

# Heat Treatment Methods Applied To AISI 431 Martensitic Stainless Steels

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**Abstract:** Martensitic stainless steels are widely used in industrial applications due to their ability to be heat treated to different strength levels, coupled with good corrosion and oxidation resistance. AISI 431 is one of the most potentially attractive steels in this class used extensively for parts requiring a combination of high tensile strength, good toughness and corrosion resistance. However, high alloy content of these steels causes the transformation to be so sluggish, and the hardenability to be so high, that maximum hardness is produced by air cooling. By applying suitable heat treatment procedures, the properties of martensitic stainless steels are greatly modified. This paper reviews the various heat treatment methods applied to AISI 431 martensitic stainless steels and their influence on the microstructure and mechanical properties.

**Keywords:** Martensitic stainless steel, heat treatment, austenitizing, tempering.

## 1.0 INTRODUCTION

Martensitic stainless steels occupy a unique status as engineering materials by virtue of their excellent combination of properties such as high strength, adequate ductility, toughness and good corrosion resistance. These steels find extensive application in chemical plants, power generation equipments, in gas turbines as turbine and compressor blades and discs, aircraft engine components and fittings and in marine components [1]. These steels can be heat treated to obtain a wide range of mechanical properties to meet the requirements of specific application [1, 2].

AISI 431 is one of the most potentially attractive steels in this class used extensively for parts requiring a combination of high tensile strength, good toughness and corrosion resistance [3].

Unlike other types of stainless steels, the properties of martensitic stainless steels are greatly modified by normal heat treatment procedures. The heat treating of martensitic stainless steel is essentially the same as for plain-carbon or low-alloy steels, in that maximum strength and hardness depend chiefly on carbon content. However, high alloy content of these steels causes the transformation to be so sluggish, and the hardenability to be so high, that maximum hardness is produced by air cooling.

The various heat treatment methods applied to martensitic stainless steels, in particular to the AISI 431 type steel and their influence on microstructure and mechanical properties, are reviewed in this paper.

## 2.0 AUSTENITIZING

Martensitic stainless steels are normally hardened by heating in the austenitizing range of 925 to 1065°C and then cooled in air or oil. When maximum corrosion resistance and strength are desired, the steel should be austenitized at the high end of the temperature range. For alloys that are to be tempered above 565°C, the low side of the austenitizing range is recommended because it enhances ductility and impact properties.

In structural steels it is observed that higher austenitizing temperatures greater than 900°C can be beneficial to the mechanical properties [4-6]. By high temperature (>1100°C) treatment, coarse alloy carbides can be dissolved completely, and a compositionally homogeneous structure can be achieved [5-6]. However, a very high austenitizing temperature leads to an increase in grain size. Yield strength and fracture toughness (CVN) values increase and DBTT decreases with a decrease in prior austenite grain size [7]. Once a compositionally homogeneous structure is achieved by heat treatments, grain refinement increases the amount of retained austenite. [5] Therefore, double austenitizing, i. e., high temperature austenitizing and quenching followed by low temperature austenitizing, can be applied to obtain the benefits of both treatments. [8]

### 2.1 Soaking times:

Soaking times employed in the hardening of martensitic stainless steels represent a compromise between achieving maximum solution of chromium-iron carbides for maximum strength and corrosion resistance, and avoiding decarburization, excessive grain growth, retained austenite, brittleness, and quench cracking. For sections of 13 mm thick and under, a soaking time of 30 to 60 min is

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sometimes recommended. For most parts, adding 30 min for each additional inch of thickness or fraction thereof has proved adequate. However, soaking times should be doubled if parts to be hardened have been fully annealed or isothermally annealed.

## 2.2 Quenching.

Because of their high hardenability, martensitic stainless steels can be quenched in either oil or air. These steels may precipitate carbides at grain-boundary areas if heavy sections are cooled slowly through the temperature range of about 870°C to 540°C. Although oil quenching is preferred, air cooling may be required for large or complex sections to prevent distortion or quench cracking.

## 3. TEMPERING

In the hardened condition, the strength and hardness of martensitic stainless steels are high but the ductility and toughness are low. In order to obtain useful engineering properties, these steels are normally tempered. The tempering temperature range for martensitic stainless steels is normally from 480-750°C. [9] With in this range, the hardness of the martensite decreases as a function of time, with more rapid tempering occurring at higher temperatures. Care must be taken not to temper higher-Cr alloys for excessive times since sigma phase precipitation in the ferrite is possible. This will result in embrittlement of the structure. [9]

## 4. PROBLEMS IN AISI 431 (16CR-2NI) STEELS

By virtue of its high chromium content, 16Cr-2Ni steel would invariably contain considerable amount of  $\delta$ -ferrite when cooled to room temperature from liquid metal during solidification or while processing at high temperature [10].  $\delta$ -ferrite is known to reduce the transverse ductility [11] and the attainable strength of the steel [12-13]. Angstadt [10] summarized that lower strength is due to interfaces of  $\delta$  - ferrite with martensitic matrix providing weak paths for crack propagation.

Due to high alloy contents and a significant amount of carbon the 16Cr-2Ni steel requires a high austenitizing temperature to allow carbides to go into solution. This would result in lower Ms and Mf temperatures resulting in retention of high levels of austenite on quenching [12]. It is reported that the steel could retain as high as 20% austenite when quenched from 1060°C [14] which is known to decrease the yield strength [15].

Due to the presence of nickel, the Ac<sub>1</sub> temperature of the steel is low (about 600°C) [16, 14]. Lower Ac<sub>1</sub> imposes a restriction on tempering temperatures since high temperatures could result in re-austenitization [16, 9]. The austenite formed during tempering can transform to martensite on cooling thereby reducing the ductility of the steel. Thus the two problems posed by 16Cr-2Ni steel are

(a) formation of  $\delta$ -ferrite and (b) retention of austenite. Compositional balance and optimum processing parameters are essential requisites to achieve the desired properties.

Table 1 Chemical composition (Wt %) [Brownrigg, 1976]

Heat No.	C	Si	Mn	P	S	Ni	Cr	N
N9657	0.14	0.35	0.80	0.030	0.024	2.6	16.2	0.032
N9765	0.15	0.41	0.79	0.023	0.026	2.6	15.4	0.035
N9927	0.14	0.27	0.77	0.030	0.029	2.6	15.8	0.032

## STEELS

### 5.1 Hardening:

Brownrigg [14] and Liu Ning et al. [17] have studied on the heat treatment methods applied to these steels. The composition of the steels chosen for study by Brownrigg and Liu Ning et al are given in Table 1 and 2 respectively.

Table 2 Chemical composition (Wt %) [Liu Ning et al., 1991]

C	Si	Mn	P	S	Cr	Ni
0.16	0.37	0.45	0.025	0.010	16.52	2.25

The austenitization temperature of 16Cr-2Ni steel has been

reported typically as 1050°C [Brownrigg, 1976]. Despite the fact that the Ac<sub>1</sub> and Ac<sub>3</sub> temperatures in Brownrigg's study were 607°C and 835°C, the selection of a much higher austenitizing temperature was to allow dissolution of all the carbides in the solid solution. The variation in hardness with increasing austenitizing temperature is shown in Fig. 1. There is a pronounced hardness peak found between 1000°C-1100°C for all the three steels. The increased hardness in this temperature range is explained to be due to carbon enrichment of the austenite resulting in a harder martensite. The lower hardness below 1000°C is due to undissolved carbides resulting in softer martensite. The decrease in hardness above 1100°C was attributed to increased amount of  $\delta$ -ferrite and / or retained austenite formation.

In the studies carried out by Brownrigg [1976] Heat nos. N 9657 and N 9927 contained varying amounts of  $\delta$ -ferrite at different austenitization temperatures (Fig.2), which can be attributed to variation in their Cr concentration.  $\delta$ -ferrite content was found to increase in the steel with increase in austenitizing temperature.

Retained austenite content of only one composition N 9765 (Table 1) has been reported which was less than 2.0% after austenitizing at 1050°C and quenching. Ms temperature reported for the steels N 9765 and N 9657 were 188°C and 162°C respectively.

The volume fraction of all the major phases, as function of austenitization temperature is shown in Fig. 3. [Liu Ning et al., 1991]. The volume fraction of  $\delta$ -ferrite was not found to change when the austenitizing temperature was less than 1100°C, thereafter it increased with austenitizing temperature. The volume fraction of retained austenite increased with austenitizing temperature between 950°C and 1200°C, while the martensite content decreased.

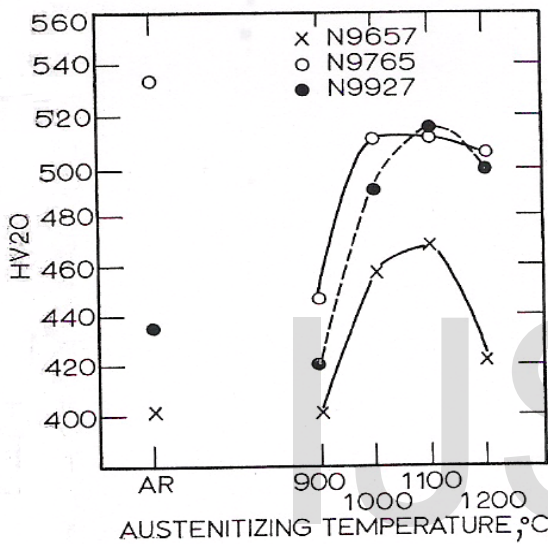


Fig. 1. Variation in hardness as a function of austenitization temperature in as-quenched 16Cr-2Ni steel [Brownrigg, 1976]

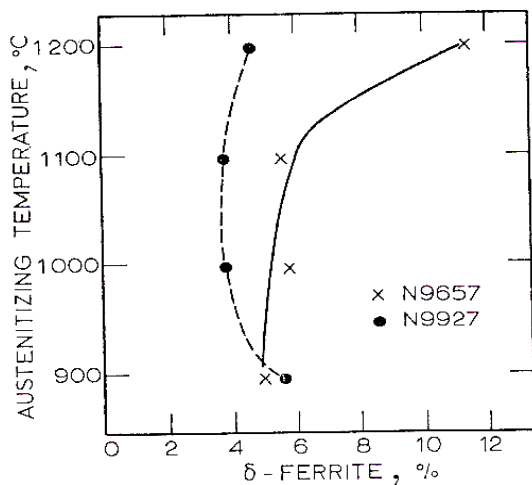


Fig. 2. Volume fraction of major phases as a function of austenitization temperature in 16 Cr-2 Ni steel [Brownrigg, 1976]

Comparing Brownrigg's data [1976] with Liu Ning et al.'s data [1991] it is seen that for a given austenitizing temperature of 1050°C, the  $\delta$ -ferrite content in Liu Ning et al.'s steel was about 15% whereas it was only 4.7% in Brownrigg's steel.

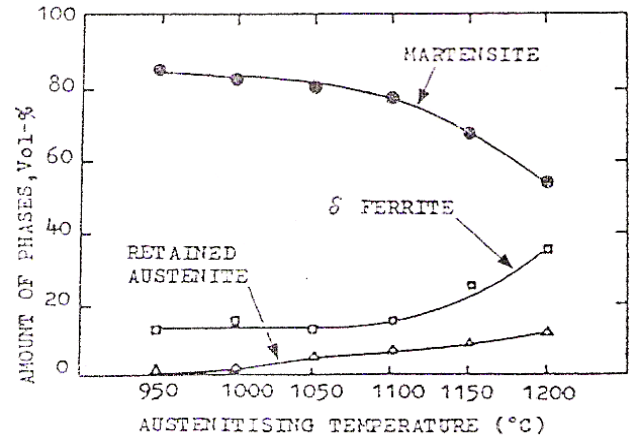


Fig.3 Variation in  $\delta$ -ferrite content with austenitization temperature for 16Cr-2Ni steel [Liu Ning et al., 1991]

The significant difference could only be attributed to chemical composition of the steels [Table 1 and 2]. In the case of Liu Ning et al., [1991], the steel had about 16.52% Cr whereas the Cr content was only 15.4 to 16% in the steels studied by Brownrigg [1976]. This indicates that increase in chromium content has a marked effect on increase in  $\delta$ -ferrite content in these steels.

The retained austenite content of Brownrigg's steel N 9765 is relatively less (2%) compared to 7% reported by Liu Ning et al., [1991]. It is also observed from Liu Ning et al.'s [1991] data that retained austenite content increases with increase in austenitizing temperature. At constant austenitizing temperature of 1050°C, the only variable affecting retained austenite content is the composition of the steel. Alloying additions constituted about 19.5% in Brownrigg's steel compared to 19.75% in Liu Ning et al.'s steel. In addition, the individual content of major alloying elements viz., C, Cr and Ni being at similar levels, their individual effects on Ms temperature in case of the steels studied by them is expected to remain the same. Ms temperature reported by Brownrigg is 188°C while Liu Ning et al., have reported it to be 355°C. Thus, there is contradiction on the effect of alloying elements on the Ms temperature, and calls for critical reassessment.

Liu Ning et al. [1991] have reported increase in strength of the steel with increase in austenitizing temperature reaching a peak value at 1100°C; thereafter the strength is found to be decreasing with further increase in austenitizing temperature. The hardness is reported to be 510 HV when austenitized at 1050°C for steel N 9765

[Brownrigg, 1976]. The hardness obtained for the same austenitizing temperature is reported to be about 425 HV (converted from tensile strength value) by Liu Ning et al. [1991]. The difference in hardness reported by the two authors could be attributed to the difference, again, in chemical composition of the steels.

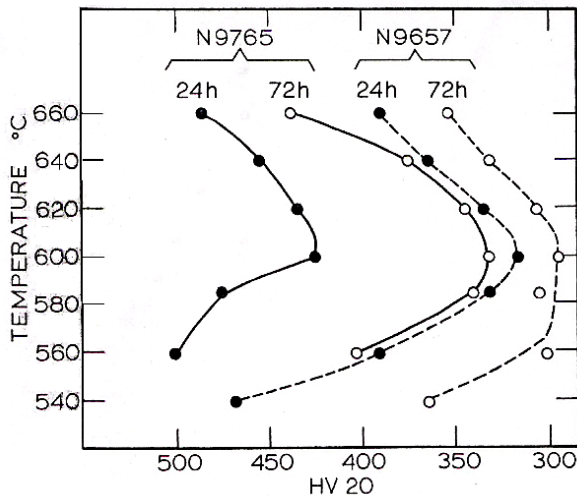


Fig. 4 Kinetics of isothermal softening in 16 Cr- 2Ni steel austenitized at 1050°C for 30 minutes [Brownrigg, 1976]

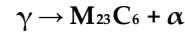
Brownrigg's steel contained lower chromium and higher nickel content resulting in lower  $\delta$ -ferrite content in the microstructure. Liu Ning et al.'s steel contained higher chromium and lower nickel content resulting in about 15%  $\delta$ -ferrite in the steel. The decrease in hardness could be attributed to lower dissolution of carbides during austenitization coupled with higher amount of  $\delta$ -ferrite content in Liu Ning et al.'s steel. Whereas higher amount of carbides in solution coupled with negligible amount of  $\delta$ -ferrite resulted in higher hardness of Brownrigg's steel.

Thus, it can be seen from the studies of Brownrigg [1976] and Liu Ning et al., [1991] that chemical composition plays a major role on the microstructure of 16Cr-2Ni steel for a given heat treatment which influences the mechanical properties. Therefore, a critical control over the chemical composition remains a prime criteria in the alloy design of 16Cr-2Ni steels.

## 5.2 Isothermal transformation behavior

Isothermal transformation experiments were carried out by Brownrigg [1976] by dilatometry, metallography and hardness measurements. 4 mm disc specimens were austenitized at 1050°C for 30 minutes and then immediately transferred to lead bath in the temperature range of 540°C-660°C. Specimens were removed at different intervals and then characterized.

The experiments showed that there was no  $\gamma \rightarrow \alpha$  isothermal transformation and the bulk of the austenite transformed to martensite on cooling to room temperature. The transformation on long holding periods caused carbon depletion of austenite by the reaction-



This caused rise in the  $M_s$  temperature allowing transformation of  $\gamma$  to martensite. The precipitation showed C-curve kinetics (Fig. 4), with a maximum rate at 600°C. It was also observed that the alloy which contained some amount of  $\delta$ -ferrite along with austenite softened more rapidly on isothermal holding compared to the one having only austenite in its microstructure. This was probably due to larger nucleation site available at  $\delta$ -ferrite/austenite boundaries apart from the prior austenite grain boundaries. Moreover, the  $\delta$ -ferrite containing steels showed finer prior austenite grain boundaries thereby providing greater nucleation area for the precipitates.

Isothermal transformation of 16% Cr steels has been studied by Castro and Tricot [1974][18] in detail and a comprehensive report has been published which is summarized below.

### 5.2.1 Decomposition between 950-800°C:

During isothermal holding of the steel at any temperature between the ranges of 950-800°C, a fine intergranular precipitation occurs very rapidly at the  $\gamma \rightarrow \delta$  and  $\delta \rightarrow \delta$  interfaces due to the transformation of  $\delta$ -ferrite which follows the reaction-



(the notation ' is used here only to differentiate this transformation product from the initial austenite). The product  $M_{23}C_6$  carbides +  $\gamma'$  austenite is lamellar and has been called as delta eutectoid or generally as D-aggregate.

Simultaneously outside these areas the regression of the austenite to  $\delta$ -ferrite takes place by the reaction  $\gamma$ -austenite  $\rightarrow \delta$ -ferrite.

The identification of lamellar carbides has shown that these are  $(Cr, Fe)_{23}C_6$  with a Cr: Fe ratio of about 2.3. The inter lamellar spacing of the carbides decreases with the isothermal holding temperature. The D-aggregate nucleus forms at grain and phase boundaries and the number of nuclei increases with decreasing temperature. This results in more numerous and finer precipitation of D-aggregate.

### 5.2.2 Decomposition between 700-550°C

During short holding periods (1-3 minutes) a very fine and granular precipitation takes place on the boundaries of austenitic areas and edges of  $\gamma$ - $\delta$  boundaries which is termed as the G-aggregate

$\gamma \rightarrow$  fine carbides  $M_{23}C_6 + \alpha$

The carbides are of the type  $(Cr, Fe)_{23}C_6$  with a Cr: Fe ratio of about 1.6 at 650°C. The morphology and position of the G-aggregate indicate the limited diffusion rate of carbon at these temperatures. The growth of this aggregate, of limited extent, ceases after about 10 minutes. The remaining austenite transforms either to ferrite by regression, or an aggregate of a pearlitic nature consisting of  $Cr_2N$  and ferrite, which is also called as the nitrogen-pearlite.

$\gamma \rightarrow \alpha$ -ferrite and  $\gamma \rightarrow Cr_2N +$  ferrite

The pearlitic transformation exhibits all the characteristics of reaction by nucleation and growth.

**5.2.3 Decomposition below 550°C**

Below 550°C, decomposition is very slow. At 550°C, 24 hours holding produced a fringe of G-aggregate and incipient regression.

**5.3 Tempering behavior**

The reported data on the variation of mechanical properties with tempering temperature [19-20] are shown in Fig. 5.

The results reported [Harvey, 1982][19] show that there is a drop in tensile strength and hardness up to 300°C tempering beyond which a secondary hardening peak is attained at 450-500°C tempering (Fig.5.a). Whereas, the yield strength more or less remains constant up to 400°C, tempering beyond which causes the yield strength to follow a similar trend as those of hardness and tensile strength. In all the three properties viz., hardness, yield strength and tensile strength, there is a steep fall beyond 500°C and up to 600°C tempering. Between 600-700°C tempering, the properties stabilize. Percentage elongation (%El) shows gradual increase with increasing tempering temperature, while the percentage reduction area (%RA) gradually increases up to 400°C tempering.

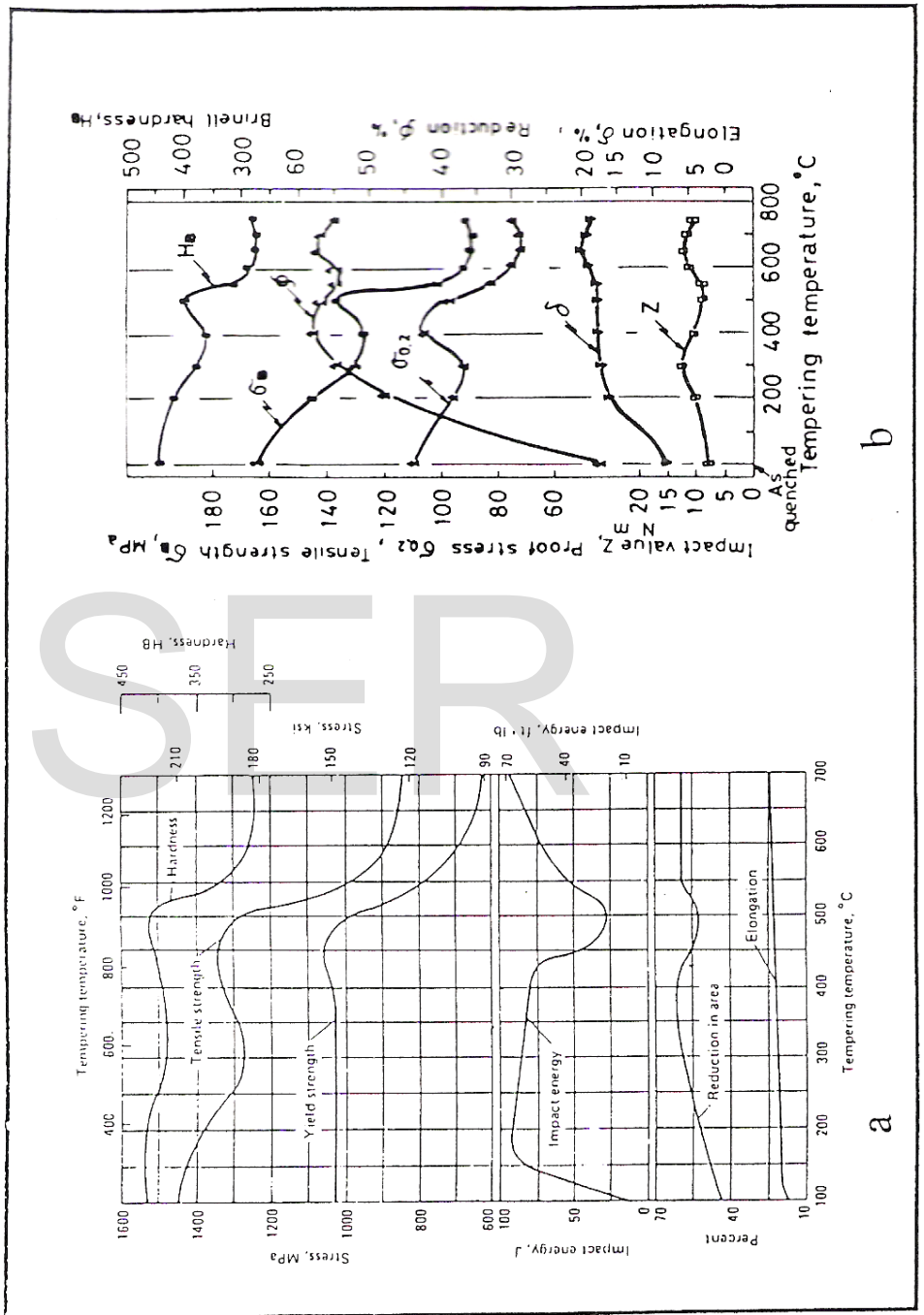


Fig. 5. Effect of tempering temperature on the mechanical properties of 16Cr – 2Ni steel. (a) Harvey[1982], (b) Ogino et al.[1987]

The results of Ogino et al. [1987][20] show that hardness, tensile strength and yield strength initially decrease on tempering at all temperatures up to 300°C, after which they increase. The strength parameters reach a peak between 400-500°C. On tempering beyond 500°C, there is a steep fall in strength and hardness up to 600°C tempered

Tempering between 400 to 550°C causes a slight decrease in %RA, beyond which the ductility is restored and remains unchanged when tempered up to 700°C.

condition. The values more or less stabilize between 600-700°C tempering.

With increase in tempering temperature, %EI shows a progressive increase. %RA increases steeply up to tempering temperature 400°C. Tempering between 400 and 600°C causes a dip in %RA, beyond which the ductility gets restored condition. The values more or less stabilize between 600-700°C tempering. With increase in tempering temperature,.

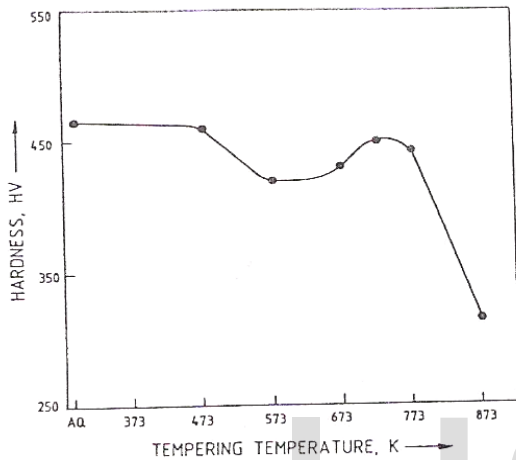


Fig. 6. Variation in hardness with increasing tempering temperature.

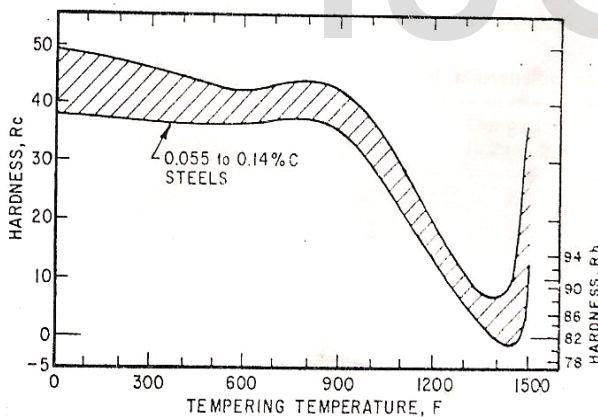


Fig. 7. Effect of tempering temperature (2-hour temper) on the hardness of 12 % Cr steels [Rickett, et. al., 1952]

It is understood from these plots that it is difficult to control the strength between 500-600°C during tempering. Since it is a critical range, tempering within this temperature interval is not practiced [BS 5 S 80, 1976].

The plots in Fig. 5.(a and b) show that the impact energy progressively decreases between 300-500°C temper conditions reaching a minimum at 500°C, beyond which the

energy increases. The steel shows poor notch toughness at room temperature when tempered between 300-500°C.

The variation of hardness with increasing tempering temperature for 16%Cr – 2%Ni martensitic stainless steels is shown in Fig. 6 [21]. The graph suggests that as quenched hardness dropped on tempering at 573 K (300°C), secondary hardening occurs when tempered between 673 K-773 K (400 - 500°C) and finally, the hardness decreases sharply on tempering above 773 K (500°C). Similar trends are observed on tempering 12% Cr steels as shown in Fig. 7 [22]. Tempering below 600°C is essentially ineffective in reducing the hardness.

The tempering temperature also has a large influence on the retained austenite content. The variation of retained austenite content with tempering temperature for 16%Cr – 2%Ni martensitic stainless steels is shown in Fig. 8 [21]. The retained austenite content decreases on tempering at 573 K, increases dramatically on tempering between 673-773 K and finally decreases to below 2% on tempering at 873 K.

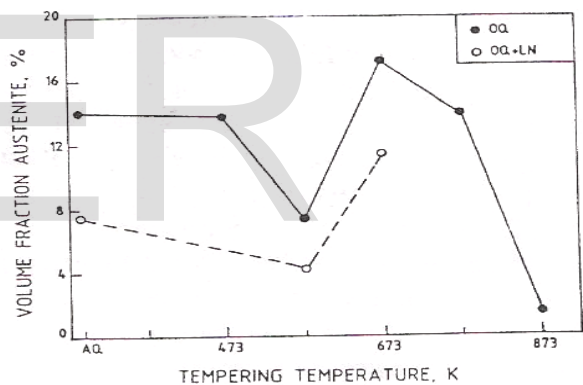


Fig. 8. Variation in austenite content with increasing tempering temperature. [Balan, 1998]

#### 5.4 Temper embrittlement

16Cr-2Ni steel is stated to be susceptible to temper embrittlement between 370-595°C [23]. Although the

specification BS 6S80 [1990] has indicated the susceptibility of the steel to temper embrittlement above 350°C, the exact temperature range has not been indicated. In the study carried out by Liu Ning et al. [1991], the author has reported temper embrittlement of the steel on tempering at 550°C. The embrittlement has been manifested in the steel by a minimum in room temperature charpy impact energy and fracture toughness when tempered at 550°C. Typical intergranular fracture of the CVN impact specimen and Auger spectroscopy confirmed the temper embrittlement of the steel following tempering at 550°C. The temper embrittlement was not attributed by the author to either precipitation of fine carbides ( $M_{23}C_6$  or  $M_7C_3$ ) in the

microstructure or to the transformation of retained austenite (as retained austenite transformation was complete on tempering at 500°C).

The embrittlement is believed to be caused by segregation of phosphorus to prior austenite grain boundaries during austenitizing of the steel. The susceptibility of the steel to temper embrittlement is also enhanced by segregation of alloying elements, particularly manganese and chromium, to prior austenite grain boundaries. Apparently the embrittling elements are arranged near the grain boundaries and move to the embrittling configuration only in the temperature range 370°C-565°C. Below about 370°C the mobility of the embrittling elements is restricted and above about 565°C they return to the un-embrittling configuration [24]. Auger spectroscopy confirmed the segregation of Cr, Ni and P on prior austenite grain boundaries during 550°C tempering, which is therefore concluded to be the cause of temper embrittlement of the steel.

## 6.0 CONCLUSIONS

A comprehensive review of present published information on heat treatment of AISI 431 martensitic stainless steels indicates that the mechanical properties of this material can be greatly modified by careful control of heat treatment methods. The major factors which influence the mechanical properties are formation of delta ferrite and retention of austenite. They can be well addressed by careful selection of austenitising temperatures and tempering temperatures. Further it is noted that the chemical composition has a vital influence on the volume fraction of the phases existing and hence a critical control over the chemical composition remains a prime criteria in the alloy design of 16 Cr-2Ni steels.

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