High Nitrogen Stainless Steels
-A New Generation of Steels-

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Abstract
Cronidur 30 is a hardenable, martensitic Cr-steel of 15%Cr, 1% Mo, and 0.30%C. It has been nitrided under pressure to 0.40% N. Compared to the well-known steel quality 1.4112, the material exhibits superior corrosion resistance as well as a good combination of strength and toughness. This is achieved through the optimum combination of Cr-, Mo-, and N-additives. By lowering the C-content while at the same time adding 0.40% N an even distribution of the deposited Cr-carbonitrides with a size of ≤ 15-20 μm has been achieved, and thus the risk has been eliminated that coarse Cr-carbides might chip off and decrease the fracture toughness anyway. The maximum hardness of Cronidur 30 is above 700 HV (60 HRC), depending on the conditions under which it was hardened. It is recommended to quench it quickly in oil or under streaming gas. By selectively setting the hardening temperature (e.g. lowering it to 970°C) the residual ductility can be improved so that later bending is possible. Because of the finely deposited Cr-carbonitride Cronidur 30 exhibits excellent wear behaviour. Therefore this steel is especially suited for the manufacture of bearings as well as cutting tools and instruments. Today Cronidur 30 is used especially in medical technology for manufacturing drills and surgical tools, as well as in the ball bearing industry and in precision engineering. More areas of application inevitably present themselves in situations where wear resistance, reliability and long lifetime are required. Some examples are threaded components, extrusion dies, screwdrivers, highly wear resistant axles and points for precision measuring tools.

P 2000 is a Ni-free austenitic CrMnMoN-steel with 17% Cr, 12% Mn and 3.5% Mo being electro-slag remelted under pressure leading to a Nitrogen content of 0.9%. This steel shows an outstanding corrosion resistance and an excellent combination of strength and ductility, even after cold deformation. By cold working the strength can be raised from 930 MPa to values over 2000 MPa. The fatigue properties are influenced in the same way. Applications for this austenitic steel type are the fastener- as well as the watch- and medical industry. This Ni-free steel grade shows good biocompatibility and will be used mainly in contact with the human body, for the production of spectacle frames, watch cases, jewellery and as wire for orthodontia. After biological evaluation and testing additional examples are prosthesis for orthopaedics, bone screws and plates for osteosynthesis.

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1. Introduction

The development of high nitrogen stainless steels (HNS) concentrated in the past on martensitic and austenitic grades. Most of the papers have been published in the proceedings of the last 5 conferences on High Nitrogen Steels (HNS) [1-5)]. History and developmental aspects are mentioned in the following papers[6-15].
The high nitrogen steels contain nitrogen levels up to about 1%, which must be introduced by electro-slag remelting under pressure up to 40 bars (PESR).

What was the reason to develop new high nitrided stainless steels? Was there a need for special properties? What are the requirements?

- Higher yield strength (austenite)
- High strength in combination with good ductility
- Higher cyclic load
- Homogeneous distribution of Cr-carbide precipitations (martensite)
- Better corrosion resistance (stress corrosion, pitting corrosion)
- Ni-free because of Ni-allergy (austenite)
- Biocompatibility (austenite)
- Antimagnetic, also in cold worked condition (austenite)
- High strain hardening capability for spring production (austenite)
- Higher resistance to wear (martensite)
- High cleanliness for good polish ability (austenite)

There are a variety of different applications where the above mentioned properties will be most interesting for the use of the new generation of high nitrogen steels.

Answers to all of these questions will be given within this paper.

2. Metallurgy of high nitrided stainless steels

The melting of HNS steels poses two problems: how to get the high nitrogen contents into the melt and how to keep them in solution during the process of solidification. It may come from molecular or ionised gas atmospheres at normal or elevated pressures, it may be offered by nitrided ferro-alloys or highly concentrated ceramic nitrides. Introduction may be directly into the melt or indirectly through the slag. According to the Sievert's equation a high nitrogen content may be either reached by a suitable choice of alloying elements, decreasing nitrogen activity, by nitrogen pressure or by ionising the nitrogen containing atmosphere[16)]. In pure iron for example only 0.04%N is disolved under normal pressure[17)].
Holzgruber[18)] has proposed various processes for the industrial production of HNS steels, among them an electroslag ladle heating system for operation under increased pressure which could be operated up to pressures beyond 36 bar.
An old and established way to introduce nitrogen into a steel melt is the addition by ferro-alloys. Typical alloys are FeMnN, MnN, FeCrN, CrN, and FeVN.
The advantage of the addition of nitrogen by ceramic nitrogen compounds is their considerably higher nitrogen content as compared with ferro-alloys. Their disadvantage arises in the introduction of possibly unwanted elements into the steel melt. One example is the addition of Silicon nitride Si_3N_4. with the main advantage of its high nitrogen content and the low density of 3,18 g/ cm^3, which allows floating and good mixing in the PESR-slag. This is the reason why most of the HNS-steels are pro-

duced by adding Si_3N_4 to the melt. A schematic shows the PESR equipment[17)] for the melting of HNS-steels (figure 1). The disadvantage of this method is the fact, that silicon lowers the nitrogen solubility and must be therefore counterbalanced by the addition of elements [16)] that are enhancing the solubility of nitrogen, such as Cr, Mo and Mn. Other elements leading to a higher solubility of nitrogen like V, Nb can only be added in small quantities because of their high potential forming nitrides.

3. Chemical Composition

3.1 Martensite

Table 1 gives details about the chemical composition of 3 industrial hardenable martensitic steel grades and Cronidur 30 (1.4108). Steel 1.4034 is a well known steel for surgical cutting instruments and tools for oral implantation. If higher hardness is requested steel 1.4112 has a preference because of its higher C-content. Particularly with this steel the problems of broken tools and corrosion attack arises. Cronidur 30 has been designed in such a way lowering the C-content to about 0.30% and adding 0.40% N with the aim of precipitating fine dispersed Cr-carbonitride particles for a higher ductility and better corrosion resistance.

3.2 Austenite

Table 2 compares the compositional limits of 3 implant steels inclusive REX 734 (ISO 5832-9) with P 2000. The HNS-type P 2000 contains Mn and N up to 1,0% instead of Ni. The Cr- and Mo-contents are at the same level as the CrNiMo-steels. To get N in full solution HNS-steels must be solution heat treated with subsequent rapid quenching.

Table 3 gives an overview on the new austenitic HNS-steels which have been developed by different companies. The Mn-contents are varying from 10 to 25% and the N-content from 0.5 to1.0%. In some cases Nb and C have been added in order to influence the corrosion and mechanical properties.

4. Heat Treatment

4.1 Martensite

Martensitic CrMn-steels are hardened at temperatures between 1000 and 1050°C at a low vacuum or under an inert gas atmosphere, followed by subsequent fast cooling.

The maximum hardness of Cronidur 30 is above 700 HV (60HRC), depending on the conditions under which it was hardened. It is recommended to chill it quickly under streaming gas. By selectively setting the hardening temperature (e.g. lowering it to 970°C) the residual ductility can be improved so that later bending is possible.

After hardening a subzero refrigeration at –80°C is recommended for transformation of small amounts of austenite to martensite. Stress relieve annealing should be done between 150 and 250°C.

Machining of martensites should be done in the soft annealed condition (770-820°C/2h + subsequent furnace or air cooling). After this treatment tensile strength values of 700-800 MPa can be reached.

4.2 Austenite

Under pressure nitrided steels should not be annealed at high temperatures (e.g. solution anneal) under high vacuum as removal of nitrogen can take place. In addi-

tion fast cooling after solution annealing is necessary in order to avoid the precipitation of nitrides. Therefore the following heat treatment parameters are:
Solution annealing temperature: 1150°C/ 0,5-1 h depending on cross section
Furnace atmosphere: air, alternative: Nitrogen (0,4 - 0,8 bar) or NH_3 or 95% Nitrogen + 5% Hydrogen.
Note! Never anneal under high vacuum

5. Corrosion Resistance

Nitrogen represents an economical and environmentally attractive and versatile alloying element, which has been shown for some time to be a powerful austenite stabilizer as well as a strengthener. Of particular importance is the well-known, but poorly understood, improvement to corrosion resistance, especially pitting resistance, attributable to N alloying of Mo-bearing austenitic stainless steels. Fundamental work on the passivity of high-nitrogen stainless alloys has been done by C. R. Clayton et al.[19,20]. It was shown that nitrogen, nickel and molybdenum additions stimulate selective dissolution of iron, resulting in a significant enrichment of chromium beneath the passive film. The build-up of a protective ferrous molybdate layer was seen tobe most strongly enhanced with additions of nickel and to a lesser extent, nitrogen.

5.1 Pitting Resistance Equivalent

The corrosion resistance of stainless steels usually is characterised by their Pitting Resistance Equivalent (PRE)

5.1.1 Martensite

The PRE in case of Cronidur 30 is 24 while that of the reference steel 1.4112 only amounts to 19, which indicates that the resistance against pitting corrosion of the high nitrogen steel, under the assumption that all alloying elements are not combined in precipitates, is higher than the resistance against pitting corrosion of the reference steel[21)].

5.1.2 Austenite

Table 4 shows the PRE of a selection of stainless CrNiMo-steels compared with the high nitrided CrMnMoN-steel P 2000 and the Co-base alloy Nivaflex. It can be clearly seen that the PRE of the CrNiMo-steels is below 40 in contrast to P 2000 with a PRE of 42,5. Only the PRE of the Co-base alloy Nivaflex is higher. It should be taken into account that the factor used for the N-calculation is 16 and not 30, that can be found in literature, too.

5.2 Pitting Corrosion

5.2.1 Martensite

Cronidur 30 is one of the best martensitic, hardenable steels with excellent corrosion resistance in Cl-containing mediums, as the following current density-potential-curves in 0,9%-NaCl-solution (pH = 4) at 40°C show (see figure 2). There is an extended passivation plateau until the breakthrough starts at a potential of 60 mV.
For the reference material 1.4112 a pitting potential of –240 mV was measured (see figure 3). So it is understandable that surgical tools corrode in an environment containing chloride ions or in contact with blood after short time.

5.2.2 Austenite

The current density/potential-curves of P 2000 and the reference material REX 734 (ISO 5832-9) in 3,2%-NaCl-solution (pH = 4) at 40°C show figures 4/5. Surprisingly both curves are identical in respect to the passivation plateaus and the pitting potentials which have been measured 936 mV for P 2000 and 904 mV for REX 734. Especially the re-passivation potential with exactly the same values as for the pitting corrosion shows that pitting corrosion will not take place under the above mentioned conditions. Consequently it can be said that the corrosion resistance of the two materials is equal.

A comparison with CrNiMo steels like DIN 1.4435 and 1.4539 (figures 6/7) show the superior reaction against corrosion attack of the implant steel REX 734 and the new Ni-free material P 2000. The 2 CrNiMo-steels that are successfully used in the watch industry show a moderate and good pitting potential but the re-passivation potential which is a measure how pits are healed on the surface are inferior in comparison with the values of P 2000 and REX 734.

An overview on corrosion data of metallic materials gives figure 8. The highest pitting potentials show the two CrNiMo-steels 904L and 1.4529 and the HNS-steels REX 734 (ISO 5832-9), P 2000, P 558, and Macrofer 2515 MoN. The pitting potential of the Heymark material 17-15 with a N-content of 0.5% lies between that of the HNS-steels and the Co-base alloys to ISO 5832-8 and 5832-12. The predecessor material of P 2000 with the brand name P 900 + Mo has a comparatively low pitting potential which will be unacceptable for most of the applications with hard corrosion attack.

5.3 Crevice Corrosion

Crevice corrosion tests were made according to ASTM G48, method B. For both materials P 2000 as well as P 558 a critical crevice corrosion temperature $T_{CCC} > 25°C$ was measured.

5.4 Intercrystalline Corrosion

Both materials P 2000 and P 558 were tested in respect to intercrystalline corrosion: corrosion resistance is in accordance with Strauss-test DIN 50914, (P 2000) and BS 970 Part 4 (P 558).

6. Biocompatibility, Biological Evaluation

In the ISO 5832 standards series we find an introduction related to the requirements of biocompatibility:

"No known surgical implant material has ever been shown to cause absolutely no adverse reactions in the human body. However, long-term clinical experience of the use of the material referred to in this part of ISO 5832 has shown that an acceptable level of biological response can be expected, when the material is used in appropriate applications."

What does this statement mean? It says that adverse reactions in the human body do occur. The precise questions are:

how severe are these reactions, e.g. the quantity of the corrosion products and
what are the interactions of the corrosion products with the living tissue[22].

The consensus conference on definitions in biomaterials[23] defines the biocompatibility as

"the ability of a material to perform with an appropriate host response in a specific application".

In this definition, *"host response"* is taken to mean "the response of living systems to the presence of a material".
More than 30 years ago S. G. Steinemann and M. Perren[24)] started their fundamental work in respect to the understanding of biocompatibility of metallic materials "in – vitro" and "in-vivo". The unexpected results of the experiments showed that a strong tissue reaction is not substantially base on a high corrosion velocity. The corrosion of aluminium and iron is stronger than nickel but the reaction is harmful.
Nickel ions are the most widespread skin contact allergen in Europe[25)]. Allergic reactions to Ni-containing alloys have become a serious medical problem in industrialized countries[26)]. In Europe, for example, more than 20% of young females and 6% of young males suffer from Ni allergy. Statistics indicate that this trend has been increasing dramatically for both men and women over the last decade[27)].
Ni-free, high corrosion resistant, austenitic CrMnN-steels therefore have been developed for medical applications like medical implants as well as for jewellery and watch applications. P 2000 as well as P 558 and Panacea have passed the standard zytotoxicity-test to ISO 10993-5[19,27,28)]. Additional biological evaluations to DIN EN ISO 10993-1 have do be done and are under way in order to get an approval as an implant material.

7. Physical Properties

7.1 Martensite
Physical properties of Cronidur 30 are assembled in table 5.

7.2 Austenite
Physical properties of P 2000, which are representative for high nitrogen austenitic steels, are assembled in table 6.

7.2.1 Magnetic Permeability
Absence of ferromagnetism in implants is important because of its role in diagnostic machines (MRI). Standard stainless steels show an increase of the magnetic permeability with cold work because of the formation of deformation martensite[27)]. In contrast, the high nitrogen and Mn- contents of the CrMnMoN-steels stabilize the face centered cubic crystal lattice and thus, no deformation martensite can be formed. Consequently, the magnetic permeability μ_R remains always below 1.004 determined at field intensities ranging from 2000-240.000 A/m, no matter whether the material is solution annealed or cold worked to a high degree (Figure 9).

8. Mechanical Properties
8.1 Static Test
8.1.1 Martensite
Mechanical properties of hardened and stress relieve annealed Cronidur 30, are presented in table 7. For those applications where geometrical stability is requested and in case of highest hardness subzero refrigeration at –80°C with subsequent stress relieve annealing is recommended.
8.1.2 Austenite
Mechanical properties of high nitrogen austenitic steels in the solution annealed condition are compared with the values of wrought stainless steel implant materials (ta-

ble 8). It easily can be seen that high nitrogen stainless steels show much higher yield strength and tensile strength in combination with high ductility. Even the good impact properties of the standard implant steel 1.4441 are measured for high nitrogen stainless steels. REX 734 (ISO 5832-9) is a material with properties lying between 1.4441 and the Ni-free high nitrogen CrMnMoN-steels.

8.2 Strain hardening

8.2.1Austenite

Due to the high nitrogen contents HNS-steels exhibits a high work hardening capacity and can be cold worked to strength levels above 2000 MPa, preserving a good ductility[27,28]. Figure 10 shows the strain hardening behaviour of typical spring alloys like the standard steel grade 1.4310 and the Co-base alloys Nivaflex and MP35N in comparison with the high nitrogen steels P 2000 and P 558. Strain hardening of REX 734 is not efficient for the production of springs.
Strain hardening factors are separately illustrated in figure 11. It can be seen that P 2000 has comparable strain hardening effect to MP35N, while P 558 shows the highest value.

8.3 Fatigue

8.3.1. Austenite

It is a difficult task to compare literature fatigue data of materials, because of the variety of testing conditions[14,27,29,30,31], e.g. rotating bending or pulsating tensile stress, different R-factors, testing in air or in 3% NaCl, with pH-values varying from 7 to 1, and test frequency from 0.5-125 Hz and more. Table 9 gives a rough overview on the data of the two implant steels 1.4441 and REX 734 and the HNS-steels P 2000, Panacea and P 558. Additional information and comparison with other metallic materials gives table 10.
The endurance fatigue strength is influenced by different factors like material condition (solution annealed or cold worked), testing method (rotating bending or pulsating tensile stress), medium (air or NaCl-solution). Therefore a correct comparison is only obtained, when the testing conditions are the same. In case of P 2000 it was demonstrated that by cold working the fatigue strength could be raised from 320 to >450 MPa.
More important is the fact that strain hardened standard implant steels 1.4441 and REX 734 loose most of their fatigue strength when they are tested under NaCl-solutions. In contrast to these results cold worked HNS-steels only show a minor effect when tested under corrosive environments.

9. Microstructure

9.*1 Martensite*

Martensitic steels harden by precipitation of Cr-nitrides. The higher the C-content the higher is the tendency of the formation of large, broken Cr-nitride particles (see Fig. 12 for the steel 1.4112). By lowering the C-content while at the same time adding 0.40% N an even distribution of the deposited Cr-carbonitrides with a size of ≤ 15-20 μm has been achieved (see Fig. 13 for Cronidur 30), and thus the risk has been eliminated that coarse Cr-carbides might chip off[9,32].

9.2 Austenite

Austenitic steels normally show an even γ-phase grain structure. The δ-ferrite-problem does not occur with HNS-steels because the austenite phase is strongly stabilised by the addition of Mn and N.
HNS-steels must be remelted by PESR techniques which leads inevitably to a material with a low content of impurities and therefore to a high cleanliness. On the other hand low quantities of impurities results in higher grain size compared with normal CrNiMo-steels.
HNS-steels must be heated to temperatures of about 1150°C in order to dissolve the whole amount of N. the N-concentration therefore has to be limited because more nitrogen in the face centered solid solution results in brittle cleavage fracture along crystal lattice planes[27)]. A further metallurgical limitation is the rapid cooling (quenching) rate which has to be imposed on HNS-steels in order to avoid decomposition into nitrides. J. W. Simmons et .al.[33,34)] and M. O. Speidel et. al.[27)] give information about the cooling (quenching) velocity, that is the time limits within which the HNS-steels must be cooled in order to avoid precipitation of the Cr_2N-phase. The diagrams show a maximum of precipitation force at temperatures of about 950°C. Ageing procedures at 700°C caused grain boundary precipitation of Cr_2N, with the degree of sensitisation increasing systematically with ageing time[34)].
J. A. Cotton et al.[35)] report on the influence of Nb and V on the microstructure of high nitrogen stainless steels. Nb and V additions result in the formation of precipitates both during solidification and after ageing at 1100°C, and in both cases these precipitates are characteristic of niobium and vanadium carbonitrides. The precipitates that form during solidification are large and as a result of their size and volume fraction, probably remove a significant amount of nitrogen from solid solution. The formation of precipitates at 1100°C, which are insoluble at elevated temperatures, improves the hardness at the expense of ductility. Because of the reduction of nitrogen in solid solution corrosion resistance will be influenced negatively.

10. Machining

10.1 Martensite

Martensitic steels normally are machined in the soft annealed condition. In such a condition Cronidur 30 and 1.4112 show hardness of about 230 HB. Because of the very fine and homogeneous Cr carbonitride-precipitations Cronidur 30 is an ideal material for the drilling of deep and narrow holes.
After hardening and stress relieve annealing with hardness values between 55 and 60 HRC only grinding is suitable.

10.2 Austenite

Because of their higher strength HNS-steels are more difficult to machine. Therefore it is recommended to use hard metal or Cermet tools. Details are given in table 11.

11. Applications

11.1 Martensite

Today Cronidur 30 is used especially in the ball bearing industry as well as in medical technology for manufacturing drills and surgical tools, and in precision engineering[36-46)] (see table 12). More areas of application inevitably present themselves in situations where wear resistance, reliability and long lifetime are required. More examples are threads, extruders, screwdrivers, highly wear resistant axles and points for precision measuring tools.

11.2 Austenite

HNS austenitic stainless steels will be mainly used as generator retaining rings, in the medical field, e.g. in orthopedics, osteosyntheses, dental implants, orthodontia, coronary stents, and in many other applications at and in the human body where absence of nickel is requested[47-56] (see table 13).
The Ni-free steel grade P 2000 shows excellent biocompatibility and will be mainly used in contact with the human body, for the production of spectacle frames, watch cases and jewellery and after biological evaluation for the production of prosthesis for orthopaedics, bone screws and plates for osteosynthesis and high-strength wire for orthodontia[27,17].
For applications in the watch- and medical industry there is a high request for excellent polishability which can be reached by special metallurgical means.

Additional applications result inevitably in cases where corrosion resistance, reliability and a high fatigue resistance are required. Examples are ultra high strength screws, nuts and bolts for the fastener industry.

12. Wear

12.1 Martensite

Throughout the performed testing Hucklenbroich et al.[40] demonstrated the superior bearing performance of Cronidur 30 over all conventional bearing steel. In full lubrication conditions Cronidur 30 shows 80 times the calculated L 10 bearing life, whereas M50 and SAE 52100 reach the expected lives. This improved performance characteristics of Cronidur 30 is attributed to the unique chemistry and pressure remelting process (PESR), the fine microstructure combined with balanced properties regarding hardness, toughness and corrosion resistance.
The advantages of this new type of martensitic steel for the bearing industry are obvious[40-42,44-46]:

- Higher corrosion resistance
- Higher life-time
- Lower failure-probability
- Higher operating temperatures
- Higher operational safety
- Minimum maintenance costs

It was shown by A. Toro[57] that nitrogen also improves the resistance of martensitic stainless steels to slurry erosion.

13. Availability of materials

13.1 Martensite

The martensitic steel grade Cronidur 30 was developed in 1984. Since that time production has grown to hundreds of tons/year mainly for supplies for the bearing industry in aviation and space industry. The medical industry as a new field of application has been developed within the last two years with increasing success. Wire rolling and drawing is now under control so that new markets can be supplied with small dimension >1 mm diameter.

13.2 Austenite

The availability of metallic implant materials is limited to the standard alloys, e.g. the so called “implant steel” 316L (DIN 1.4441), the established Co-base alloy Co Cr28 Mo6, the commercially pure titanium grades 1-4 and the “work horse” of the titanium alloys Ti Al6 V4 (ELI), see table 14.
The steel grade ISO 5832-9 (REX 734) is nowadays produced by several steel companies world-wide. The high technical requirements on the one hand and the complexity of production processes on the other hand led to quality- and related supply-problems. Because of an increasing market for this steel for the production of hip-stems shortages of delivery can occur.
The Ni-free high nitrogen-containing CrMnMoN-variants of austenitic stainless steels are now appearing on the market. It seems that the serious production problems related to difficulties in metallurgy and processing have been overcome. The extraordinary combination of high strength, ductility and fracture toughness of this non-magnetic steel type justifies an additional attempt by the steel producers to start regular production

14. Conclusion

A survey on martensitic and austenitic high nitrogen stainless steels is given and the interactions between applications, requirements, properties and last but not least availability are presented.
The martensitic stainless HNS steels now have found their niche in the market:

- Bearings for the aviation– and space industry
- Surgical cutting instruments.

Other new applications are now under exploration taking into consideration their excellent corrosion- and wear resistance and thus resulting higher life-time and operational safety.
Because of demands for higher stresses and temperatures by the electricity generating industry, the HNS steel P 2000 was first designed as retaining ring material.
Allergic reactions to nickel containing alloys have become a serious medical problem in industrialized countries. Therefore the austenitic HNS grades with their good combination of high strength and ductility even in cold worked condition and excellent corrosion resistance are predestined as a potential successor for the implant steels 316L (1.4441) and REX 734 (ISO 5832-9).
The availability of a material mirrors the interest of the customer in this material: is there a specific need for new materials with improved properties or is it only a question of “nice to have”. If a new material has been developed it must be asked what are the advantages in comparison to the existing implant materials.
We must bear in mind that a customer will only pay a higher price for a product that shows clear advantages against the standard material. What does that mean for the presented high nitrogen martensitic and austenitic stainless steels?
In case of the martensitic grade Cronidur 30 the advantages of this new steel are so obvious that it has got its breakthrough.
There is a growing demand for Ni-free austenitic steels for use in medical applications and in the watch industry. Now the suppliers must show their ability of producing the different forms and dimensions with the requested properties.

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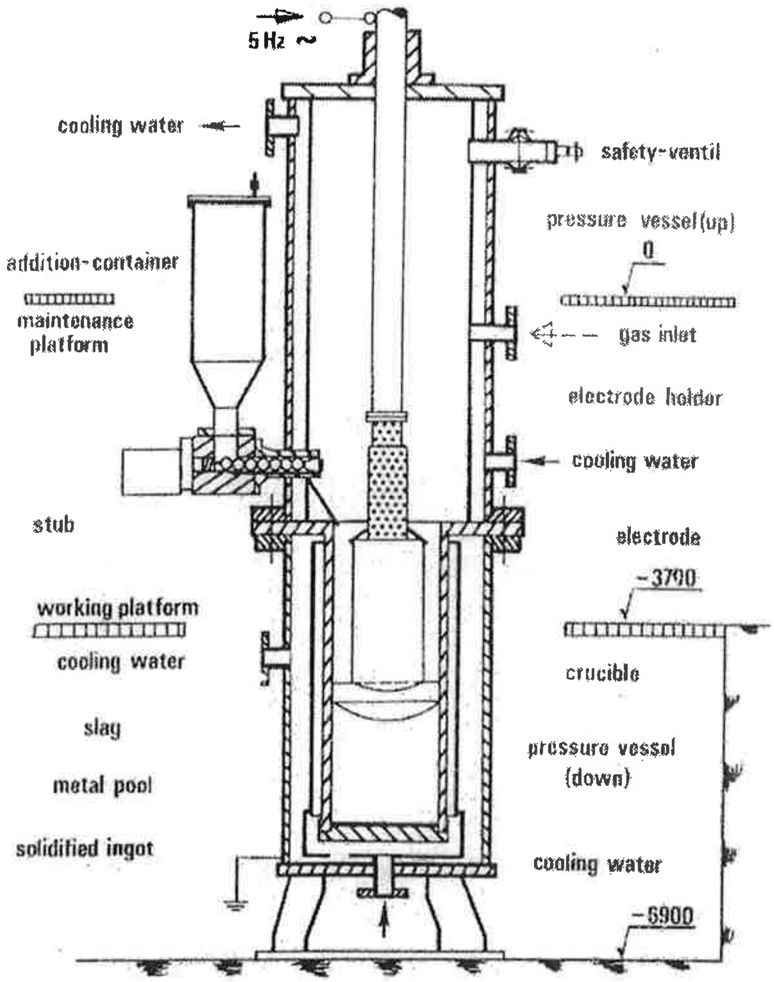


Figure 1: Scheme of pressure-electro-slag remelting equipment (PESR)

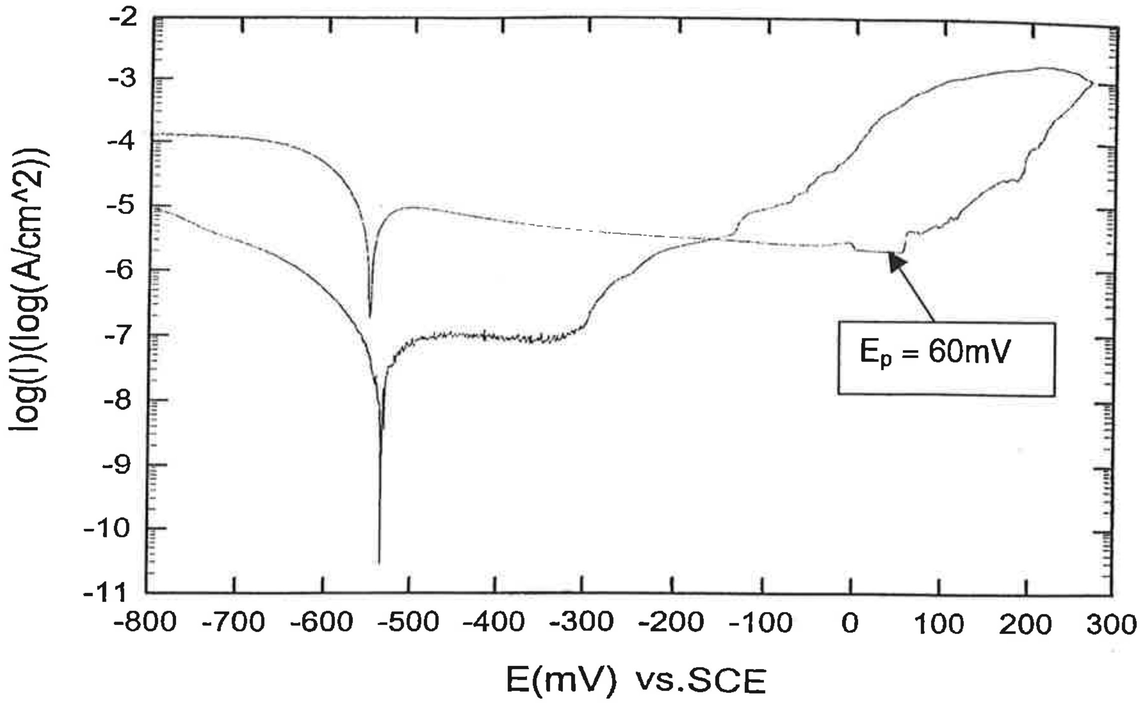


Figure 2: Current density/Potential Curve Cronidur 30
Testing conditions: 0,9% NaCl, pH4, 40°C

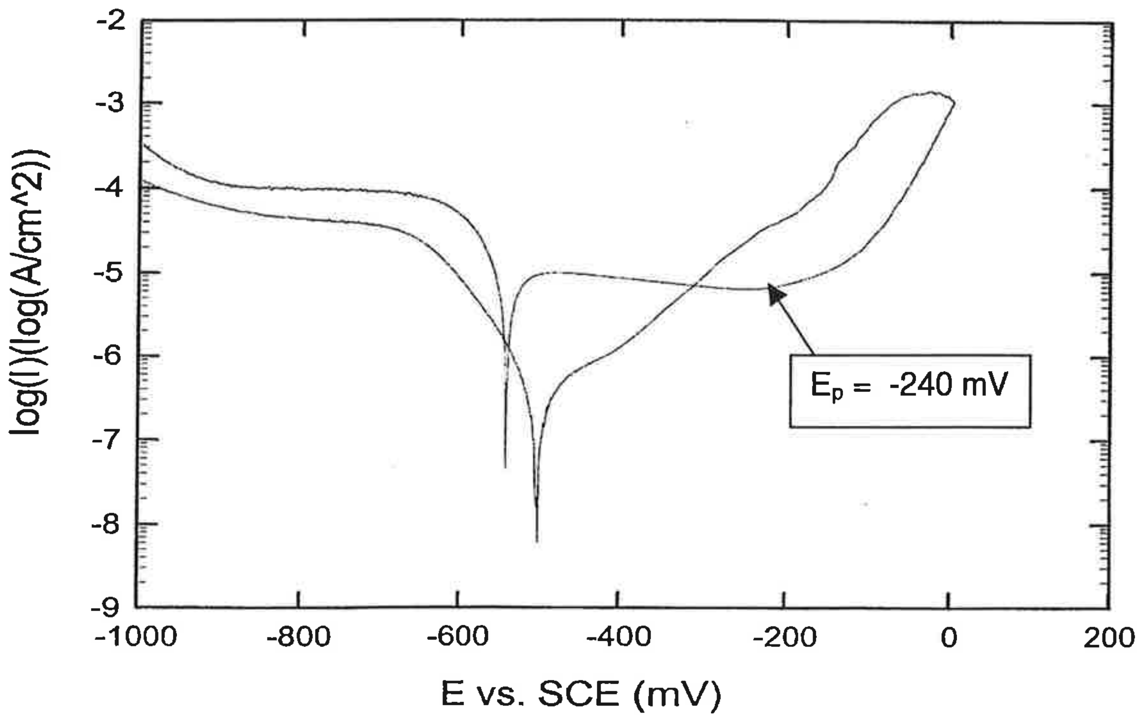


Figure 3: Current density/Potential Curve 1.4112
Testing conditions: 0,9% NaCl, pH4, 40°C

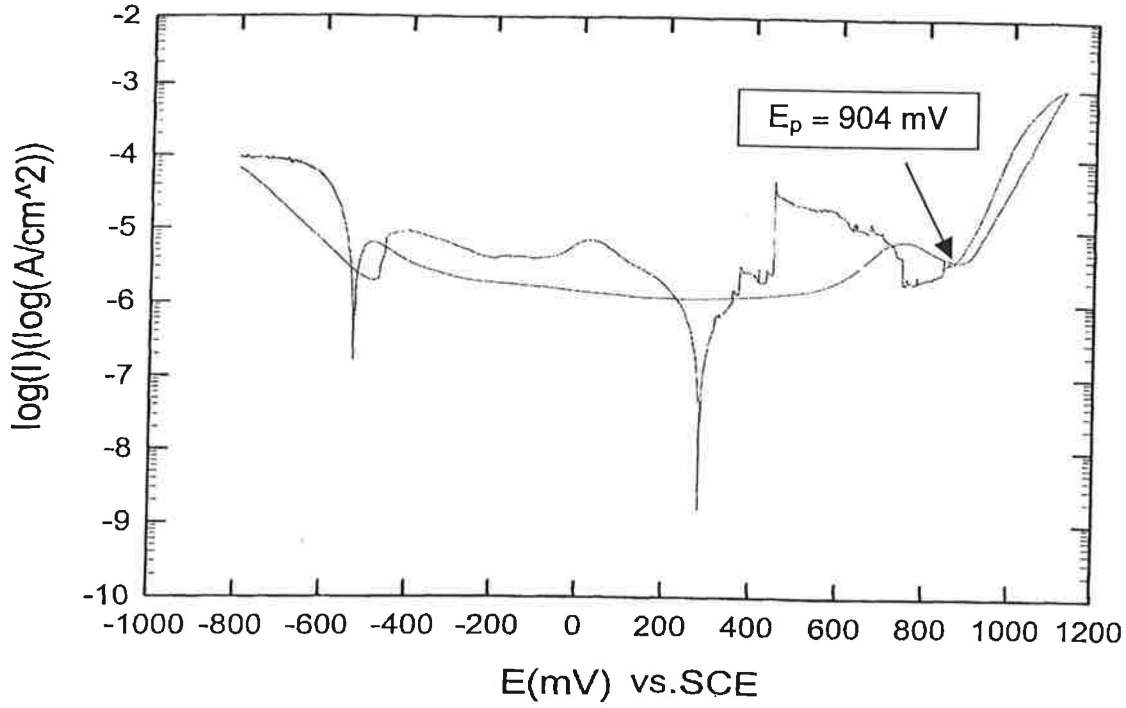


Figure 4: Current density/Potential Curve REX 734
Testing conditions: 3,2% NaCl, pH4, 40°C

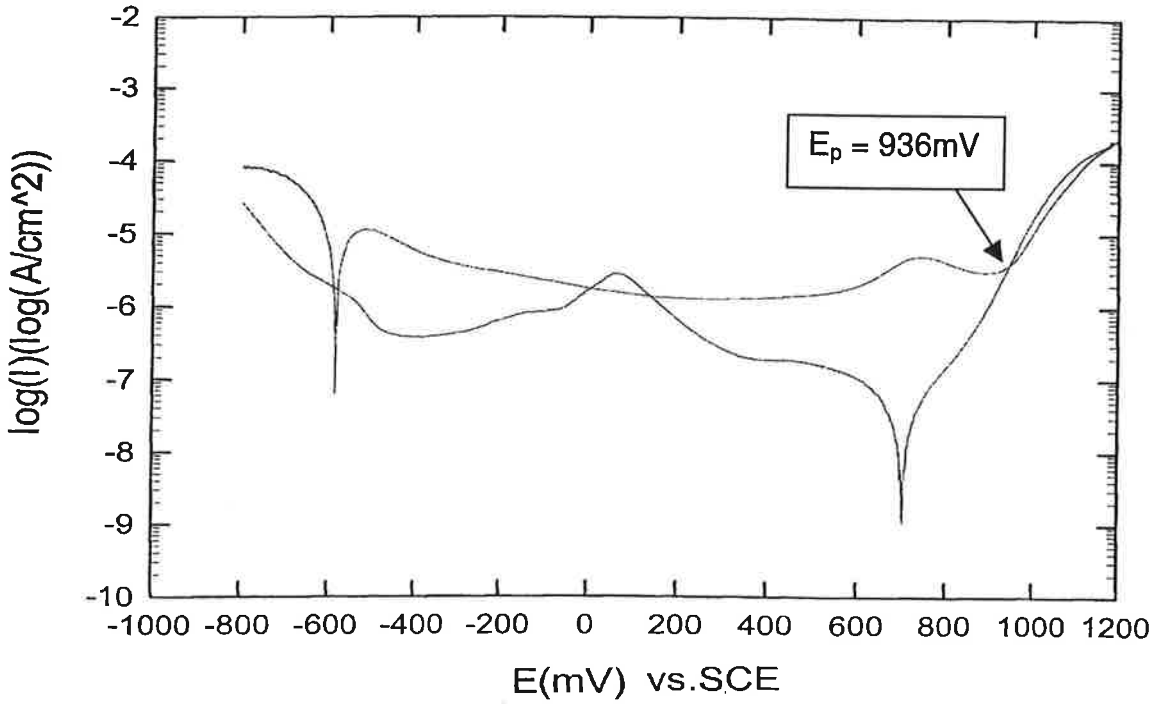


Figure 5: Current density/Potential Curve P 2000
Testing conditions: 3,2% NaCl, pH4, 40°C

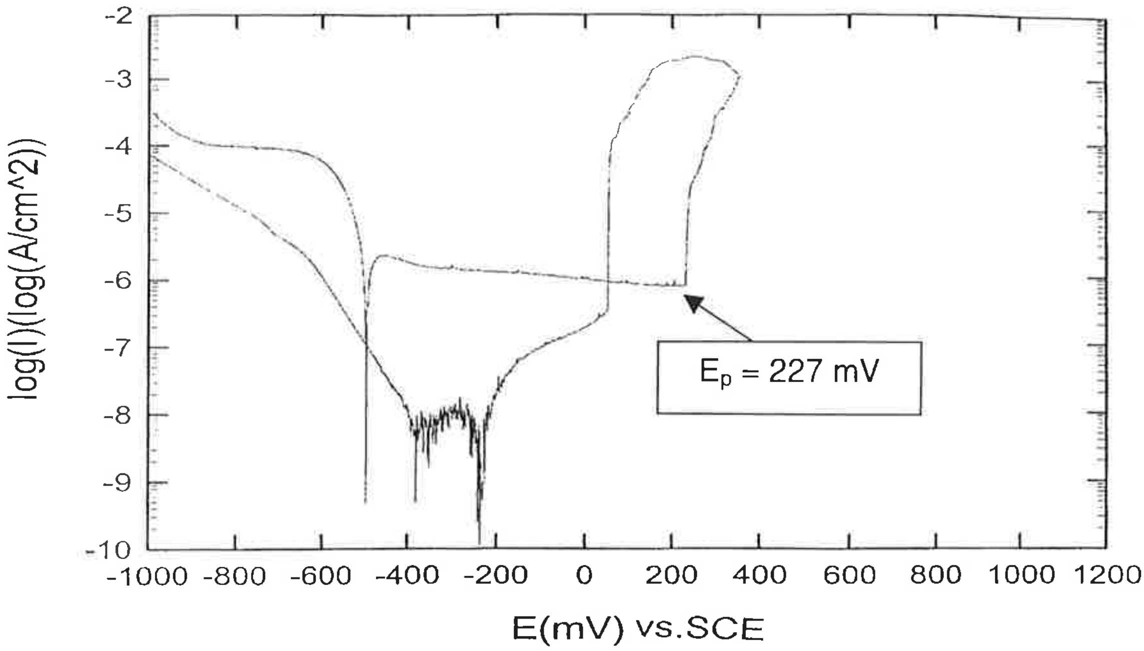


Figure 6: Current density/Potential Curve 1.4435

Testing conditions: 3,2% NaCl, pH4, 40°C

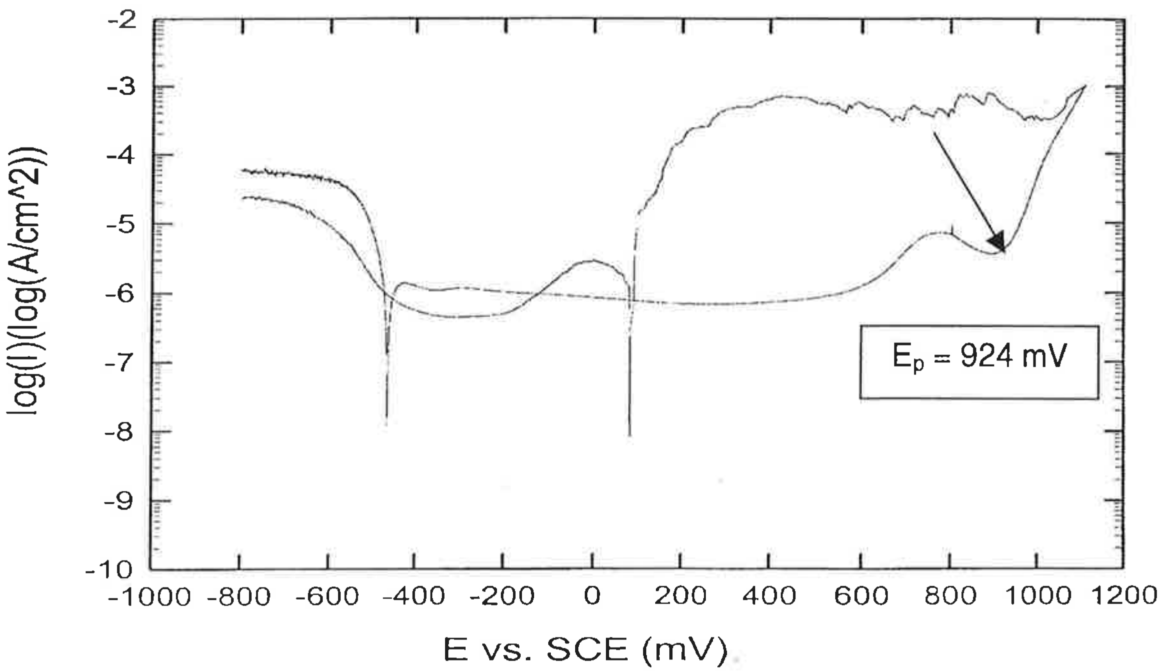
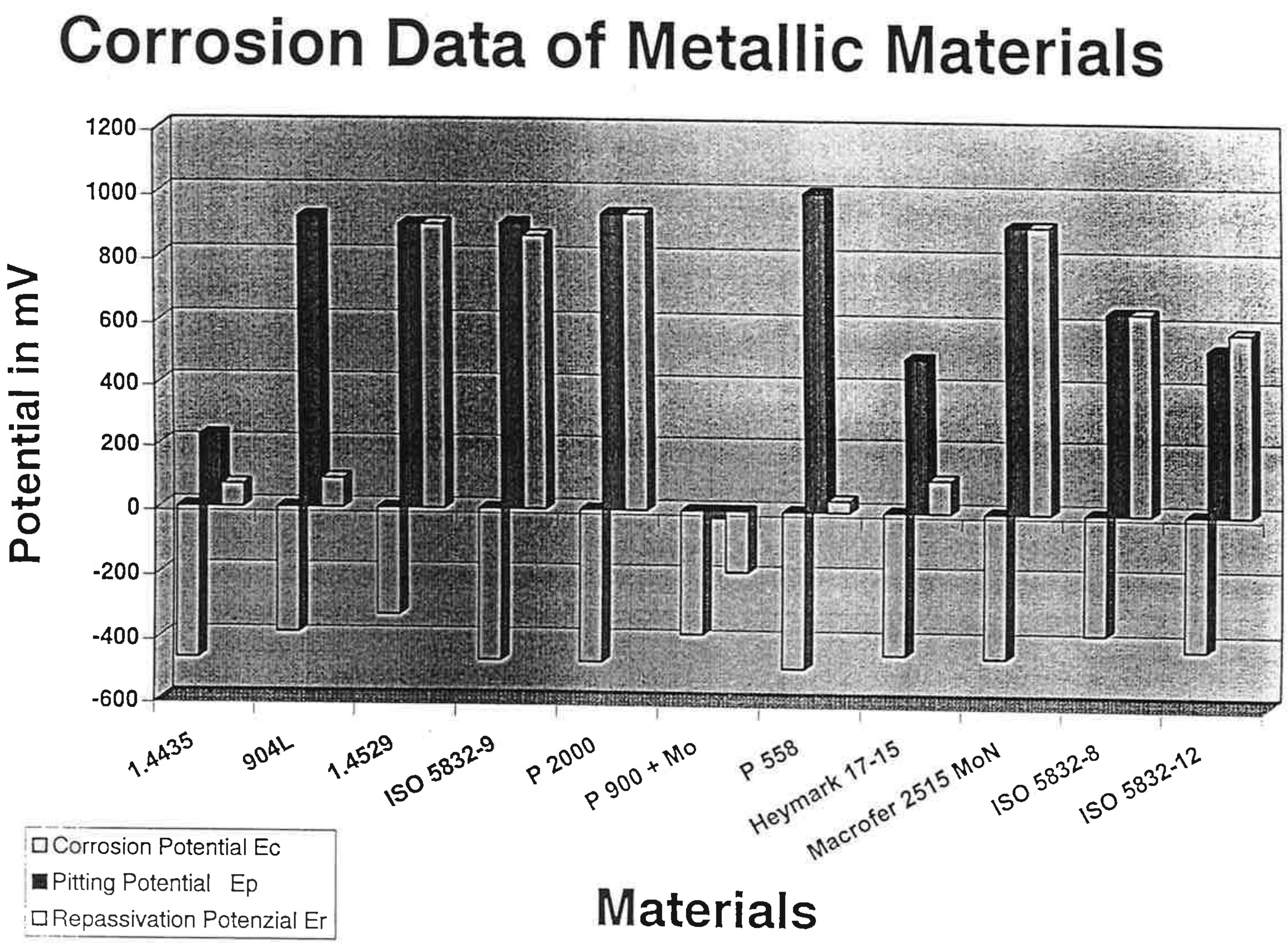


Figure 7: Current density/Potential Curve 1.4539

Testing conditions: 3,2% NaCl, pH4, 40°C

Figure 8:


Corrosion Data of Metallic Materials
Potential in mV
1200
1000
800
600
400
200
0
-200
-400
-600
1.4435
904L
1.4529
ISO 5832-9
P 2000
P 900 + Mo
P 558
Heymark 17-15
Macrofer 2515 MoN
ISO 5832-8
ISO 5832-12
Materials
Corrosion Potential Ec
Pitting Potential Ep
Repassivation Potenzial Er

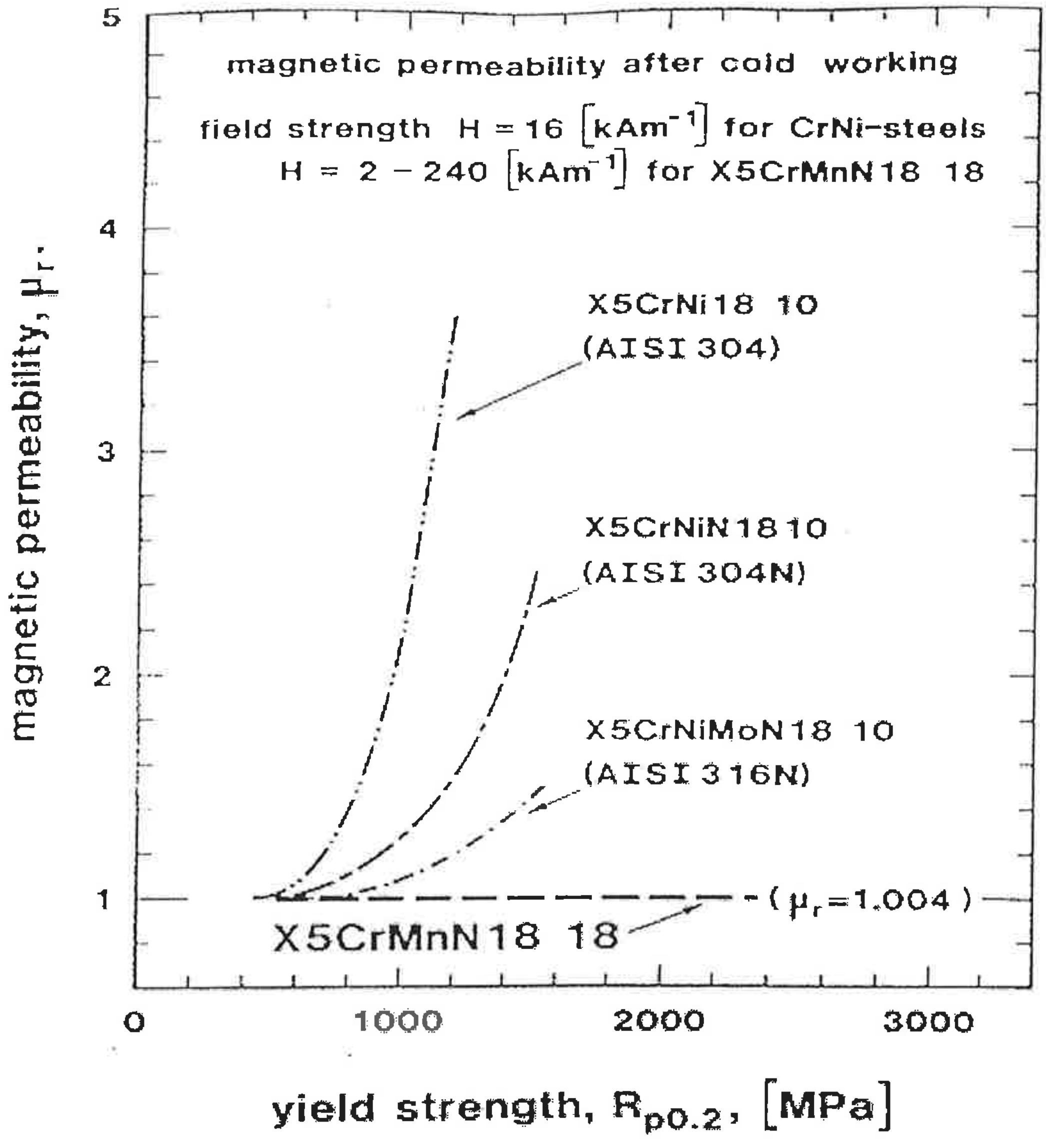


Figure 9: Magnetic Permeability of different steels

Figure 10:

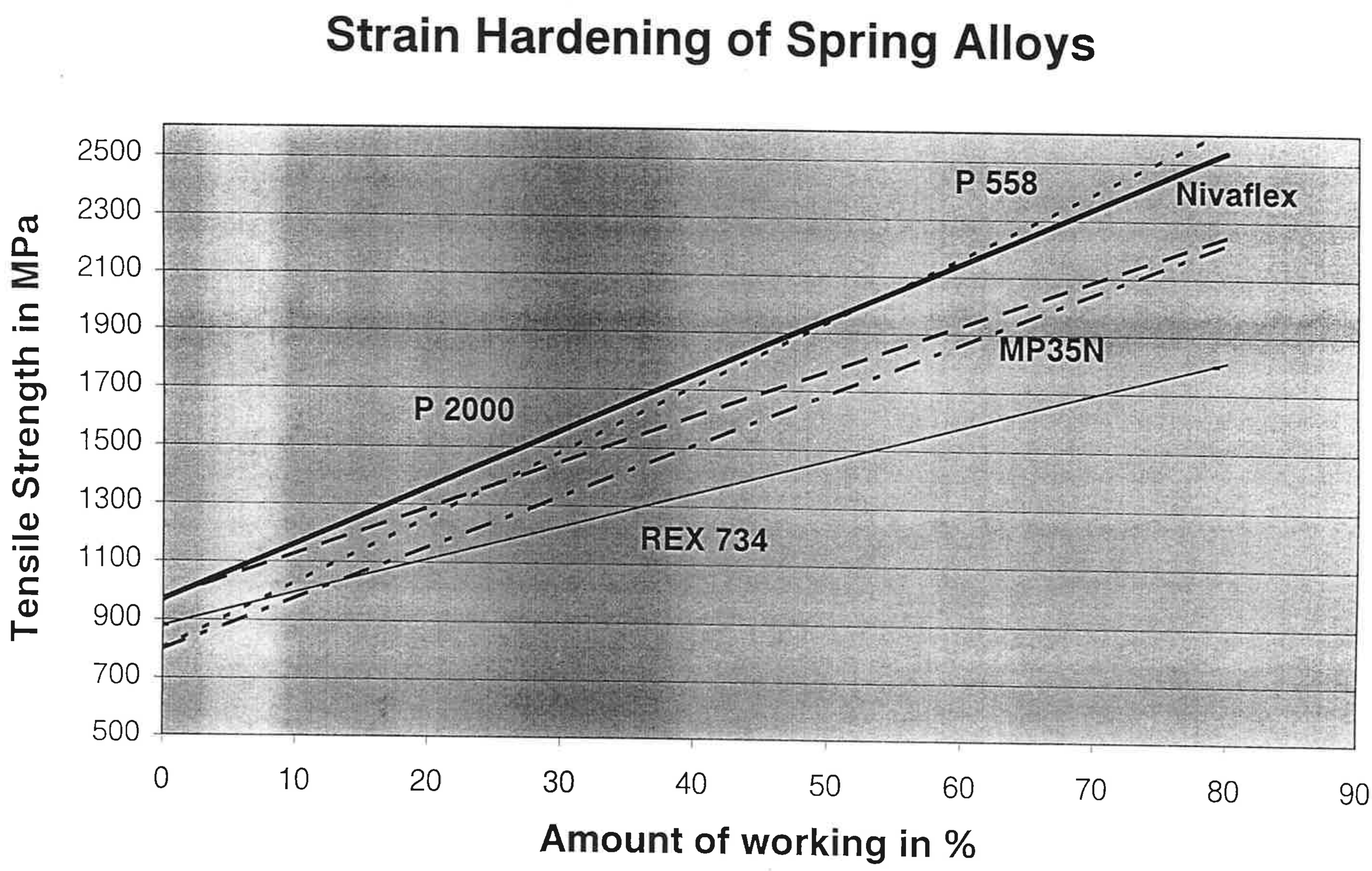
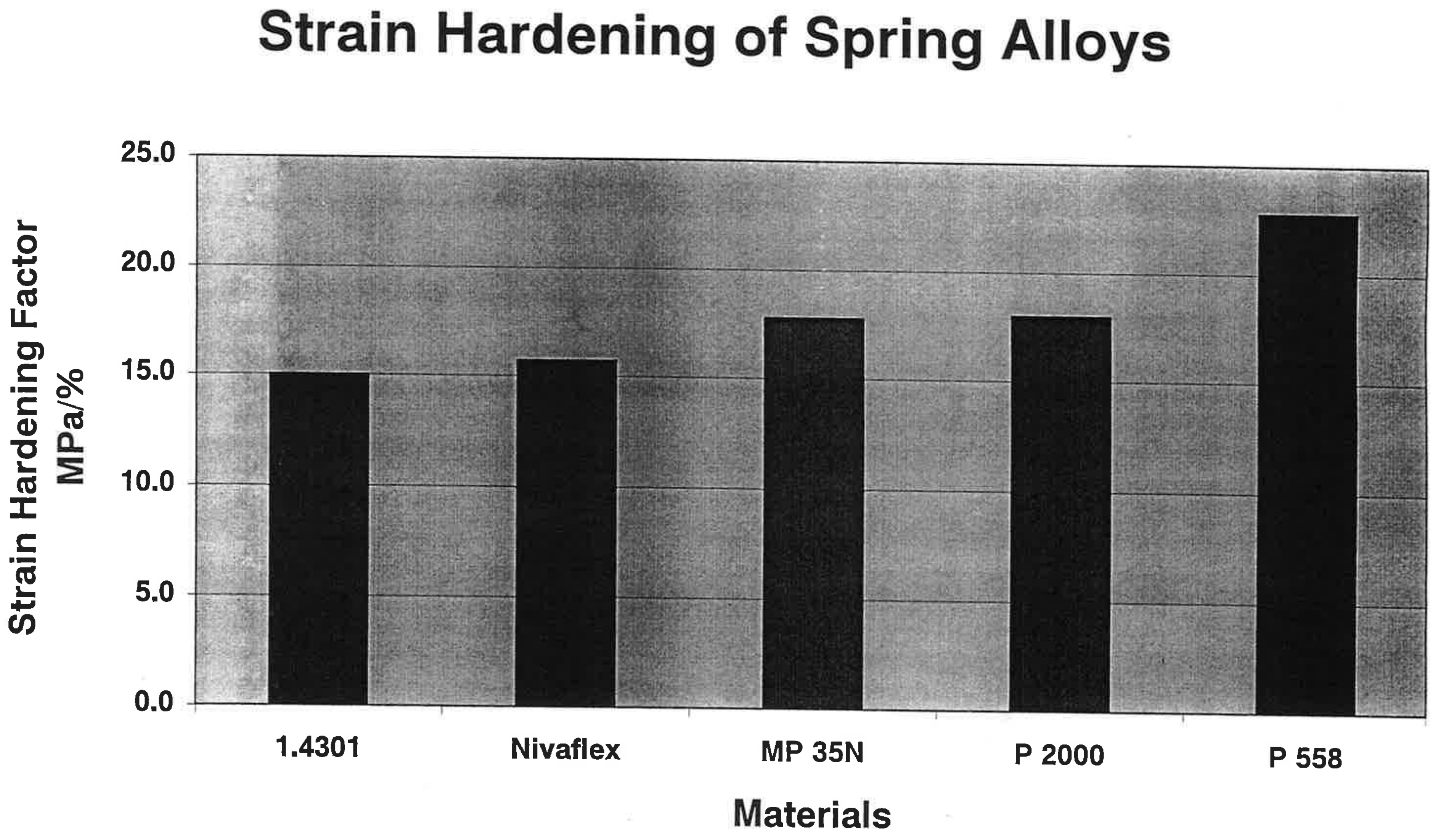

Strain Hardening of Spring Alloys
Tensile Strength in MPa
2500
2300
2100
1900
1700
1500
1300
1100
900
700
500
0
10
20
30
40
50
60
70
80
90
Amount of working in %
P 558
Nivaflex
MP35N
P 2000
REX 734

Figure 11:


Strain Hardening of Spring Alloys
Strain Hardening Factor
MPa/%
25.0
20.0
15.0
10.0
5.0
0.0
1.4301
Nivaflex
MP 35N
P 2000
P 558
Materials

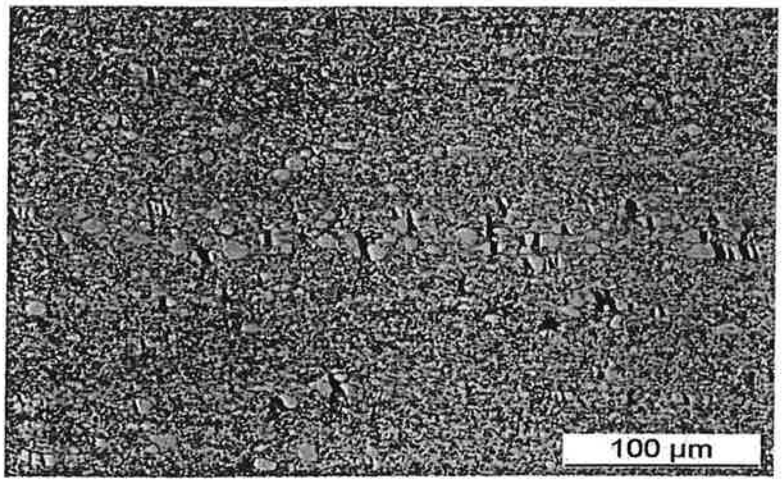


Figure 12: Microstructure of 1.4112

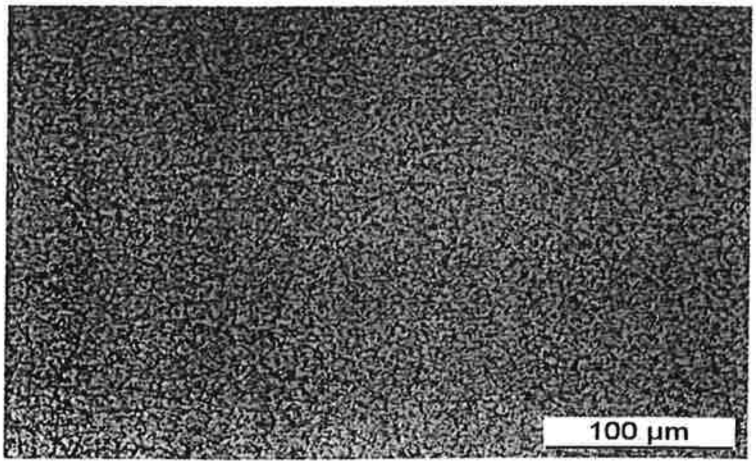


Figure 13: Microstructure of Cronidur 30

Table 1: Chemical Composition

Hardenable Martensitic Steels

DIN - mat. no.	DIN - symbol	C	Si	Mn	P	S	Cr	Mo	N	V
1.4034	X46Cr13	0.42-0.50	≤ 1.00	≤ 1.00	≤ 0.045	≤ 0.030	12.5-14.5		-	
1.4112	X90CrMoV18	0.85-0.95	≤ 1.00	≤ 1.00	≤ 0.045	≤ 0.030	17.0-19.0	0.90-1.30	-	0.07-0.12
1.4125	X 105CrMo17	0.95-1.20	≤ 1.00	≤ 1.00	≤ 0.045	≤ 0.030	16.0-18.0	0.40-0.80	-	
1.4108*	X30CrMoN15-1	0.25-0.35	≤ 1.00	≤ 1.00	≤ 0.030	≤ 0.025	14.0-16.0	0.85-1.10	0.30-0.50	

* = Cronidur 30

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Table 2: Chemical composition of implant steels

Element	Compositional limits %, (m/m)			
	AISI 316 L	DIN 17443 1.4441	ISO 5832-9 REX 734	P 2000[1)]
Carbon	0.030 max	0.030 max	0.08 max	0.15 max
Silicon	1.00 max	1.00 max	0.75 max	-
Manganese	2.0 max	2.0 max	2 - 4.25	12 - 16
Phosphorus	0.045 max	0.025 max	0.025 max	-
Sulfur	0.030 max	0.010 max	0.01 max	-
Chromium	16.0-18.0	17.0-19.0	19.5 - 22	16 - 20
Molybdenum	2.0-3.0	2.5-3.2	2 - 3	2.5 - 4.2
Nickel	10.0-14.0	13.0-15.5	9 - 11	Ni-free
Niobium	-	-	0.25 - 0.8	0.25 max
Nitrogen	-	0.10 max	0.25 - 0.5	0.75 - 1.00
Copper	-	-	0.25 max	-
Iron	Balance	Balance	Balance	Balance

1) until now not standardised as implant steel

Table 3: Chemical Composition

Ni- free austenitic Steels

Company	Trade mark / brand	Ni	Cr	Mo	Mn	Si	S	C	N / C+N	Nb	Cu	V	Al	Ti	Fe
VSG	P 2000	0.11	16.00	3.92	11.77	1.09		0,07	0.85	0.01	0.03	0.09	0.009		bal.
VSG	P 900 + Mo	≤ 0.30	16-19	1.8-2.5	17-20	< 1.0			0.8-1.0						bal.
ETH	Panacea	0.03	17.1	3.3	12.3	1.0	0.007	0.017	0.9	0.11					bal.
Krupp VDM	Macrofer 2515 MoN	0.37	18.95	2.83	24.75	0.80		0.021	1.05		0.79			≤ 0.01	bal.
Aubert & Duval	Nonic 7007	≤ 0.25	16-19	2.5/3.3	20/24	<0.25		≤ 0.20	0.65/0.90						bal.
Böhler	P 558	0.08	17.4	3.1	10.2			0.2	0.48	0.051					bal.
Heymark	17-15 extra low Ni	≤ 0.05	17.0	2.2	15.0			≤ 0.10	0.50						bal.
Carpenter	Biodur 108	0.141	20.3	0.68	23.8	0.167	0.001	0.062	0.96	0.001	0.03	0.03	0.001	0.003	bal.
Columbus	Cromanite	1.37	18.98	0.22	10.35	0.47	0.003	0.064	0.50						bal.

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Table 4: Pitting Resistance Equivalent

Definition of PRE : %Cr + 3,3 X %Mo + 16 X %N

Material			Cr	Mo	3.3 X %Mo	N	16 X %N	PRE
AISI/Trade mark	DIN - no.	Heat-no.						
316 L	1.4404	73635	16.7	2.07	6.83	--	--	**23.5**
4435 NTK	1.4435	8N6665	17.7	2.62	8.65	--	--	**26.3**
904 L	1.4539	Nominal analysis	20	4.5	14.9	0.05	0.8	**35.7**
REX 734	ISO 5832-9	--	20.65	2.12	7.0	0.41	6.56	**34.2**
P 2000	1.4452	77077	15.95	3.92	12.94	0.85	13.6	**42.5**
----------	1.4653	Nominal analysis	19.0	3.00	9.9	1.0	16.0	**44.9**
Nivaflex	--	Nominal analysis	18.0	8.00*	26.4	--	--	**44.4**

*) = Mo + W

To DIN 17443 PRE ≥ 26 is requested for the implantat-steel 1.4441

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Table 5: Cronidur 30 Physical Properties

Physical Properties		
Modulus of elasticity (Young)	218	kN/mm^2
Poisson's Ratio at RT	0,3	
Density (soft annealed)	7,67-7,72	g/cm^3
Electric Resistance	$1{,}0 \times 10^{-4}$	Ω/cm

Temperature °C	Thermal Conductivity W/m °K	Linear Expansion Coefficient mm/mm °C ($x10^{-6}$)
-129	11,872	8,8
-73	12,939	9,5
-46	13,242	9,7
-18	13,545	9,9
+10	13,848	9,9
+66	14,425	10,6
+121	15,002	10,8

Table 6: P 2000 Physical Properties

Physical Properties		
Modulus of elasticity (Young)	180-220	kN/mm^2
Poisson ´s ratio at RT	0,28-0,30	
Coefficient of thermal expansion	16×10^{-6}	1/°K
Density (soft annealed)	7,7	g/cm^3
Specific electric resistance	0,725	µΩm
Permeability (determined at field intensities ranging from 2000-240.000 A/m)	≤ 1,004	
Thermal conductivity at 87°C	14,9	W/m °K

Table 7: Cronidur 30 Mechanical Properties

Mechanical Properties hardened and stress relieved (as per following table)		
Yield Strength $R_{p0,2}$	1650	N/mm^2
Ultimate Tensile Strength R_m	2036	N/mm^2
Elongation after Fracture A	1-2	%
Hardness HV / HRC	700/60	
Shear-Yield-Strength at 32-34 HRC	665	N/mm^2

Table 8:
Mechanical properties of different austenitic stainless steels, solution annealed (Typical values)

	1.4441 ISO 5832-1	REX 734 ISO 5832-9	P 2000	PANACEA	P 558
Yield Strength $R_{P0.2}$ in MPa	220-260	420-500	610-720	610-720	600-660
Tensile Strength R_m in MPa	500-540	850-900	930-1120	980-1120	1010
Elongation A in %	55-65	40-45	55-65	55-65	50
Reduction in Area in %	65-75	60-65	70-75	65-75	65
Hardness HV 10	130-160	220-240		280-310	
Notch Impact Strength in J	> 300	210-250	303	220-280	> 150

Table 9: Fatigue strength of different austenitic stainless steels (Typical values)

	1.4441 ISO 5832-1	REX 734 ISO 5832-9	P 2000	PANACEA	P 558
Fatigue Strength σ_a (solution annealed)	179	400-420	385	480	480
Fatigue Strength σ_a (work hardened)	379 (30%) 448 (60%)		>450		
Testing conditions	Reversed bending $N_f = 10^7$ f = ? air		R = -1 $N_f = 10^6$ f = 0.5 Hz air	R = -1 $N_f = 10^7$? air	

Table 10: Fatigue resistance of different materials

Material	DIN-no. / Symbol	Condition	Rotating bending fatigue resistance in MPa
steel	1.4441	annealed	230
steel	1.4441	cold worked	400
steel (REX 734)	ISO 5832-9	annealed	420
P 2000	1.4452	annealed	385
P 2000	1.4452	cold worked	>450
Co Cr Mo - alloy	ISO 5832 - 4	cast	300
Co Cr Mo - alloy	ISO 5832 - 12	forged	600
cp titanium	grade 4	annealed	230
cp titanium	grade 4	cold worked	400
titanium alloy	Ti-6Al-4V	annealed	540
titanium alloy	Ti-6Al-7Nb	annealed	540

Table 11: P 2000® Machining data

Pre-machining

Cutting conditions:		
Cutting speed	35 m/min	
Feed	0,5 mm	
Cutting depth	4 mm	
Cutting tool	SNMM 190646	SNMM 190646
Type	CP2 or CP3	4025
Supplier	Kennametal/Hertel	Sandvik

Final machining

Cutting conditions:		
Cutting speed	45 m/min	
Feed	0,5 mm	
Cutting depth	0,2 mm	
Cutting tool	RCTM 0803 MO	This geometry to be used for the machining of one diameter only.
Type	525 (Cermet)	
Supplier	Sandvik	

Cutting conditions:		
Cutting speed	45 m/min	
Feed	0,5 mm	
Cutting depth	0,35 mm	
Cutting tool	DNMG 150612.11	This geometry is used for stepped diameters.
Type	520 (Cermet)	
Supplier	BKW Alternative: Widia	

Sawing

Cutting conditions:	
Saw blade	Bi-metal 4570 X 34 X 1,1 X Z3
Number of teeth	3 teeth /25 mm
Sawing speed	30-35 m/min
Feed	0,1 mm/sec
Contact pressure	20 kg/cm^2
Coolant	Wellcor (Fa. KSR, Bäretschwil)

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Table 12: Fields of application for Cronidur 30

Sector	Typical components
Aviation Turbine industry Bearing industry	**Bearings for:** Aviation turbines Cryogenic rocket turbopumps Rotor head for helicopters Space mechanics Aircaft structural components Fuel pumps for space shuttle Ball screw gearing shafts (mooving aeroplanes flap tracks) Small size rolls Miniature bearings for turbines for dentists Precision bearings for machine tool Wire rolling mill
Surgical cutting instruments	Drills (with laser markings), milling cutters, saws, scalers, chisels, dental curettes, taps, countersink cutters
Surgical non-cutting instruments	Filling instruments, dental explorers, laboratory and orthodontic pliers
Precision engineering	Temper-resistant gears, threads, highly wear resistant axles and points
Mechanical engineering	Needles for injection pumps, screwdrivers
Traffic	Wheel tire for high-speed trains
Food-, chemical- and pharmaceutical industry	Wear-resistant parts for processing of food, polymers, pharmaceutics, paper and pigments
Cutlery industry	Corrosion resistant knives, scissors, pliers for professional use

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Table 13: Fields of application for Ni-free austenitic HNS steels (e.g. P 2000)

Sector	Typical components
Energy	Generator retaining rings
Fastener industry	Ulta high-strength screws, nuts and bolts
Automotive industry	Screws and bolts, springs
Medical engineering	**Orthopedics:** hip-joint endoprostheses (hip, knee, shoulder, elbow) **Osteosyntheses:** bone plates, screws, marrow-nails for use in bone fractures, dynamic compression screws/plates **Dental applications:** implants, supra-structures, dentures **Orthodontia:** high-strength wire, brackets, braces **MRI:** operations in high magnetic field **Pacemakers:** cables (non-magnetic) **Injection:** needles
Stents	**Coronary stents:** mesh stents, coil stents, tubular stents, ring stents, multidesign stents
Surgical cutting tools	Drills, milling cutters, saws
Watch industry	Casings, backs, bracelets, pivots
Body piercing	Rings, ear-rings, pins (Nickel content <0,05%)
Fashion jewellery	Rings, bracelets, chains, brooches (scratch-proof)
Food chain	Knives, spoons, forks, cooking pans
Textile fittings	Buttons, buckles, studs
Optical industry	Spectacle frames
Daily use	Coins, scissors
Decorative applications	Dark appearance, due to absence of Nickel
Wear resistance	Parts with high capacity against impact abrasion

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Table 14: Availability of austenitic implant materials

Group	Grades	Availability	Remarks
Conventional implant steels	316L (1. 4441)	+ + + +	common implant steel
	REX 734	+ + +	increasing applications
HNS Ni-free steel	P 2000	++	approval as implant material started
Co-base alloy	Co Cr 28 Mo6	+ + + +	prefarably used for hip stems
Titanium	CP grades	+ + + +	grade 4 also in cold worked condition
	Ti Al6 V4 (ELI)	+ + + +	( ) both grades are on the market

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