hardness measurements were also taken.

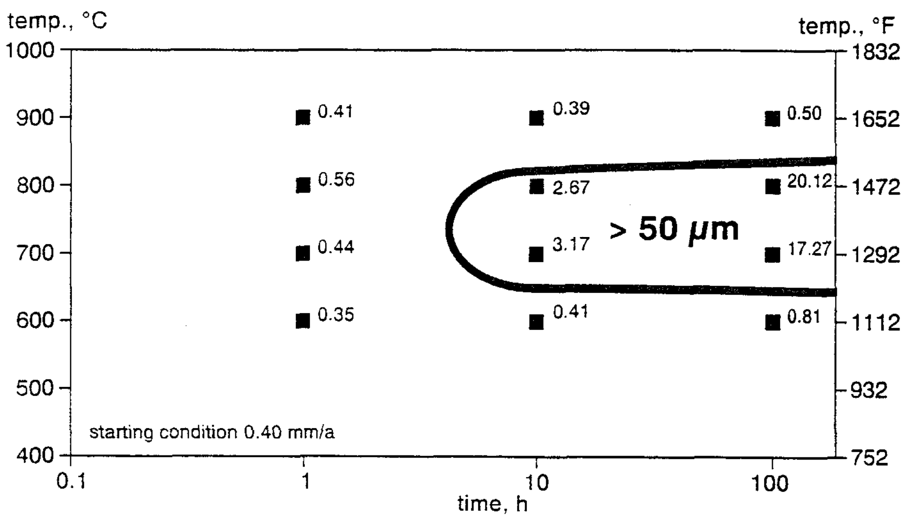
The initial mechanical properties of the material investigated are shown in Table 2. As would be expected, in the soft annealed condition, mechanical strength and hardness are higher and ductility is somewhat lower than in the solution annealed condition. These differences are mainly due to the differences in grain size of ASTM 8 (20 μm mean grain diameter) for the soft annealed condition and of ASTM 6 (60 μm mean grain diameter) for the solution annealed condition.

TABLE 2
INITIAL MECHANICAL PROPERTIES OF ALLOY 625 INVESTIGATED

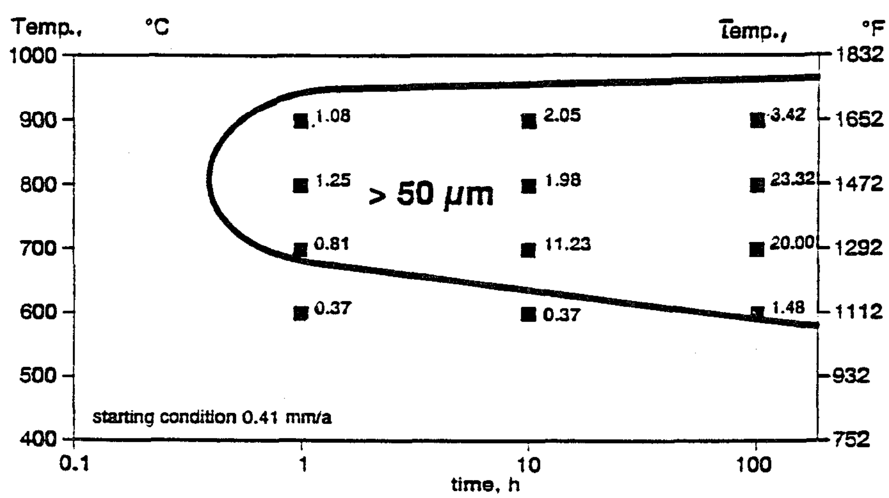
	$Rp_{0.2}$ N/mm^2	$Rp_{1.0}$ N/mm^2	Rm N/mm^2	A_5 %	Brinell hardness
soft annealed	451	501	910	45	244
solution annealed	376	415	843	55	208

TIME-TEMPERATURE-SENSITIZATION BEHAVIOR

Fig. 2 shows the Time-Temperature-Sensitization diagrams established a) for the soft annealed condition and b) for the solution annealed condition of alloy 625. In the soft annealed condition sensitization in terms of the 50 μm (2 mils) intercrystalline penetration criterion, occurs fastest at about 750°C starting already after about 3 h aging at this temperature. The whole temperature range of sensitization as shown in Fig. 2a is in good agreement with the results of previous investigations[3] where a distinct increase of corrosion rate in ASTM-G-28 A solution had been observed after 3 h aging at 700 / 750°C.



a) soft annealed condition (15 min at 980°C)



b) solution annealed condition (15 min at 1120°C)

Figure 2: Time-Temperature-Sensitization (TTS) diagram of Alloy 625, composition as indicated in Table 1, when tested according to ASTM G 28, method A[5] over 120 h on a plate of 5 mm thickness. Numbers indicate corrosion loss (mm/year)

However, on the previously tested low iron-containing alloy (2 wt. % Fe) [3] start of intercrystalline corrosion in terms of the 50 μm (2 mils) intercrystalline penetration criterion only occurred after about 50 h aging at 750°C. This difference might be due to the increased iron content of the alloy of the present investigation since iron is known to accelerate the effects of thermal instability of alloy 625 [4]

Contrarily, as Fig 2b shows, in the solution annealed condition sensitization in terms of the 50 μm (2 mils) intercrystalline penetration criterion starts within less than 1 h at about 800°C. In addition, the whole range of sensitization is extended to both higher and lower temperatures than is observed for the soft annealed condition.

So the term "stabilized" as designated for the soft annealed condition has been proved to be correct with respect to intercrystalline corrosion of alloy 625. This is not so self-evident as might be expected from the general observations on stainless steels since according to Fig. 1 ductility loss as another aspect of thermal degradation is delayed not by soft annealing but by solution annealing of alloy 625 [2] which, therefore, is the stabilizing heat treatment with respect to ductility.

TIME-TEMPERATURE-PRECIPITATION BEHAVIOR

Fig. 3 exhibits selected examples of the microstructure of alloy 625 in the soft annealed condition after various aging treatments. After 1 h at 600°C optical microscopy reveals no change of the microstructure with respect to the soft annealed starting condition. Fig. 3a shows some carbides and carbonitrides in a fine grained austenite matrix only. After 10 h at 600°C a somewhat more pronounced decoration of grain boundaries by carbide particles is seen as shown in Fig. 3b. This kind of precipitation is still more pronounced after 100 h at 600°C. In the same way precipitation occurs at 700°C where after 100 h grain boundaries are covered by a dense network of carbides, Fig. 3c. After 10 h at 800°C again a preferred precipitation of carbides on grain boundaries is seen (Fig. 3d) whereas after 100 h at this temperature, as shown in Fig. 3e, precipitation of a needle-like phase, probably Ni_3 (Nb, Mo) [2] covers all the microstructure. Contrarily after 100 h at 900°C much less precipitation occurs as is apparent in Fig. 3f.

The microstructure of alloy 625 in the solution annealed condition after various aging treatments is shown in Fig. 4. Again Fig. 4a reveals no visible change of the optical microstructure after 1 h at 600°C compared to the solution annealed starting condition. After 10 h at 600°C some grain boundary precipitation is discernible as shown in Fig. 4b, it is somewhat more pronounced after 100 h at 600°C. As with the soft annealed condition the grain boundaries are completely covered by carbide precipitation after 100 h at 700°C as Fig. 4c demonstrates. After 10 h at 800°C (Fig. 4 d) this carbide coverage is less, but becomes more dense after 100 h at 800°C (Fig. 4e). As Fig. 4f shows there is less precipitation at 900°C than at 800°C.

When comparing Fig. 4e with Fig. 3e a major difference between the soft annealed and the solution annealed condition after 100 h at 800°C becomes apparent: there is much less general precipitation in the solution annealed material. Apparently in addition to grain boundary precipitation this general precipitation of Ni_3(Nb,Mo) phase affects very strongly the ductility of the material [2] . Hence, the solution annealed condition is favoured if a delayed loss of ductility during aging is the prerequisite requirement whereas the soft annealed condition is preferred if a high resistance to sensitization is the primary requirement.

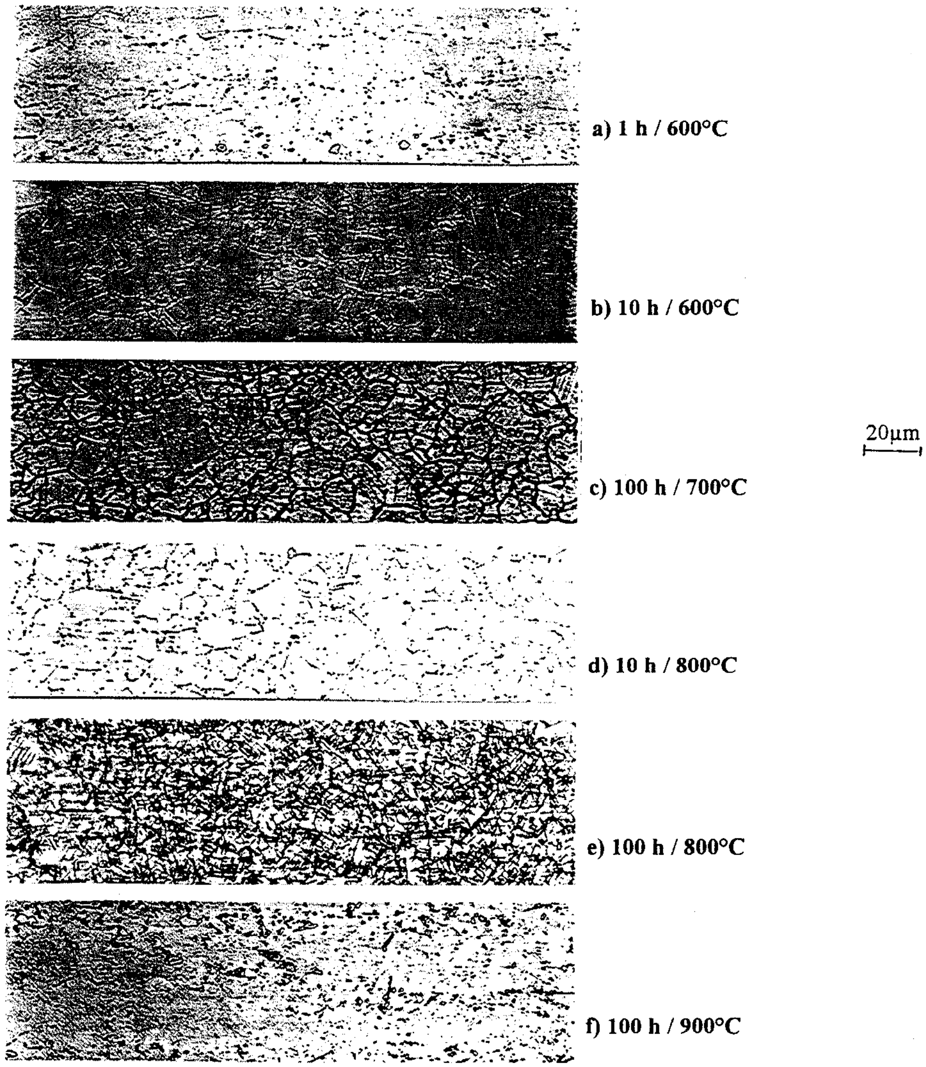


Figure 3: Microstructure of Alloy 625, soft annealed (15 min at 980° C) and aged, magnification x 500

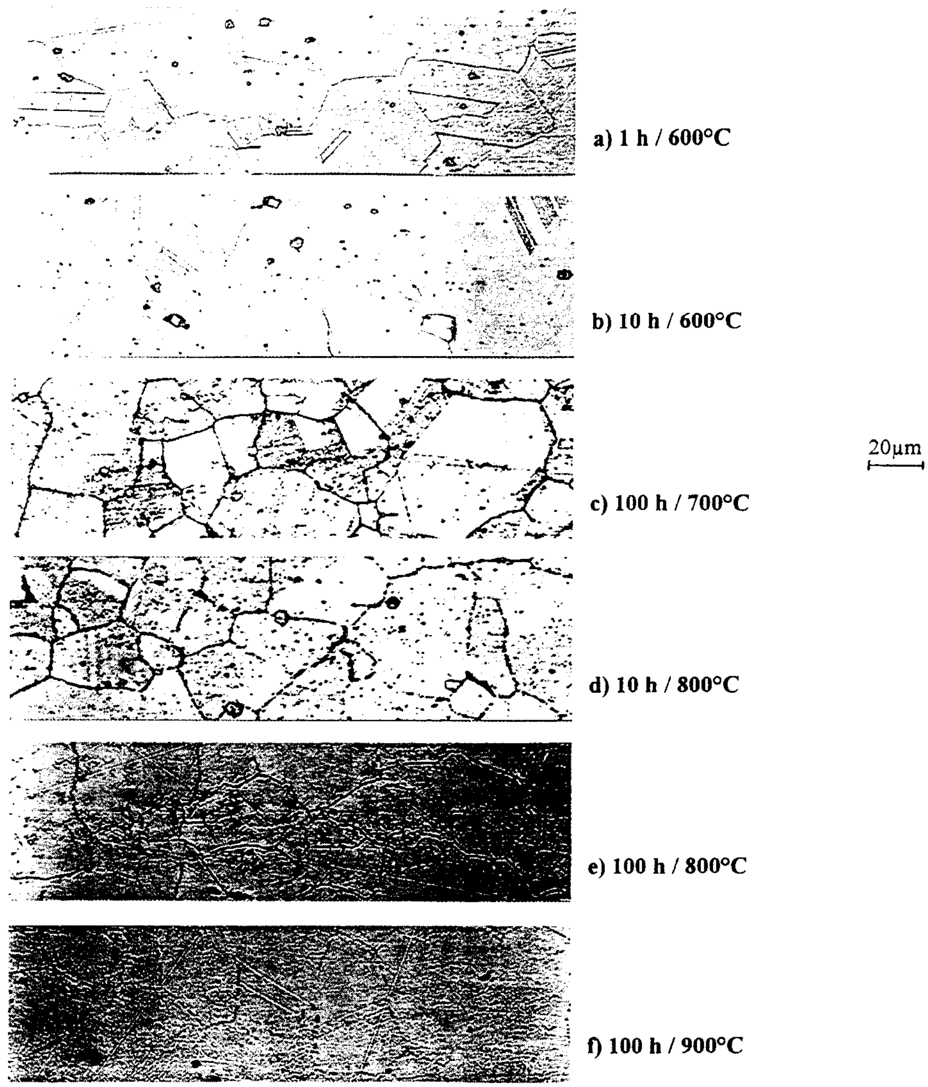
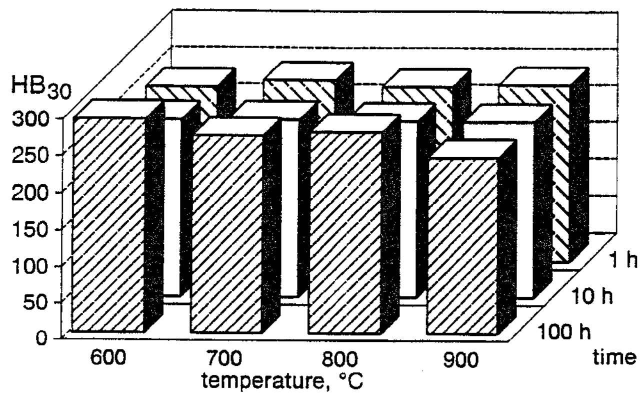


Figure 4: Microstructure of Alloy 625, solution annealed (15 min at 1120° C) and aged, magnification x 500

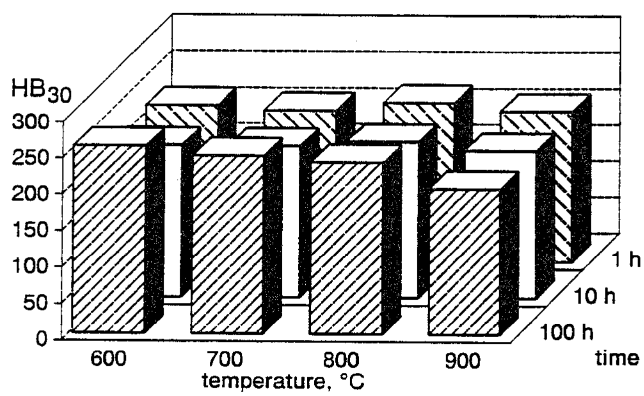
TIME-TEMPERATURE-HARDNESS CHANGE

The results of Brinell hardness testing are demonstrated in Fig. 5. As already shown in Table 2 the hardness of the soft annealed condition is higher than the hardness of the solution annealed material mainly due to the smaller grain size. As is obvious from Fig. 5 during a subsequent aging treatment at 600, 700 and 800°C hardness is increasing. At 900°C hardness remains constant or slightly decreases even in case of the solution annealed condition.



1 h	**235**	**245**	**236**	**239**
10 h	**240**	**240**	**239**	**238**
100 h	**291**	**268**	**274**	**239**

a) soft annealed condition (15 min at 980°C) HB = 244



1 h	**215**	**207**	**220**	**208**
10 h	**209**	**207**	**215**	**203**
100 h	**258**	**245**	**236**	**200**

b) solution annealed condition (15 min at 1120°C) HB = 208

Figure 5: Brinell hardness numbers of Alloy 625, composition as indicated in Table 1, after aging at temperatures between 600 and 900° C

1. Alloy 625 in the soft annealed condition (15 min at 980°C) exhibits sensitization of 50 μm (2 mils) intergranular penetration after about 3 h aging time at 750°C or, in the solution annealed condition (15 min at 1120°C), after less than 1 h aging time at 800°C when tested according to ASTM-G 28, method A.

2. Whereas soft annealing of alloy 625 is a stabilizing heat treatment with respect to sensitization, solution annealing of alloy 625 is a stabilizing heat treatment with respect to ductility.

3. Grain boundary precipitation occurs during aging of alloy 625 in both its solution annealed and its soft annealed condition. The more pronounced loss of ductility of the soft annealed condition is due to more general precipitation of Ni_3 (Nb, Mo).

4. Sensitization as well as loss of ductility during aging of alloy 625 may be retarded by lowering the iron content of the alloy.

ACKNOWLEDGMENT

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REFERENCES

1. ASTM-B 443-93: Standard Specification for Nickel-Chromium-Molybdenum-Columbium Alloy (UNS N06625), Annual Book of ASTM Standards, Vol. 2.04 Philadelphia, PA., 1995

2. M. Köhler: Effect of the Elevated Temperature-Precipitation in Alloy 625 on Properties and Microstructure, Superalloys 718, 625 and Various Derivatives, Edited by E.A. Loria, TMS, 1991, pp. 363 - 374

3. U. Heubner, M. Köhler: Time-temperature-precipitation and time-temperature-sensitization behavior of highly corrosion resistant nickel-chromium-molybdenum alloys (in German), Werkstoffe und Korrosion 43 (1992), pp. 181 - 190

4. U. Heubner, M. Köhler: Effect of Carbon Content and Other Variables on Yield Strength, Ductility and Creep Properties of Alloy 625, Superalloys 718, 625, 706 and Various Derivatives, Edited by E. A. Loria, TMS, 1994, pp. 479 - 488

5. ASTM-G 28 A-94: Standard Test Methods of Detecting Susceptibility to Intergranular Corrosion in Wrought Nickel-Rich, Chromium-Bearing Alloys, Annual Book of ASTM Standards, Vol. 3.02 Philadelphia, PA., 1995

6. SEP 1877 / 79, Method II: Standard Test Method of Detecting Susceptibility to Intergranular Corrosion in Corrosion Resistant Materials (boiling ferric sulfate - 40 % sulfuric acid test), Verlag Stahleisen, Düsseldorf, 1994