THE MAGNETIC PROPERTIES OF A PRECIPITATION HARDENING AND A SOFT MARTENSITIC STAINLESS STEEL

T. Ceccon, P. Belloli, P. Ramina

Tiziano Ceccon, Acciaierie Valbruna SpA, Viale della Scienza 25, 36100 Vicenza (Italy). tceccon@valbruna.it
Paolo Belloli, Acciaierie Valbruna SpA, Viale della Scienza 25, 36100 Vicenza (Italy). pbelloli@valbruna.it
Paolo Ramina, Acciaierie Valbruna SpA, Viale della Scienza 25, 36100 Vicenza (Italy). pramina@valbruna.it

Abstract
Ferritic stainless steels, known as “soft magnetic”, find applications in all those sectors of industry where high values of magnetic permeability and low values of coercive force are required. The choice of the most suitable type is, normally, a function of its magnetic properties and of its resistance to corrosion in operation. Among all the ferritic steels taken into account in the various ASTM and Euro Norm, or in their “ tailor-made “ specific or free machined versions, the grade that combines high magnetic properties with a good behaviour in corrosive environments can be identified and located. On the other hand, the ferritic structure, softened and with a grain size enlarged by magnetic annealing, is characterised by low values of $Rp_{0,2}$, Rm and very low values of KV. Hence, whenever there is a requirement for higher mechanical properties, the use of martensitic chrome steels with a low carbon content enables higher values of kV to be obtained but reduces considerably the magnetic properties and resistance to corrosion, because of the high temperature of tempering, with no guarantee of toughness at low temperatures. The choice of soft martensitic and precipitation steel grades such as W 1.4418 and W 1.4542 (AISI 630), respectively, permits the obtaining of extremely good mechanical properties and KV together with excellent corrosion resistance, at the detriment, however, of the magnetic properties. This memo proposes to study the analytical and structural conditions that influence their magnetic and mechanical properties as a function of the conventional heat treatment provided for by EN 10088 and ASTM A564.

THE BEHAVIOUR OF HARDENED AND TEMPERED MARTENSITIC STEELS

The mechanical properties of martensitic stainless steels with 12 ÷ 17 % chrome are obtained by two processes: hardening and tempering.
The first provides the steel with its maximum hardness, the second stretches the structure until the expected or required properties are obtained. A correct hardening process provides for the attainment of the austenitizing temperature and its being maintained for the time necessary for the carbides to go into solution, followed by a period of cooling in air or in oil, in order to convert the austenite into martensite. The more carbon is present in the alloy, the greater will be the hardness of the martensite and the more subject to tension or stress will be its structure.
It is essential to carry out the process of tempering as quickly as possible in order to transform the martensite into tempered martensite, that has a more stable structure. The temperature of tempering (or that of a number of tempering processes in the case of the presence of retained austenite) is a function of the properties required, bearing in mind that at high temperatures of tempering there is generally a corresponding reduction of corrosion resistance. The behaviour of soft martensitic steel W1.4418 and of precipitation hardening martensitic steel W1.4542 (AISI 630) is not unlike that of the known chrome-martensitic steels, but shows some significant differences such that exceed the known limits of normal martensitic stainless steels and enhance other properties that belong to certain austenitic and duplex steels, in terms of toughness and resistance corrosion, providing higher values of $Rp_{0,2}$ and Rm.

Table I. Chemical analysis % W 1.4542 (AISI 630)

C	Mn	Si	Cr	Ni	Mo	Cu	Nb	P	S
0.07 max	1.00 max	1.00 max	15.0 17.0	3.00 5.00	0.60 max	3.00 5.00	0.15 0.45	0.04 max	0.03 max

Table II. Chemical analysis % W 1.4418

C	Mn	Si	Cr	Ni	Mo	N	P	S
0.06 max	1.50 max	0.70 max	15.0 17.0	4.00 6.00	0.80 1.50	0.02 min	0.04 max	0.03 max

Table III. Chemical Analysis % W 1.4313

C	Mn	Si	Cr	Ni	Mo	N	P	S
0.05 max	1.50 max	0.70 max	12.0 14.0	3.50 4.50	0.30 0.70	0.20 max	0.04 max	0.015 max

HEAT TREATMENT OF W 1.4542 (AISI 630) STEEL

The mechanical properties of this precipitation hardening steel are obtained with an ageing process that hardens the martensitic structure through the precipitation of a phase rich in copper coherent with the matrix. In detail, the complete cycle consists of a solution treatment at 1040°C, that brings the copper in solution in the austenitic matrix, followed by a rapid cooling. The austenite begins the transformation into martensite at about 130°C and the change is completed below 30°C. When the transformation has taken place, re-heating at a suitable temperature according to the mechanical properties required tempers the martensite and hardens the structure because of the precipitation described. Examining the

various structures obtained with the heat treatment, it can be observed that the one after solution treatment and cooling (Condition A) is composed of untempered martensite supersaturated with Copper (HB<360) with a possible presence of bands of ferrite but without austenite [1].
Ageing at 480°C for one hour (H900) enables the maximum hardness to be obtained but gives low values of impact strength. Already in condition H1025 (550°C), the formation of stable austenite begins to become apparent, that reaches its maximum at about 620°C (H1150) giving rise to proportionally advantageous effects on the impact strength but to an inevitable reduction of $Rp_{0,2}$, and Rm. This situation is due both to the progressive softening of the martensite at higher temperatures, and to the formation of globules of copper with a loss of coherence with the matrix [1] .

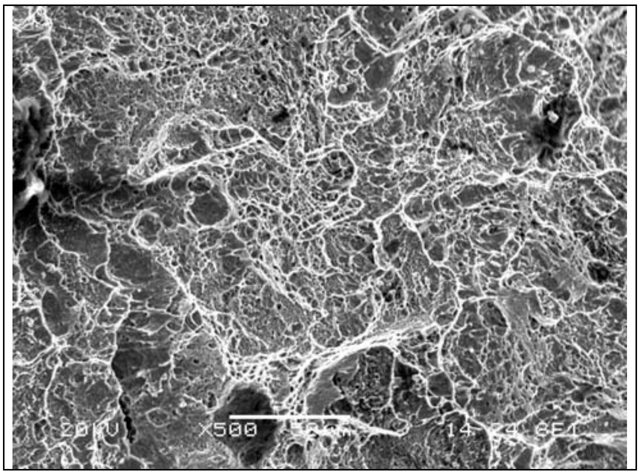


Fig1: W1.4542 Cond.H1150

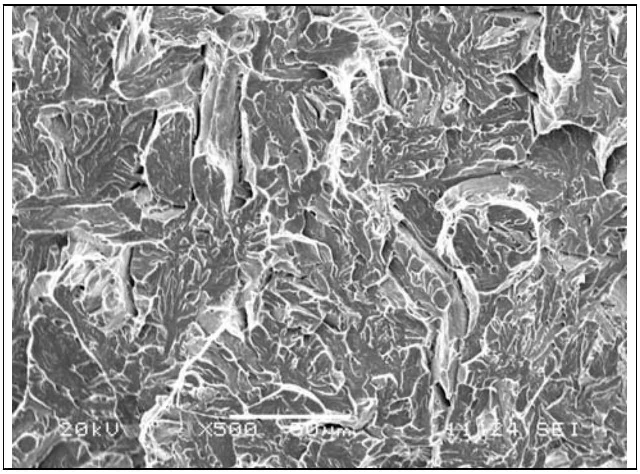


Fig2: W1.4542 Cond.H900

HEAT TREATMENT OF W 1.4418 STEEL

Like all martensitic steels, it is used in the hardened and tempered condition showing a structure made up of tempered martensite, austenite, and small quantities of ferrite . The quantity and distribution of these phases depend on chemical balance. In as quenched condition (1040 C° , air cooling) , the structure is made up of martensite, traces of ferrite and less than 10 to 15 % of retained austenite. Because of the delayed pearlitic change, due basically to the presence of nickel, cooling in air is sufficient to obtain a complete martensitic change [2] even in the case of items of large section. In the same way, the transformation temperatures A_1 and A_3 and those of M_s and M_f are strongly influenced by nickel and molybdenum. In particular, with Ni>4%, there is a considerable reduction in temperature at point A_1.
In as quenched condition, high values of Rm and HB are obtained that reach their maximum after tempering at about 450°C. When the temperature increases beyond 500°C the formation of finely dispersed stable austenite begins, reaching its maximum at about 620°C.
It is important to note that this stable austenite creates a favourable situation in terms of toughness even at low temperatures and it does not change into martensite after cooling.
On the other hand, above 620°C a part of the austenite becomes unstable and changes into martensite after cooling, that requires further tempering to avoid a stress situation that could cause quenching cracks.
For this reason, stable austenite plays a fundamental role in the behaviour of this steel.

COMPARISONS

The two steels show similar but not identical behaviours. In common they have the gradually increasing formation of stable austenite with increase in temperature of tempering or ageing. In both cases the austenite becomes unstable above 620°C but their structures after hardening is completed differ also in terms of hardness. Whilst AISI 630 (W 1.4542) shows a martensitic matrix supersaturated with copper but without retained austenite [1] , W 1.4418 contains 10 to 15% of this. It follows that if AISI 630 (W 1.4542) starts to form austenite only above a certain temperature, while W 1.4418 adds more austenite to the existing one [1].
The highest values of Rm, $Rp_{0,2}$ and HB are in any case provided by the AISI 630 (W 1.4542) after ageing at 480°C (H900). We would recall that selective variations in analysis, within the range permitted by the Standards, permit the obtaining of well-defined structures and particular temperatures of heat treatment with the scope of optimising the properties of the finished product [3].

MAGNETIC BEHAVIOUR

It is known that these two types of steel have were designed to provide high mechanical properties and impact strength combined with a resistance to corrosion that, in certain environments, approaches that of the austenitic steels. In their magnetic behaviour, they rank in between the magnetically soft and the magnetically hard materials. They are a long way from the very high permeability of Silicon - Iron (ASTM A867) or the ferritic stainless steels used for solenoid valves (ASTM A 838) and from the coercive forces of the order of K A/m of permanent magnets. Interest in the use of Soft Martensitic and Precipitation Hardening for magnetic applications is comparatively recent and lies in those sectors in which are required high strength, toughness and stainless properties combined with ferromagnetic behaviour. It is clear that the limited "*Iron*" part of these steels, the interstitial elements and the structures that they acquire through heat treatment are factors that oppose a good magnetic response. It is nevertheless possible to obtain appreciable compromises between magnetic properties and mechanical ones like KV and $Rp_{0.2}$/Rm.

DESCRIPTION OF TESTS

Mechanical tests were carried out in accordance with the Standards in force.

A complete characterisation of the magnetic properties was carried out with a Permeameter using a Sanford – Bennet yoke with which the reluctance of the system is minimised with respect to that of the sample examined. It permits the carrying out of tests on straight samples of circular or rectangular section, the length of which (>200 mm) renders negligible the demagnetisation or degaussing factor. The following magnetic quantities were determined: Magnetisation Curve, Saturation Induction B_s(Tesla), Intrinsic Induction J (Tesla), Residual Induction B_r(Tesla), Saturation Field H_{sat} (A/m), Coercive Force Hc(A/m), Maximum Magnetic Force H_m (A/m), Absolute Permeability μ_0 (H/m), Hysteresis Loop and the Maximum Permeability μ_{max} .

Since the utilisation in magnetic devices of the steels under consideration necessitates a behaviour that is closer to that of magnetically soft materials, it is better correct to evaluate the Magnetisation Curve(fig.3), the Maximum Permeability(fig.4), and J_{sat} rather than the Hysteresis Loop and its area, and the Residual Induction , which are important parameters in materials for permanent magnets. In fact, the Magnetisation Curve shows the increase of B as the Magnetising Force H increases and is a function of the magnetic properties of the material [4].

$$B = \mu_0 H + J \qquad (1)$$

where µ0H is the effect of the external magnetising field and J is characteristic of the material.

In brief, absolute permeability is given by:

$$\mu_0 = B/H \qquad (2)$$

whilst the relative magnetic permeability or maximum permeability is given by:

$$\mu\ max = \mu_0/\mu a \qquad (3)$$

where µa is the permeability of space :

$$\mu_a = 4\ \pi x 10^{-7} \qquad (4)$$

Heat treatment for ageing and hardening and tempering was carried out in the laboratory on samples from which were obtained the test specimens for the mechanical and for the magnetic properties. The latter, of circular or rectangular section between 105 and 195 mm^2, were ground with Ra<1µm without under-going any deformation nor overheating which would have markedly affected the values of magnetic permeability [5].

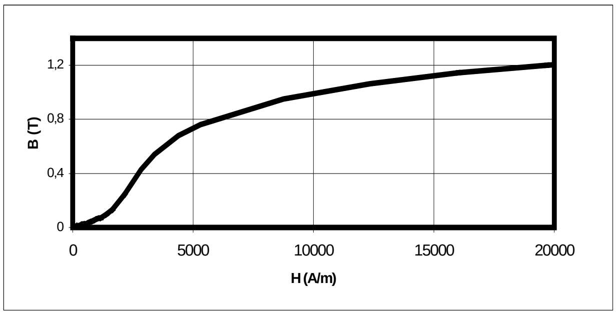


Fig.3: W1.4542_Magnetisation Curve cond.H925 (Creq/Nieq=1.82)

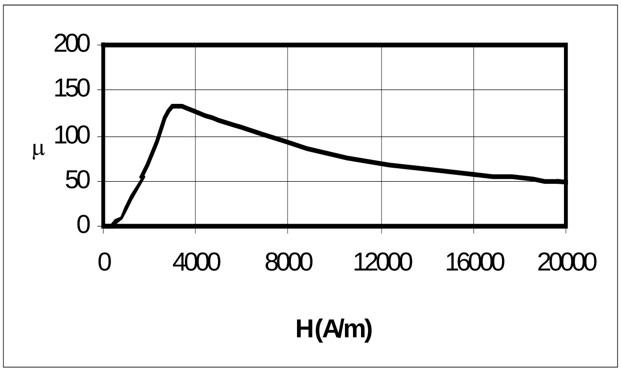


Fig.4: W1.4542_Magnetic Permeability curve cond.H925 (Creq/Nieq=1.82)

AISI 630 (W 1.4542) : RESULTS OF TESTS

It is known that the chemical analysis, heat treatment and structural conditions affect both the mechanical and the magnetic properties of all types of steel. To determine if, and to what extent, the three quantities mentioned can be correlated, a method was chosen that has already been used in previous work.[3],[7] and extensively experimented with positive results. Heats were studied that had an analytical balance that made them suited for giving the finished product certain well-defined properties. The evaluation of this balance was made utilising the ratio of Chromium equivalent to Nickel equivalent, using the Suutala-Moisio formula for the Austenitic grades [6] while the temperatures in the ageing tests were in accordance with ASTM A564. Since these temperatures were common to all the test specimens it follows that structural, mechanical and magnetic differences depend on the analytical balance Cr_{eq}/Ni_{eq}.

Creq= Cr% +1,37Mo% +1,5Si% +2Nb% +3Ti% (5)

Nieq= Ni% +0,31Mn% +22C% +Cu% +14,2N% (6)

The information provided by this report must not concern only its numerical value but must be completed by evaluating the effect of each individual element.

The evaluation of the data obtained permits the observation that:

(a) Magnetic Permeability increases as the value of Cr_{eq}/Ni_{eq} increases and decreases with the increase of ageing temperature.

With high values of Cr_{eq}/Ni_{eq} there is no austenite present at the minimum ageing temperature (H900-480°C) whilst with low values , this phase already starts to appear and the lower the ratio mentioned, the higher the content . This situation can be verified in figure 5. With ageing at H900 (480°C) the heats with Cr_{eq}/Ni_{eq}=1,90÷1,94 show a permeability that is peculiar to a tempered martensite structure even if the maximum hardness for this type of steel is attained. This martensite displays a ferromagnetic behaviour. The heat that has the ratio Cr_{eq}/Ni_{eq}=1,69 shows the same structure but with a higher percentage of stable austenite which is a non-magnetic phase. Increasing the ageing temperature, the permeability of all the heats reaches the maximum value at H1025(550°C) and show a faster drop in the heats with a lower value of Cr_{eq}/Ni_{eq} because of the progressive increase in the austenite content. On the other hand, the heats with a high ratio do not show appreciable drops until reaching H1100(595°C). Beyond this temperature, and until they reach condition H1150(620°C) the permeability drops to minimum values and is practically equal for all the heats because of the quantity of stable austenite that forms and reaches a maximum at about this temperature [1]. To check to what extent the austenite has a negative effect on the magnetic properties in martensitic structures in the absence of important quantities of Cr, Mo, Cu, Nb, magnetic tests were carried out on the well-known 100Cr6 steel with the traditional treatment of hardening + tempering and with cryogenic treatment + tempering. The values of permeability with the latter treatment were three times higher than with the former. (μ max = 338 against μ = 108).

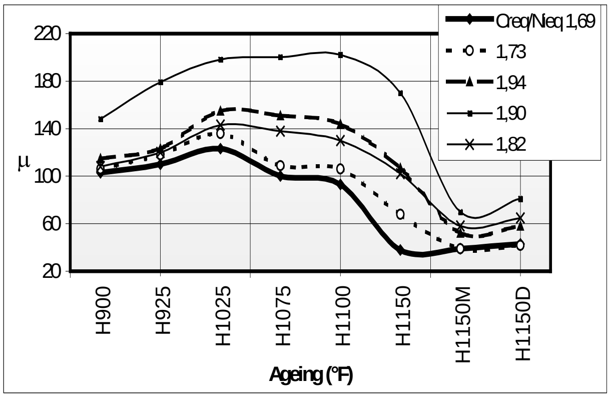
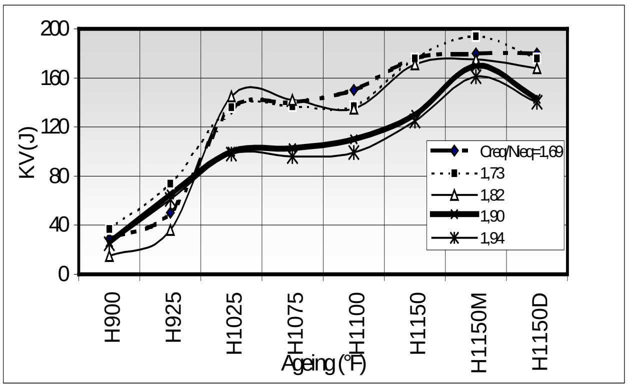


Fig.5: W1.4542_Maximum permeability for different Cr_{eq}/Ni_{eq} and Ageing temperatures.

(b) The impact strength KV increases as the ratio Cr_{eq}/Ni_{eq} decreases. The lowest values occur at H900 since at this temperature there is the maximum precipitation of the copper-rich phase and hence the maximum hardness. It should be noted that the highest values of the ratio Cr_{eq}/Ni_{eq} correspond to the lowest values of KV because of the absence of stable austenite and of the presence of ferrite. The Magnetic Permeability reaches its maximum at H1025 (550°C) and starts to drop after this temperature has been reached, whilst the impact strength remains fairly constant until it increases appreciably starting from H1100 (595°C) reaching a maximum at H1150 (620°C). The reasons for this behaviour lie in the stable austenite that forms progressively as the temperature rises, and the fact that a larger quantity of this phase improves the values of impact strength KV.

Fig.6: W 1.4542_Impact Strength for different Cr_{eq}/Ni_{eq}



and Ageing temperatures.

(c) The values of the mechanical properties and the ratio $Rp_{0.2}/Rm$ increase as the ratio Cr_{eq}/Ni_{eq} increases. The values of $Rp_{0.2}$ and Rm given in figure 6 show their maxima at condition H900 (480°C) whilst the best value for the ratio $Rp_{0.2}$ /Rm occurs at condition H1025 to which also corresponds the maximum value of magnetic permeability.

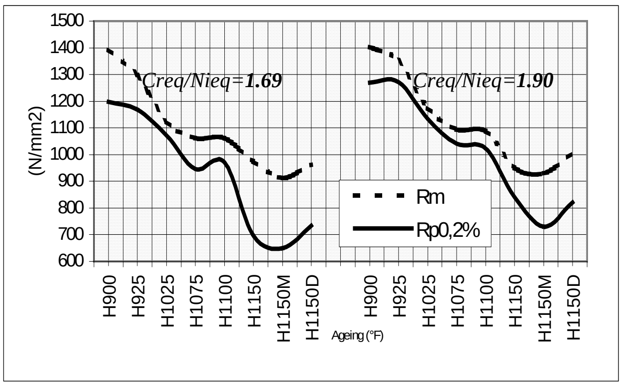


Fig.7: W 1.4542_ $Rp_{0.2}$ and Rm values for different Cr_{eq}/Ni_{eq} and Ageing temperatures.

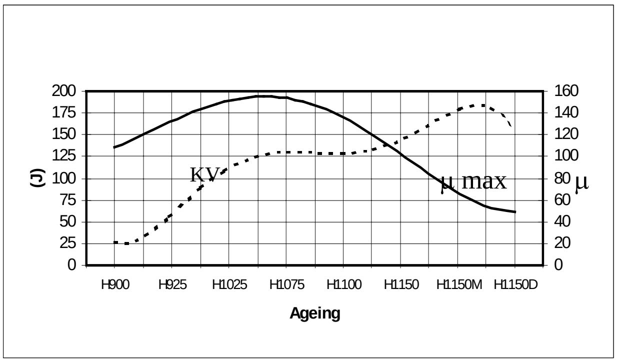


Fig.8: W 1.4542_ Maximum magnetic permeability and impact strength at different ageing temperature.

(d) The values of J_{sat} (Tesla) measured in the conditions of maximum permeability increase with the increase in the value of the ratio Cr_{eq}/Ni_{eq} whilst at condition H1150 (620°C) the values are equal.

(e) The lower the magnetic permeability , the higher the coercive force.

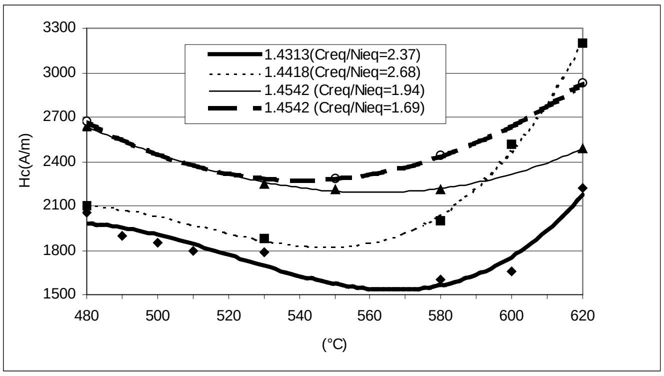


Fig.9: Coercive Force Variation at different tempering/ageing temperatures.

W 1.4418 : RESULTS OF TESTS

The use of the ratio Cr_{eq}/Ni_{eq} and the information that can be obtained from the values it supplies can be extended, within certain limits, to this type of steel also. It is clear that the ratios are higher in absolute value and, as a consequence, they cannot be compared with those of AISI 630 (W 1.4542). Hence, a value of the ratio Cr_{eq}/Ni_{eq}=2,30 for W 1.4418 provides a behaviour, in terms of magnetic permeability and impact strength, similar to that for a ratio of Cr_{eq}/Ni_{eq}=1,60 for AISI 630 (W 1.4542) but very far from a ratio of Cr_{eq}/Ni_{eq}=1,95 even if closer in numerical terms. Similarly, a value of ratio Cr_{eq}/Ni_{eq}=2,30 for W 1.4313 is not comparable with a value of Cr_{eq}/Ni_{eq}=2,30 of the W 1.4418, but with a value of Cr_{eq}/Ni_{eq}=1,80 of AISI 630 (W 1.4542). Therefore, the ratio Cr_{eq}/Ni_{eq} must not be considered separately in isolation but must be integrated by a careful evaluation of the content of all the elements and, in particular, Carbon and Nickel. In other words, if between Cr_{eq}/Ni_{eq}=2,60÷2,80 the values of Magnetic Permeability, mechanical properties and $Rp_{0.2}$/Rm are practically equal and very high for the same temperature of heat treatment, in certain particular conditions of the chemical balance this steel demonstrates a behaviour such that important changes in the parameters for the heat treatment are required in order to obtain specified mechanical properties. In fig. 10 -11, it can be noted how, with Cr_{eq}/Ni_{eq}=2,30, there is a drastic drop of $Rp_{0.2}$ even at low tempering temperatures even if the values of Rm are maintained constant and high, with a consequent detrimental effect on the $Rp_{0.2}$/Rm ratio associated with low values of magnetic permeability.

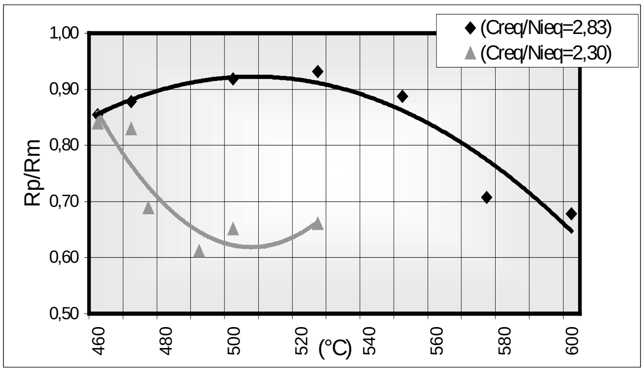


Fig.10: W1.4418_ Tempering Curves of two Heat with different Cr_{eq}/Ni_{eq} values.

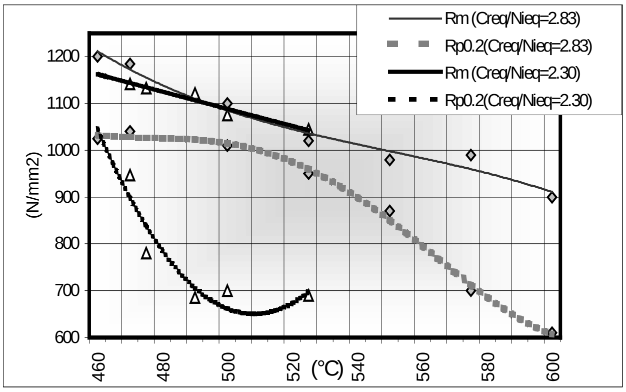


Fig.11: W1.4418_ Rp/Rm tempering curve variation on two Heat with different Cr_{eq}/Ni_{eq} values.

An evaluation of the results of tests of mechanical properties on 215 heats shows that, for the same values of Cr(%) and of a total of the percentages of the elements Ni, C, and N that lies between 5,10 and 5,20, good values of KV are obtained and high values of Rm and $Rp_{0.2}$ .On the other hand, a total between 5,80 and 5,90 causes a drastic reduction of the yield point. The magnetic permeability of W 1.4418 steel is 15 to 20 % higher than that of AISI 630 (W 1.4542) at the tempering/ageing temperature at which $Rp_{0.2}$/Rm and KV are the same for both.

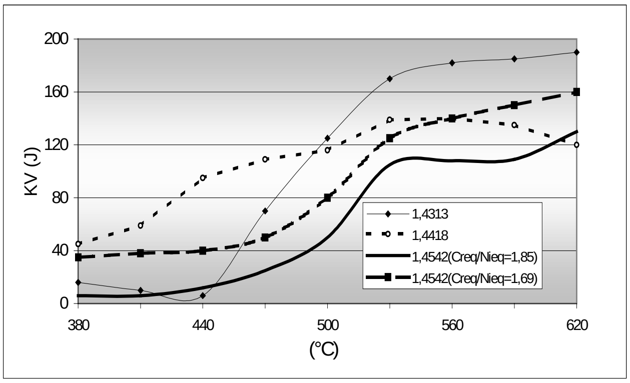


Fig.12: Impact Strength (KV) variation at different ageing/tempering temperatures

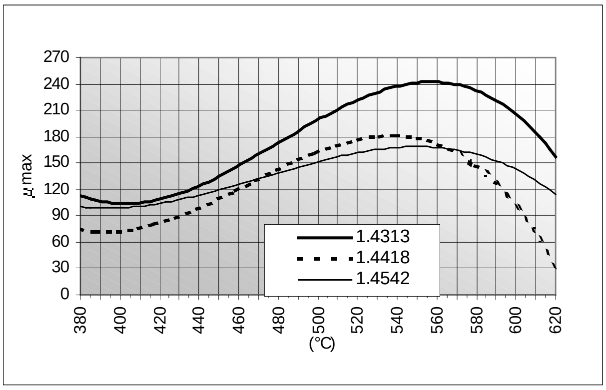


Fig.13: Maximum Permeability variation at different tempering/ageing temperatures.

It should be noted that the element "*Iron*" in W 1.4418 is a couple of points higher than in AISI 630 and this difference makes itself felt for the same interstitial elements like carbon and nitrogen. This is confirmed by the better magnetic properties of W. 1413 which is much less alloyed. In fact, the values of J_{sat} for this type are higher because of the low amount of stable austenite present at 550°C.

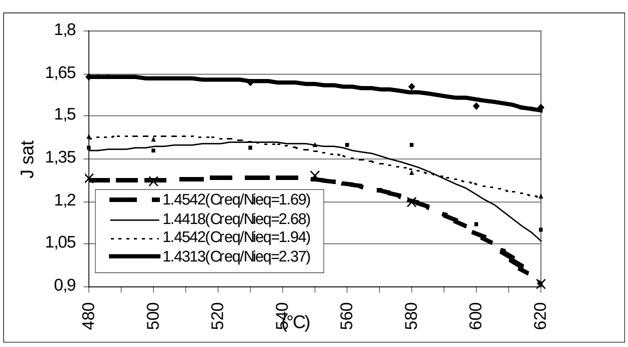


Fig.14: Intrinsic Induction variation at different tempering/ageing temperatures

The permeability of AISI 630 (W1.4542) becomes equal to that of W1.4418 only in the presence of higher values of Cr_{eq}/Ni_{eq}, partially sacrificing its impact strength, even if it maintains values that are still satisfactory. Moreover, it is opportune to recall that for both types, high values of this ratio favour or facilitate the formation of bands of delta-ferrite that penalise the values of KV.

CONCLUSIONS

A) Both the two steels have very close magnetic properties that are affected by their chemical balance and heat treatment.
B) The ratio Cr_{eq}/Ni_{eq} permits the behaviour of the steel to be foreseen in terms of both mechanical and magnetic properties.
C) In evaluating the influence of the ratio Cr_{eq}/Ni_{eq}, the effect of interstitial elements like carbon and nitrogen must be taken into account, and in particular the nickel content.
D) The choice between AISI 630 (W1.4542) and W1.4418 from the economical point of view must take into consideration the continual changes in alloying elements like Mo and Cu, seeing that Cr and Ni are practically equal. AISI 630(W1.4542) steel, that is produced by a longer and more complex process compared with W1.4418, enables higher hardness values to be obtained with a consequent increase in resistance to wear.

References

[1] C.Leymonie, M.C. Lecocq,M.C.Ottoman, *Relations entre la structure et les propriètès mecanique de deux aciers à 16 Cr –4% Ni , Traitment Termique* (165-82)
[2] H.J Niderau, *State of development of soft martensitic stainless Cr-Ni steels* . Edited by K.H. Miska, Climax Mo.Co. (1977)
[3] T.Ceccon, G.Melotti, L.Pazienza, *Influenza della composizione chimica e del trattamento termico sull'indice di qualità dell'acciaio 1.4542*, Congresso AIM , Modena (Novembre, 2002)
[4] Laboratorio Elettrofisico, *Introduzione al magnetismo e Permeametro* (1992)
[5] T.Ceccon, *Magival, Soft Magnetic Steels,* Shanghay (Novembre 2000)
[6] N.Suutala, T.Moisio, *The use of Cr_{eq}. And Ni_{eq} in solidification phenomena in austenitic stainless steels* . The Metal Society (1980)
[7] T.Ceccon, *Aisi 630: un acciaio inossidabile PH martensitico multiruolo*. Convegno AIM-AIPI , Milano (Dicembre 2003)