THERMO - MECHANICAL TREATMENT OF MARAGING STEELS

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[PHYSICAL METALLURGY]

By

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CERTIFICATE

Certified that the dissertation entitled "THERMO-MECHANICAL TREATMENT OF MARAGING STEELS", which is being submitted by Sri MADAN LAL in partial fulfilment for the award of the degree of Master of Engineering in Metallurgical Engineering (Physical Metallurgy) of the University of Roorkee, Roorkee, is a record of his own work carried out by him under my supervision and guidance from 2nd January, 1971 to October 4, 1971.

The matter embodied in this dissertation has not been submitted for the award of any other degree.

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ABSTRACT

In the present investigation thermomechanical treatment comprised of marforming i.e., cold working in the martensitic condition followed by maraging at 450 and 520°C respectively. It was observed that with increase of prior deformation i.e., upto 47 per cent reduction the hardness peak shifts towards lesser aging period. The variation of hardness with aging time for any fixed aging temperature shows a maxima, which shifts towards lesser aging period, when temperature is increased. For any constant aging period the hardness of Fe-18Ni and Fe-19Ni maraging steels increases linearly with increase of prior cold deformation. However, for Fe-25Ni steel there is discontinuity in this linearity at about 8 per cent deformation. This is related to the different degree of work hardening of the martensite and the retained austenite in conjunction with the precipitation. It is striking to note that the absence of maraging does not reveal this subtle hardening difference.

ACKNOWLEDGEMENTS

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CHAPTER - I

INTRODUCTION

The necessity of developing high strength on simple heat-treatment coupled with good ductility, low notch and crack growth sensitivity, etc., led to the development of Fe-Ni maraging steels containing 18-28 per cent nickel. These steels have been developed largely to meet the demands for high speed aircraft and missiles. The maraging steels produce a martensitic matrix on cooling from austenitizing temperature and possess high strength and ductility by combining a martensitic type of hardening of the iron-nickel alloy coupled with age-hardening.

Carbon content of the maraging steels is kept very low to avoid the embrittling Fe_3C phase, and to minimize the acicular, or twinned martensite common to high carbon steels. Since the usual tempering reactions involving the formation of carbides can not occur in carbon-free maraging steels, their strength can be retained upto higher temperatures. Small additions of titanium, molybdenum, cobalt, aluminium, etc., are usually made to introduce strengthening on aging in the temperature range of 400 - 500°C. The strengthening mechanism is believed to be either due to precipitation hardening, in the form of intermetallic precipitates in the martensitic matrix or to short range order. The precipitates are of the type Ni_3Ti or Ni_3Mo.

The yield/ultimate strength ratio of these maraging steels is very high but they have good ductility with reduction in area around 60 per cent and elongations in the region of 10 per cent. The maraging steels are easier to fabricate, resistant to stress corrosion and shows better dimensional stability during maraging.

Aim and Scope:

The primary purpose of the present work was to evaluate the effects of thermo-mechanical treatments - prior cold deformation (i.e., marforming) on hardness of the Fe-18Ni, Fe-19Ni and Fe-25Ni grades of maraging steels. The effect of temperature on the hardness behaviour of these steels was also studied. In addition, photomicrographic studies were made for the hardening mechanism responsible for the high strength.

Although as evidenced in the reviewed chapter sufficient amount of work has been done on Fe-18Ni maraging steel but little or practically no information is available in case of Fe-19Ni and Fe-25Ni maraging steels. The thermo-mechanical treatment of Fe-19Ni and Fe-25Ni maraging steel is also important, since it further improves the mechanical properties. This is why the effect of thermo-mechanical treatment on hardness of Fe-19Ni and Fe-25Ni maraging steels was also carried out in addition to Fe-18Ni maraging steel. Thermo-mechanical treatment of maraging steels improves the hardness by subsequent aging. A careful selected heat-treatment combined by suitable marforming may improve strength and ductility.

Although these maraging steels because of having high content of nickel are not economical from the Indian point of view, for critical applications such as pressure vessels, air-craft industries etc., the case of thermo-mechanically treated steels is very sound. This is of still greater interest, when we notice attractive properties of such steels like good machinability and workability, absence of volume change during hardening, resistance to stress corrosion cracking and good weldability even in the fully hardened condition.

CHAPTER - II

LITERATURE SURVEY

2.1 Introduction:

The realization of a need for new ultra-high strength steels with high ductility and toughness, which would be easier to fabricate and heat-treat as required for air-craft and missile construction prompted the development of Fe-Ni "Maraging Steels". Maraging steels are new types of precipitation-hardened high alloy steels developed in recent years. These steels exhibit strength and toughness and other desirable characteristics which are un-obtainable from conventional,medium-carbon, low alloy steels.

Maraging steels are the first attempt at replacing carbon steels by practically non-carbon iron alloys (containing not more than 0.03 per cent carbon) which have high strength and good ductility. Age hardening of the ductile martensites of 18, 20 and 25 per cent

Nickel-Iron alloys form the basis of these outstanding properties.

The steels are termed maraging steels because the precipitation reaction which accounts for their ultra-high strength occurs on aging when they are in martensitic condition. Strengths in excess of 250,000 p.s.i. can be achieved[1] in the Fe-18Ni maraging steels when transformed to martensite and aged for 3 hours at 480°C. A typical composition for these steels is 18Ni, 7Co, 5Mo, 0.3Ti, 0.1Al, less than 0.03C, balance Fe. Work by Decker, Eash and Goldman[2] showed that 18/8/5 Ni/Co/Mo steels with smaller additions of titanium offer better ductility and greater resistance to fracture in the presence of sharp cracks, defects and notches. The basic strengthening is due to presence of molybdenum, titanium, and aluminium. Cobalt in the presence of these elements provides a faster hardening response but in itself does not produce appreciable hardening. The carbon is kept to a low level to increase the ductility of the martensite.

Of the four major requirements[3] for the "Perfect alloy" - strength, ductility, fabricability, and corrosion resistance - the maraging steels seem to possess at least the first three to a remarkable degree. Their ductility, in terms of notch sensitivity, is in excess of unity; a low degree of work-hardenability makes them easy to machine and form; their heat-treatment is simple, and they can be welded without preheat in both the annealed and fully heat-treated conditions. These steels show better dimensional stability during maraging.

One of the limitation of their applications to wider fields is probably the high cost of the nickel which is present in these steels in large quantities. The alloying additions made to give age-hardening are also expensive as far as Indian conditions are concerned.

2.2 Structural Aspects of Maraging Steel:

Higher strength levels are normally achieved in conventional low-alloy steels by increasing the carbon content of the martensitic structure and, in some instances, by secondary hardening in which carbides play an important part. Ductility and impact properties can normally be expected to decrease as tensile strength is raised and an increase of the carbon content tends to accentuate this trend. Accordingly, the limit to which this element may be added to obtain higher strength is determined by its adverse effect on ductility and toughness[4]

During the last few years, attempts have been made to obtain a better under-standing of the metallurgy of ultra-high-strength steels with the object of developing more reliable, stronger and tougher steels. These investigations have been prompted mainly by the requirements for aircraft and missile constructions, which demand ductility in addition to high strength to weight ratios.

2.2.1 Difference in nature of Fe-C and Fe-Ni martensites:

Since carbon additions have been shown to promote embrittlement of low and medium-alloy steels, this element was not considered as a source of strengthening[4,5].

Accordingly, instead of the iron-carbon martensite employed in conventional high strength steels, the maraging steels utilize the martensite formed in iron-nickel alloys to harden the matrix.

The martensites formed in iron-nickel alloys containing 18-30 per cent nickel possess the following characteristics[4] in comparison with iron-carbon martensites.

(i) Both are products of a diffusionless shear-transformation of austenite.

(ii) Transformation of iron-nickel alloys can proceed both athermally and isothermally, which must partly account for the variations in M_f temperature.

(iii) No tetragonality has been measured in the body centered structure of the iron-nickel martensite.

(iv) The iron-nickel martensite does not show appreciable hardness variation with nickel content, unlike iron-carbon martensites, which vary markedly with carbon content.

(v) The iron-nickel martensite is only moderately hard and very tough, in contrast with the high hardness and pronounced brittleness of untempered martensite in medium and high-carbon steels.

(vi) Martensite is formed in iron-nickel alloys with this range (18-30 per cent) of nickel contents over a wide range of cooling rates, and thus section-size effects are small. Rapid quenching is not necessary.

(vii) Iron-nickel martensites are only moderately hard, and thus lose little hardness on reheating to moderately elevated temperatures. The 18-25 per cent nickel alloys may be reheated to 450°C or above, before austenite reversion occurs.

(viii) The Iron-nickel martensites are hardened by aging at low temperatures in contrast to Iron-carbon martensites which generally soften on tempering.

2.2.2 Transformation in maraging steels during heating and cooling :

In the iron-nickel phase diagram[6] (Fig.1) the temperatures for the strat (M_s) and finish (M_f) of the transformation of austenite to martensite or ferritic type phases on cooling have been shown. The corresponding temperatures (A_s and A_f) for reversion of these phases back to austenite on heating also appear on Fig.1.

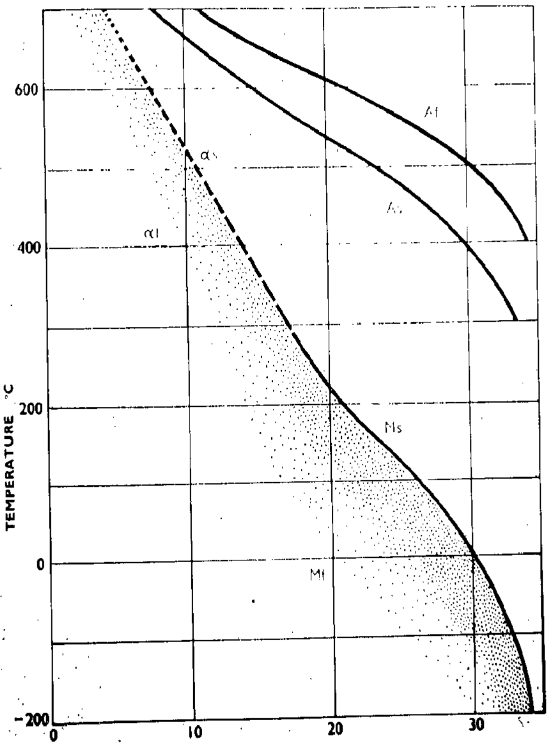


Fig.1. Transformation in Iron-Nickel alloys on heating and cooling[6].

The maraging steels belong to Fe-Ni base type and are austenitic at elevated temperatures. Those steels containing 18-20 per cent nickel transforms completely to martensite on cooling to room temperature from the austenitizing temperature; but those containing 25 per cent are semi-austenitic depending upon the M_s temperature. The amount of nickel in the maraging steel controls the M_s temperature of the alloy[6,7]. Binary iron alloys with 18-20 per cent nickel would possess M_s temperatures in the range 220-250°C. (Fig.1). The hardening additions, Co, Mo, Nb and Ti also affect the M_s temperature and their gross effect lowers[4] the start of transformation to about 130-160°C. Isothermal as well as athermal martensite formation ensure that austenite transformation is completed in the range 50-100°C. The addition of 5 per cent of nickel to the 20 per cent nickel maraging steel ensures that 25 per cent Ni-Ti-Al has an M_s temperature below room temperature and remain austenitic on cooling to room temperature[4,7].

Fe-25Ni maraging steel :

This steel is austenitic after cooling to room temperature from the austenitizing temperature. The transformation to martensite can be achieved by either of the two methods[8] described below :-

Ausaging : Martensite could be formed in the Fe-25Ni alloy by aging the austenite (ausaging) to precipitate alloying elements, particularly Ni, (as finely dispersed Ni_3 Ti phase) from solid solution, thus raising[28] the M_s temperature above room temperature, with the result that transformation-hardening occurs on cooling from the aus-aging temperature.

Cold Work :

Transformation of the austenite in this steel can be affected by cold working the annealed material. This treatment is preferably followed by refrigeration. By comparison with aus-aging, this alternative procedure tends to give, in the fully hardened steel, higher tensile and proof strengths and, within certain limits, improved notched tensile strength. After formation of martensite by either of the above procedure, the steel is hardened by aging for 1-4 hour at 430-480°C.

Fe-20Ni maraging steel :

Lowering the nickel content from 25 per cent to 20 per cent reduces the stability of the austenite formed during the solution annealing treatment and, in consequence, transformation to martensite occurs on cooling to room temperature. The necessity for aus-aging or mechanical working is thus obviated and hardening can be completed by a simple low temperature maraging treatment. Hardening of the 20 per cent nickel steel, as of the 25 per cent nickel type, depends on precipitation of a phase of the $(Fe,Ni)_3$ (Ti.Al) type.

Fe-18Ni maraging steel :

This steel also is martensitic when cooled from the annealing temperature. Hardening can be achieved by simple maraging treatment in the range of 430-480°C.

The structure[9,10] of martensite in the maraging steels resembles that of low carbon martensite and consists of bundles of martensite needles with very high dislocation density within the plates.

Floreen and Decker[11] carried out the experiments on heat-treatment of Fe-18Ni steel and found out that when the steel was annealed at 650°C, the structure contained approximately 50 per cent austenite after cooling to room temperature. This austenite had the fine lamellar appearing structure. Apparently at this annealing temperature the austenite that formed during annealing became partially stabilized and did not retransform to the body-centered-cubic structure on cooling to room temperature. This retained austenite may have been due to the transformation of the metastable body-centered cubic α_2 matrix formed on cooling into the equilibrium α and γ phases. During this transformation there was probably some partitioning of the alloying elements between the α and γ phases so that some of the austenite was enriched and did not transform back to α_2 on cooling to room temperature[12].

It is observed that annealing at a temperature below 760°C results in poor tensile strength due to considerable amount of retained austenite on cooling after annealing. As the annealing temperature was raised, the amount of austenite retained on cooling to room temperature decreased until only the body-centered cubic phase was present. The minimum annealing temperature[11] required to eliminate all of the austenite was approximately 780°C. As shown by the subsequent maraging results, it is essential to eliminate this austenite to achieve satisfactory hardening during maraging.

The micro-structural studies of Fe-18Ni steel was done by Decker, Eash and Goldman[2] after annealing for 1 hour at 820°C. In the annealed condition the alloy had excellent formability, and could be cold worked as much as 98 per cent reduction in area without intermediate annealing. The austenite ASTM grain size was 6 to 8 after annealing at temperatures upto 980°C. Above this temperature grain growth occurred, with ASTM grain size 4 resulting after annealing at 1150°C.

Since the maraging steels are usually in the martensitic condition after annealing, the volume changes associated with martensite formation donot require consideration during hardening. Actual length measurements on the steels before and after hardening, show that the 18 per cent Ni-Co-Mo steel does not alter in dimension, whilst the 20 per cent and 25 per cent Ni-Ti-Al steels actually show a contraction of 0.10-0.12 per cent.

2.2.3 Reverse transformation to austenite :

Most martensitic transformations are capable of undergoing a reverse transformation back to the austenite phase on heating. Decomposition to[5] metastable martensite of maraging steels in to equilibrium ferrite and austenite may occur, during aging fairly rapidly at temperatures above 450°C. The formation of equilibrium austenite and ferrite involves redistribution of alloying elements and occurs through the process of nucleation and growth.

The addition of titanium, aluminium, or molybdenum decreases[13] the rate of formation and the amount of austenite formed. The austenite did not appear in appreciable quantities in the alloys that undergo precipitation hardening until peak hardness is reached. The equilibrium austenite is richer in alloy content. According to Speich[13] the austenite formed on reversion may not transform back to martensite on cooling as its M_s temperature may now be below room temperature as a result of alloy enrichment.

2.2.4 Role of Precipitation in Strengthening :

The Fe-Ni martensite respond to age-hardening if a number of other elements are present. The phases taking part in the precipitation hardening of martensite have not yet been identified with certainty,because of the difficulties involved in analysing very fine particles. Table -I gives a list of precipitating phases. The precipitate particles were invariably found out as (i)very small (0.01 micron in length), (ii) two dimensional platelet or ribbons and (iii) Orthogonally oriented and evenly distributed through the martensite matrix.

It is generally agreed[3] that about one-half of the yield strength of the fully heat-treated Fe-18Ni maraging steels can be ascribed to the strength of the iron-nickel martensite formed upon cooling from the annealing temperature. The large incremental strengthening of the annealed steel that occurs upon aging is believed to be the result of precipitation of intermetallic compounds, Ni_3Mo and Ni_3Ti.

The electron microscopic investigation of Fe-18Ni steel was observed by Reisdorf[9] and it was found out that a high density of fine precipitate was formed upon aging to martensite. It was believed that the bulk of precipitate is Ni_3Mo in the form of ribbons on dislocation lines and at the martensite sub-boundaries, and the remainder as small isolated particles of Ni_3Ti uniformly distributed throughout the matrix[3,9]. Suggestions have also been made that cobalt may decrease the solubility of Ni_3Mo in the iron-nickel martensite,resulting in a more finely dispersed Ni_3Mo precipitate and, hence, greater strengthening.

Table-I

Precipitating Phases in Maraging Steels[27].

System	Precipitating Phase
Fe-20 per cent Ni-Ti	Ni_3Ti (though the stable phase is $[Fe,Ni]_2Ti$ laves phase).
Fe-18 per cent Ni-5 per cent Mo	Ni_3Mo.
Fe-20 per cent Ni-2.5 per cent Al	No precipitate ; hardening may be due to ordering or clustering.
Fe-25 per cent Ni-Al	$(Fe,Ni)_3$ (Ti,Al).
Fe-20 per cent Ni-10 percent Cu	Cu.

Speich[13] while studying the thin section transmission micrographs of aged specimen reported particles of Ni_3Ti to be present in the Fe-20Ni-1Ti martensite after aging at 500°C for 24 hours. The Ni_3Ti appears as needles about 600 A° long and 100 A° in diameter in a very fine dispersion. It is believed that Ni_3Ti particles nucleated on the dislocations are present in the as quenched structure[13]. Electron-probe micro-analysis of the precipitate in the Fe-20Ni-3Ti specimen aged 24 hours at 500°C gave 76 per cent Ni, 21 percent Ti, and 3 per cent Fe confirming the identification of the precipitate as Ni_3Ti. In the above steel hardening of martensite was associated with the formation of a fine dispersion of Ni_3Ti precipitate. The hardening of Fe-20Ni martensite containing 2.5 per cent Al is not accompanied by precipitation. The hardening may be due to ordering or to clustering. In the Fe-20Ni-10Cu alloy, particles of copper are precipitated during aging, but these particles may form after the maximum peak hardness has been reached.

Reisdorf[9], in Fe-25Ni maraging steel in the aged condition found small spherical precipitates, about 100 to 200 A° in diameter, present throughout the matrix. The crystal structure of this precipitate is also f.c.c., with a_0 equal to about 3.58 A°. Hardening in the Fe-25Ni maraging steel is due to precipitation of a phase of the $(Fe,Ni)_3$ (Ti,Al) type[7,9].

2.2.5 Effect of alloying elements :

Several elements have proved successful additions in conferring age-hardening to the iron-nickel base alloys. The basic strengthening is believed to be due to presence of 'hardner-constituent', that is, titanium, molybdenum, cobalt etc.

The addition of cobalt in Fe-18Ni steel produces no perceptible solid solution hardening, but definitely retards the softening[16] upon heating at temperatures upto 425°C. One of the hypothesis to explain the strengthening effect of cobalt is that this addition may provide a more dense and uniform distribution of dislocations in the martensitic matrix of the annealed alloys, thus providing many easy nucleation sites for the more rapid precipitation of finer and more uniformly spaced particles when the material is aged[3].

The addition of molybdenum to the iron-nickel binary alloy introduces increasing solid-solution hardening[16]. With 1 per cent Mo, the solid-solution hardening was retained through out the aging sequence ; but with 4 per cent Mo, the hardness substantially increased through out the aging sequence upto 540°C, and the alloy did not overage at 480°C upto 100 hours of aging. Molybdenum also effectively retards reversion to austenite. Increase of molybdenum content increases the hardness and accelerates the age-hardening reaction. For good toughness, however, it is necessary to limit the molybdenum content to 5.1 per cent maximum. This level of molybdenum has a marked effect in lowering the martensite transformation temperature of these steels. Molybdenum also seems to play a very important role in preserving the high toughness of maraging steels. Improvement of toughness has been ascribed in large part to the effect of molybdenum in reducing intergranular precipitation.

Cobalt and molybdenum, simultaneously added to the Fe-18Ni binary, produce additive hardening effects. Cobalt and molybdenum, together, quite effectively retard reversion, since both cobalt and molybdenum raise the A_s temperature of the Fe-Ni alloys. The effect of cobalt on the strength of the alloy can be explained by the lower solubility of molybdenum in the presence of cobalt, thus giving a larger volume fraction of precipitate[17,18].

The addition of cobalt produces a finer dispersion of precipitates in the molybdenum containing Fe-18Ni alloys, but may not significantly alter the dispersion in other alloys. This effect of cobalt apparently is more pronounced at higher molybdenum contents. The simplest explaination of this effect is that cobalt lowers the solubility of Ni_3Mo in the iron-nickel martensite. This would tend to produce a finer dispersion of Ni_3Mo, and the resultant strength increase could then be due to smaller value of the interparticle spacing, λ, in the Orowan relationship :

$$\sigma = \sigma_0 + \frac{Gb}{\lambda}$$

where σ is the yield strength after aging, σ_0 the yield strength of the precipitate-free matrix, G the shear modulus of the matrix, b the Burgers Vector, and λ the interparticle spacing.

Titanium additions above 0.5 per cent have been reported to reduce toughness, and maximum titanium content for Fe-18Ni maraging steel is restricted to this value[15]. The segregation tendencies of titanium are well known. This characteristic, in addition to the fact that titanium lowers M_s temperature 38°C for every 1 per cent, means that excessive amounts of titanium and/or insufficient homogenization may result in bands of retained austenite. Beside its role as a strengthening agent by forming uniformly dispersed particles of Ni_3Ti in the martensitic matrix, titanium is needed to scavenge the residual carbon in these alloys and so prevent precipitation of M_6C-type carbide, upon cooling from the annealing temperature. This reaction may seriously interfere with the normal, primary age-hardening reaction by effectively reducing the amount of molybdenum available for the formation of Ni_3Mo[3].

The strength of maraging steel is significantly greater than the strength produced by the sum of individual effect of cobalt, molybdenum and titanium. The result suggests that steel is strengthened by precipitation produced by molybdenum and titanium, and possibly ordering of the matrix due to cobalt[15,17].

Aluminium contributes both marked solid-solution strengthening[16] and age-hardening to the Fe-18Ni binary base. Using a 1150°C solution treating temperature all of the aluminium can be held in solid-solution, and aging produces a high hardness. However, if a standard 815°C solutionizing temperature is used, the aging is less pronounced. Aluminium raises the M_s temperature to 316°C at 2.56 per cent Al, but has no observed effect on the reversion. Aluminium is added to maraging steels as a deoxidizer.

Boron and Zirconium additions are made to these steels, since it was found in the development of the Fe-25Ni maraging steel that these additions supressed harmful grain-boundary precipitation[4]. Calcium is added to assist sulphur removal.

2.3 Strengthening of Maraging Steels :

There are many methods by which strengthening can be brought about in maraging steels. Of them the two important methods are the thermo-mechanical treatment and maraging.

2.3.1 Thermo-mechanical treatment of Maraging Steels :

Thermo-mechanical treatments can be defined as treatments whereby plastic deformation, generally below the recrystalization temperature, is introduced in to the heat-treatment cycle of a steel in order to improve the properties. With an absence of intermediate transformation products on air-cooling the maraging steels have good hardenability and hence can be readily cold-worked in the austenitic condition prior to transformation to martensite. Further, they can be worked in the martensitic condition prior to aging and even can be deformed in the fully aged condition.

Kula and Hickey[30] showed that Fe-18Ni maraging steels can be strengthened by various thermo-mechanical treatments with little decrease in fracture toughness, although the magnitude of the strength increase is not large. These results are in general agreement with those of Floreen and Decker and Bush[29]. The increase in strength induced by deformation at temperature below 870°C is shown to depend on the conditions under which transformation took place. The thermo-mechanical treatments applied to maraging steels include[30] (a) Cold-working in the austenitic condition of 330°C, followed by transformation to martensite and aging, (b) Cold-working in the martensitic condition and aging and (c)Cold-working in the aged condition with and without subsequent reaging.

(a) Cold-worked in the austenitic condition :

The tensile and hardness properties of Fe-18Ni maraging steel after aging at 480°C for 3 hour (figure2) showed that the tensile and yield strength increases as a result of reduction in thickness i.e., cold-working. The elongation and hardness show little change as shown in figure 2. The hardness changes only slightly on aging at 150°C (300°F) and 260°C (500°F) and more after aging at 370°C (700°F) and 480°C (900°F).

(b) Cold-worked in the martensitic condition (Marforming) and subsequent aging :

Kula and Hickey[30] also showed that at room temperature, the Fe-18Ni maraging steels are in the

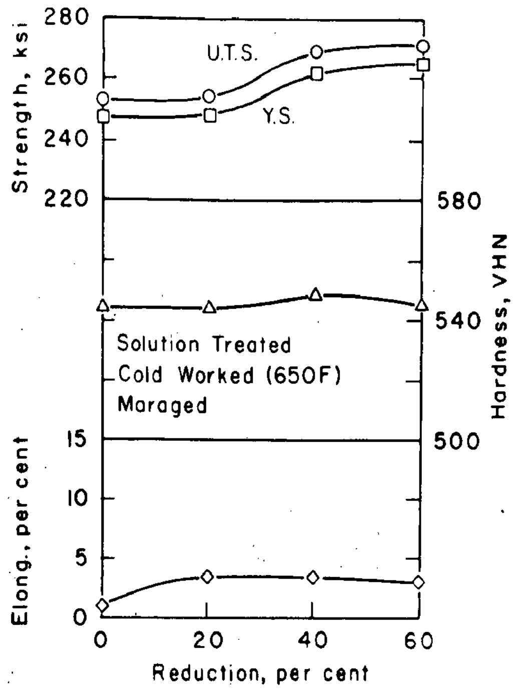
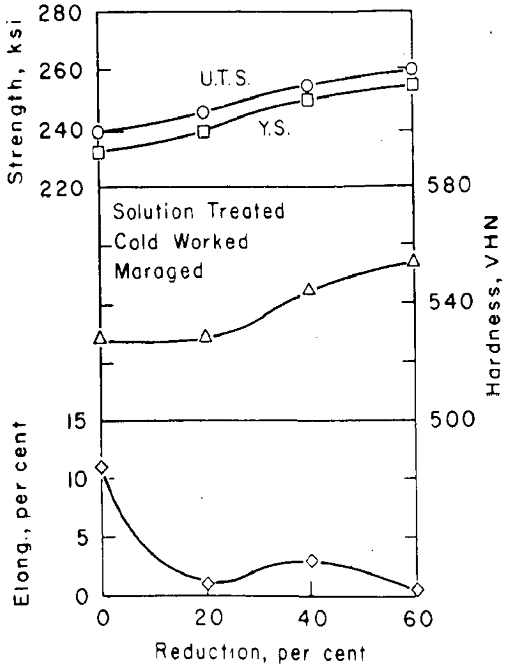


Fig.2. Effect of cold-working in the austenitic condition on tensile and hardness properties of Fe-18Ni maraging steel30.

Fig.3. Effect of cold-working in the solution treated condition on tensile and hardness properties of Fe-18Ni steel30.



martensitic condition, but are relatively soft and can be rolled readily. Tensile and hardness properties for reductions upto 60 per cent followed by the standard aging at 480°C for 3 hour are plotted in figure 3. The tensile strength and yield strength increases with cold working. Accompanying this is a decrease in ductility and increase in hardness. The hardness changes only slightly on aging at 150°C (300°F) and 260°C (500°F) and more after aging at 370°C (700°F) and 480°C (900°F) as shown in figure 4. However, there is only a slight decrease in fracture toughness accompanying the aforementioned strength improvement brought about by 60 per cent cold-work.

(c) Cold-worked in the aged-condition :

It was possible to cold-roll the aged material as much as 60 per cent without difficulty. The tensile and hardness properties after rolling are shown in figure 5. It was observed by Kula and Hickey[30] that the yield strength and hardness are unchanged or decrease slightly and there is a modest increase in tensile strength.

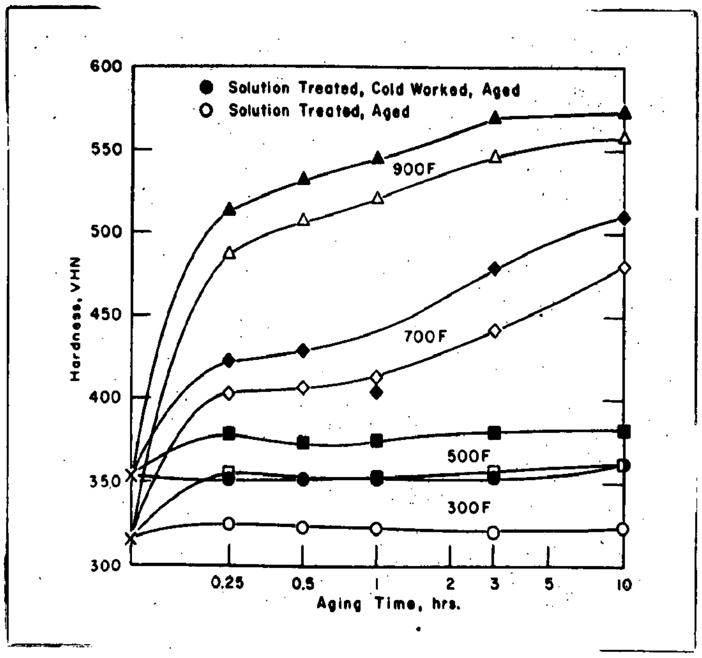


Fig.4. Effect of aging temperature and time on hardness of Fe-18Ni maraging steel, unworked and cold-worked 60 pct. in solution treated condition.[30]

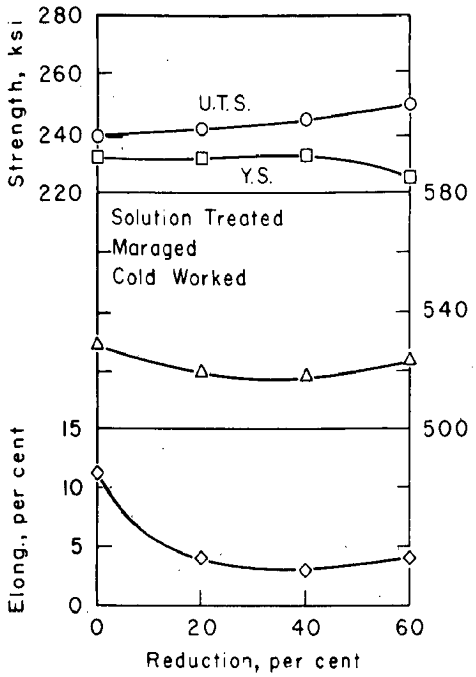
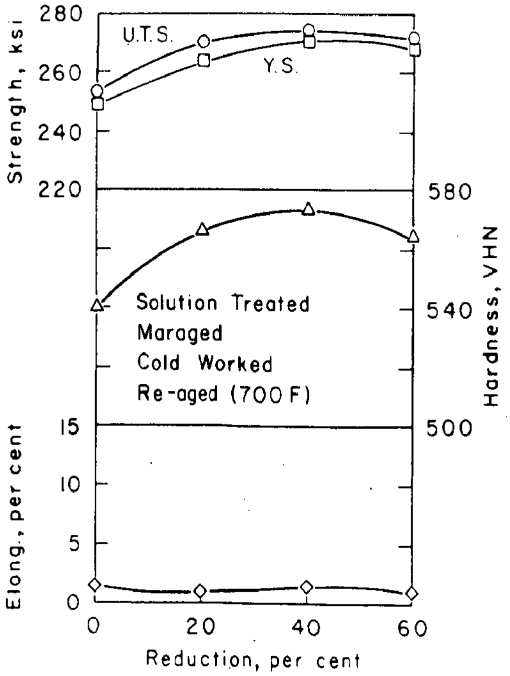


Fig.5. Effect of cold-working in the aged condition on tensile and hardness properties of Fe-18Ni maraging steel^{30}.

Fig.6. Effect of cold-working in the aged condition on tensile and hardness properties of Fe-18Ni steel. Reaged 1 hour at 370°C^{30}.



In addition to testing after cold rolling, tests were also carried out on material that had been re-aged for an hour at 370°C after rolling in the aged condition, figure 6. Here the hardness and yield and tensile strengths all increases while the ductility is low. Comparing the results, it was observed by Kula and Hickey[30] that the strength and hardness are increased as a result of re-aging after cold working and that this increase is greater with increasing amount of cold-work.

The results based on hardness measurements have led to general agreement that the role of carbides[31] is important to strengthening by thermo-mechanical process, presumably through the mechanism of an interaction of the precipitating carbides with defects produced in the austenite transformed to the martensite, leading to a more finely dispersed precipitate. The very small increase in strength which occurred when the unaged martensite was cold-worked and then aged is attributed to work hardening of the martensite. The major contribution to the strengthening in aged cold worked steels arises from strain hardening, with a smaller strengthening contribution arising during the re-aging. This aging increase is due to a re-solution and finer scale reprecipitation of carbides[32].

Cold-working of martensite followed by aging was slightly more effective in raising the strength and hardness than an equivalent amount of working in the austenitic condition. When cold-worked after aging, the tensile strength increases only slightly while the yield strength and hardness actually decrease (figure 5). Re-aging the material after cold working, figure 6, results in higher strength and hardness. The magnitude of this increase during aging increases as a function of the amount of cold work. It was observed by Nolan and Davidson[37] that the ductility as measured by elongation and reduction in area are effectively independent of the cold working. This is in contrast to the result reported by Kula and Hickey[30]. Where he observed a degradation in elongation as a result of reduction by cold-working.

2.3.2 Strengthening of Maraging Steels by Precipitation:

Age-hardening is one of the principal means of strengthening the substitutional iron-base martensites in the maraging steels[33,34]. In the maraging steels the unusual combination of strength and toughness may be obtained by age-hardening a low-carbon iron-nickel martensite matrix[35].

In contrast to Fe-C martensites, the martensite of maraging steels are relatively soft and ductile in the as-quenched condition, due to the low solid-solution hardening effect of the substitutional elements as compared to carbon. These martensites are hardened by aging at low temperatures by precipitation of the intermetallic phases in a martensitic matrix. Although the mechanism of hardening in maraging and secondary hardening is essentially similar, the two processes are different in the sense that in the latter the precipitation of carbides takes place.

The aging of substitutional iron-base martensites can be seperated in to three stages :-

(a) Recovery of the defect structure of martensite,

(b) Formation of clusters, ordering and precipitation of intermetallic compounds,

(c) Formation of Austenite.

(a) Recovery : It appears that two reactions may occur during recovery involving (i) the migration of vacancies and residual interstitials to dislocations which are, therefore, pinned down(ii) dislocation re-arrangement partially to relieve residual stresses generated by the previous martensitic transformation.

(b) Precipitation : The Fe-Ni martensite respond to age-hardening if a number of other elements are present. The addition of cobalt is very interesting. Cobalt by itself is not effective but in combination with molybdenum, a marked hardening response is produced. The precipitates are evenly distributed throughout the martensitic matrix and the fine evenly distributed dispersion of the precipitate particles appears to be related to the high dislocation density of the martensite matrix.

(c) Formation of austenite : Most martensitic transformations are reversible and get back to austenite on heating. Decomposition of metastable martensite of maraging steels into equilibrium ferrite and austenite may occur during aging fairly rapidly at temperatures above 450°C.

The formation of austenite is an important part of the aging process in all these alloys, although it does not appear in significant quantities at 500°C until after the aging peak is reached. The amount of austenite formed increased with aging time[13]. The formation of austenite must be minimized for optimum mechanical properties of maraging steels.

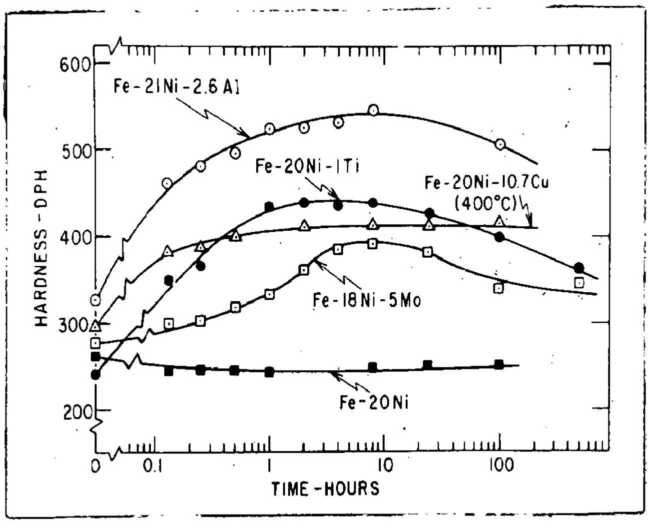
2.3.3 Aging Kinetics :

Speich[13] studied the hardness change during aging of Fe-20Ni, Fe-21Ni-2.6 Al, Fe-18Ni-5Mo, and Fe-20Ni-1Ti martensites at 500°C and the Fe-20Ni-10.7Cu martensite at 400°C. The results are shown in figure 7. The Fe-20Ni alloy, which lies in the $\alpha + \gamma$ field of the Fe-Ni system at 500°C, softened slightly. The only processes that can occur in this alloy are the formation of austenite and the recovery of the defect structure of martensite. The other alloys, all of which were aged in $\alpha + \gamma +$ compound fields, exhibited precipitation-hardening with a single aging peak. The kinetics of the aging processes is about the same for all the alloys except for the Fe-20Ni-10.7Cu alloy which appears to harden as rapidly at 400°C as the other alloys do at 500°C.

Speich[13] investigated the effect of composition on the aging behaviour of the Fe-20Ni-Ti martensite and is shown in figure 8. The peak hardness rises rapidly as the titanium content is increased from 1.1 to 5.8 per cent titanium, with a maximum hardness of 805 VPN being obtained in the Fe-20Ni-5.8Ti alloy. The time required to reach peak hardness increases slightly with increasing titanium content.

The Fe-18Ni-Co-Mo steels in fact, show very rapid hardening and during the first five minutes at 480°C. A maximum hardness[31,36] of about 540 VPN is achieved after 3 hours at 480°C. The effect of temperature on aging

Fig.7. Age-hardening of Fe-18 to 21 pct. Ni martensites with additions of Al, Mo, Ti and Cu at 500°C[13].



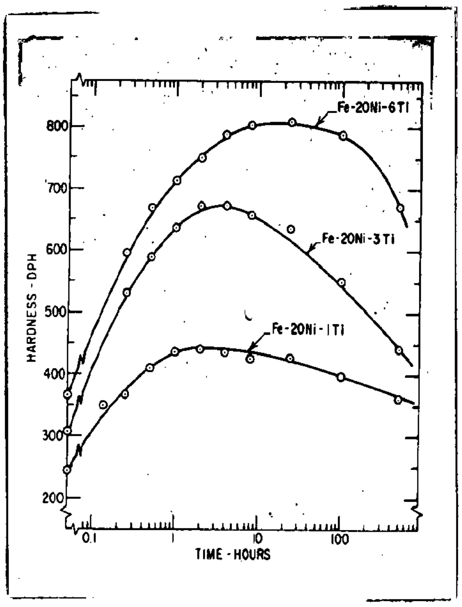


Fig.8. Effect of composition on aging kinetics of Fe-20Ni-Ti martensites at 500°C[13,27].

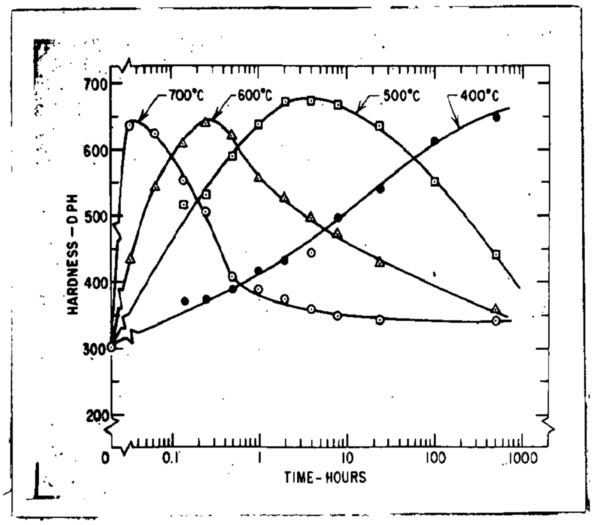


Fig.9. Effect of temperature on aging kinetics of Fe-20Ni-3Ti maraging steel[1]

behaviour of the Fe-20Ni-3Ti alloy is shown in figure 9. As expected, the time required to reach peak hardness increases with decreasing temperature. Unexpectedly, the peak hardness obtained does not increase significantly with decreasing aging temperature. Over-aging occurs very rapidly at 600°C and 700°C.

Floreen and Decker[11] studied the kinetic analysis of the Fe-18Ni maraging steel and showed that hardness results could be expressed by the simple relationship :-

$$H_t - H_o = Kt^n$$

where,

H_t = Hardness at time t.

H_o = Initial Hardness.

K = A constant.

t = Maraging time.

n = Time constant.

The values of n varied from 0.19 to 0.30 with changing initial conditions.

The maraging treatment recommended for all steels, lies between 1 and 4 hours at 460°C - 480°C.

Treatment at temperature above this range, or even prolonged soaking (1000 hours) at temperature within the range can result in a small amount of austenite reformation. The reformation of austenite has little effect on tensile strength, but does slightly impair proof stress and notched strength[4]. The effect of aging time and temperature on mechanical properties and austenite contents of Fe-18Ni-Co-Mo and Fe-25Ni-Ti-Al maraging steels are shown in figures 10 and 11, respectively. The marked decrease in notched tensile strengths of the ausaged and maraged Fe-25Ni steel is mainly due to the increase in the yield strength, with increase of maraging temperature and not to the reformation of austenite.

Aging for normal periods at temperatures below the range 430 - 480°C does not result in maximum hardening of the steel. The lower proof stress[4] and tensile strength values obtained are off-set by an increase in ductility and maximum stress.

2.4 Properties :

Some of the physical and mechanical properties data of maraging steels are presented in Table - II.

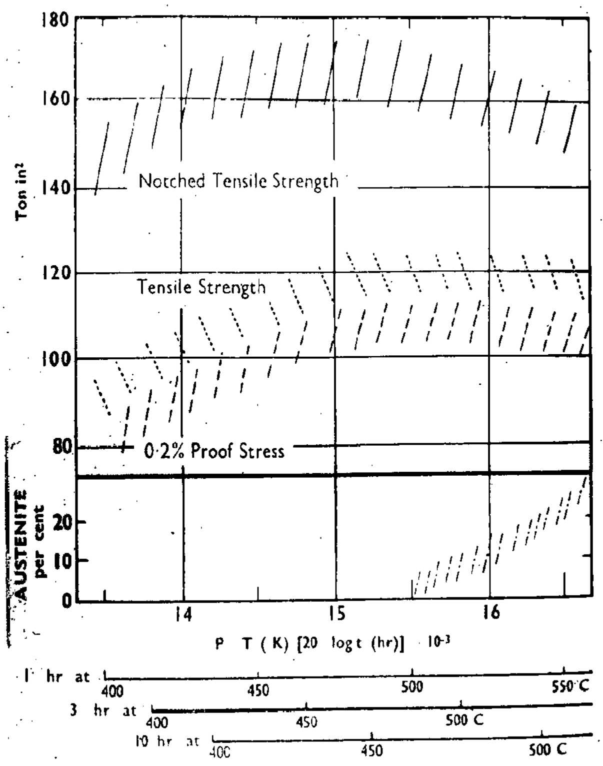


Fig.10. Effect of maraging time and temperature on the mechanical properties and reformation of austenite in Fe-18Ni-Co-Mo steels[4].

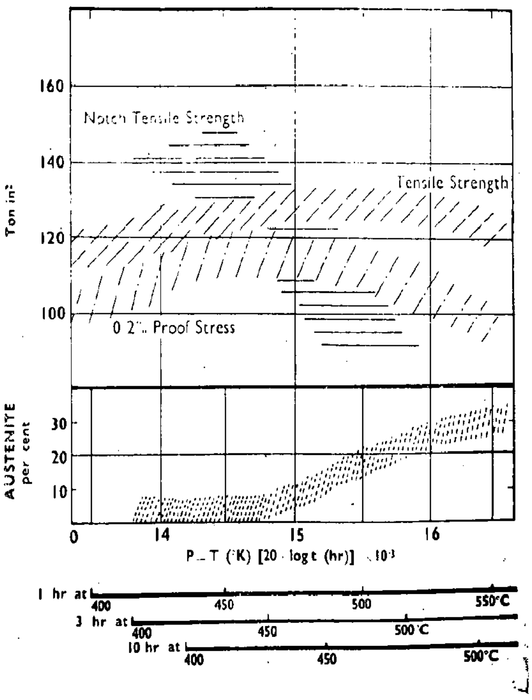


Fig.11. Effect of maraging time and temperature on the mechanical properties and reformation of austenite in Fe-25Ni-Ti-Al steels[4].

Table - II

Physical and some mechanical properties of maraging nickel steels.

Property	Fe-18Ni-Co-Mo	Fe-20Ni-Ti-Al	Fe-25Ni-Ti-Al
lus of Elasticity, 10^6lb/in^2	26.5-27.5	25.50	24.50
lus of Rigidity , 10^6lb/in^2	10.20	-	-
son's Ratio	0.30	0.31	0.31
pct. Proof stress in compression, Ton/in^2	110.00	-	-
r strength, Ton/in^2	64.00	-	-
ity, lb/in^2	0.290	0.284	0.286
mal expansion coefficient, 10^{-6}/°C (20-480°C)	10.10	11.20	11.20
ge in length caused by maraging pct.	0.00	- 0.12	- 0.10
trical Resistivity, microhm-cm.:			
Annealed from 820°C	60-61	-	-
aled and maraged, 3 hour, 480°C	38-39	-	-
etic Inductance, gauss :			
H = 2,500, Oe.	16,550	17,110	13,550
H = 5,000, Oe.	18,500	18,375	14,750
nece, Gauss	5,500	5,000	3,700
cive force, Oersteds.	28.10	15.60	25.00

2.4.1 Mechanical Properties :

The hardening reaction is not limited by section-size for the Fe-18Ni maraging steel as it is in the case of quench-hardening low alloy martensite steels. The elongation per cent/or the ductility of the steels varies with the strength levels and the type of product. As the tensile strength increases, the ductility tends to drop. For all the maraging steel grades, the average elongation ranged from 3 to 12 per cent. It is generally agreed that the vacuum-melted steel compared with the same steel air-melted has improved transverse ductility, great uniformity in tensile properties, and also better notched and un-notched fatigue strength.

The maraging steel, like most complex alloys, is an inhomogeneous material and would generally show differences between the longitudinal and transverse tensile properties relative to the rolling direction. Although these differences can be reduced, if not eliminated, by adequate cross rolling, the occurrence of segregation bonding and layers of retained austenite is often considered responsible for directionality of mechanical behaviour. It has been suggested that this directionality of tensile properties is not necessarily a reflection of the bonding but may be associated with anisotropy of prior austenite grain shape and orientation. Recently, it has been reported that a double - annealing heat-treatment consisting of austenitization at 900°C, followed by a second austenitization at about 815°C, results in equiaxed prior austenite grains of larger size and reduces differences between the longitudinal and transverse tensile properties.

Fatigue Properties :

The fatigue strength of steel is generally increased with the tensile strength and is about 50 per cent of the ultimate tensile strength. Upto a tensile strength of about 180 p. s. i, there is a more or less linear relationship between tensile strength and fatigue strength. Above this tensile strength, the increase in fatigue strength becomes progressively less as the tensile strength increases and for steels with yield strengths greater than 220 p.s.i the endurance limit (fatigue - barrier) appears to be limited to about 120 p.s.i. The fatigue properties of Fe-18Ni maraging steels indicates that vacuum-melted steel have a definite superiority over air-melted steel and the fatigue strength is reduced appreciably by the presence of notch. The fatigue strength of maraging steel is superior to conventional steel under high-stress low-cycle conditions.

Impact and Tensile Toughness :

The maraging steel offer improved fracture toughness at a high strength level in comparison to conventional high strength steel. Maraging steels are comparatively less notch-sensitive in terms of the Charpy V-notch tests than the conventional high strength steels[19].

The maraging steels have superior notch toughness above the tensile level of about 200 p.s.i. It has also been shown that the toughness (NTS/TS ratio) of Fe-18Ni maraging steel is insensitive to wide variations in annealing and maraging conditions[11]. The maraging steels do not display a sharp ductile-to-brittle transition temp., loss in toughness being gradual to as low as -250°C.

Embrittlement Characteristics :

There is enough evidence that maraging steels, like any high-strength b.c.c., steel, are subject to hydrogen embrittlement and are, consequently, subject to cracking failure at stress below the yield strength[20,21]. It has been shown that the amount of hydrogen required to embrittle Fe-18Ni maraging steel is substantially greater than the amount needed to embrittle high strength steel to the same degree in terms of ductility loss[22].

Table - III

Mechanical Properties of Maraging Steels[4].

(a) In the annealed condition

Mechanical Property	Fe-18Ni-Co-Mo.	Fe-20Ni-Ti-Al.	Fe-25Ni-Ti-Al.
Hardness, VPN	290-320	270-320	190-230
0.2 pct. proof stress, ton/in.^{2}	42-52	45-55	17-20
Maximum stress, ton/in.^{2}	62-67	60-70	50-60
Reduction of area, per cent	70-75	65-75	70-80
Elongation, per cent	17-19	20	30-35

Table - III (contd..)

Mechanical Properties of Maraging Steels[4].

(b) In the aged condition

Mechanical Property	Fe-18Ni-Co-Mo.	Fe-20Ni-Ti-Al.	Fe-25Ni--Ti-Al.
0.2 pct. proof stress, ton/in.^{2}	104-108	107-121	107-122
Maximum stress, ton/in.^{2}	107-122	110-125	116-130
Elongation on 4.5 $\sqrt{A}$, pct.	10-12	10-12	10-15
Reduction of area, pct.	50-60	45-60	40-60
Notched tensile strength, ton/in.^{2}	165-185	140-170	125-160
NTS/MS ratio	1.45-1.55	1.25-1.50	1.05-1.35
Charpy V-notch Impact value, ft-lb. at 20°C	25-30	12-20	-
Nil ductility transition temperature, °C	-	20 to-60	150-200
Maraging period	3 hrs.	4 hrs.	1 to 4 hrs.
Maraging temperature	480°C	450°C	450°C

2.4.2 Influence of Alloying Element on Mechanical Properties :

Minor additions of carbon have a marked strengthening effect on the maraged nickel-iron martensite, and an increase from 0.01-0.04 per cent will raise the strength of the Fe-18Ni-Co-Mo steel by about 9 ton/in^2. The carbon increments markedly reduce notched properties when more than 0.03 per cent carbon is present in the steel.

Manganese and silicon should each be held to below 0.1 per cent maximum, since these elements drastically reduce ductility and notched tensile strength[4]. Titanium has a more powerful hardening effect and increases the proof stress by 4.5 ton/in^2. for each 0.1 per cent addition to 18 per cent Ni-Co-Mo and 20 per cent Ni-Ti-Al steels. Large additions of titanium and aluminium can produce high levels of hardness, but alloys with much more than 1.9 per cent Ti plus aluminium tend to be susceptible to brittle failure.

Molybdenum additions in the Fe-18Ni-Co-Mo types of steel raise the 0.2 per cent proof stress value of about 0.9 ton/in^2. for each 0.1 per cent added[4].

Molybdenum also helps in preserving the toughness in the Fe-18Ni maraging steel. Increasing cobalt and molybdenum contents increases yield and tensile strength. Figure 12 shows the effect of cobalt with molybdenum on maraging, and it is great feature of these steels that only the particular Mo-Co combinations chosen have given this considerable hardening effect coupled with a very high toughness.

Sulphur and phosphorus have been found to be deleterious in conventional ultra-high strength steels, particularly in connection with ductility, weldability and hydrogen embrittlement. Apart from the control of the hardening additions to within the ranges specified above, the contents of other elements have been found to be critical to give optimum properties.

2.4.3 Corrosion Resistance Property of Maraging Steels :

The maraging steels have better resistance to atmospheric corrosion than have low alloy steels. Laboratory-made 18Ni/Co/Mo steel, when tested (U-bend specimen test) did not fracture during 240 days exposure in natural sea-water. Tests which have also been performed in industrial

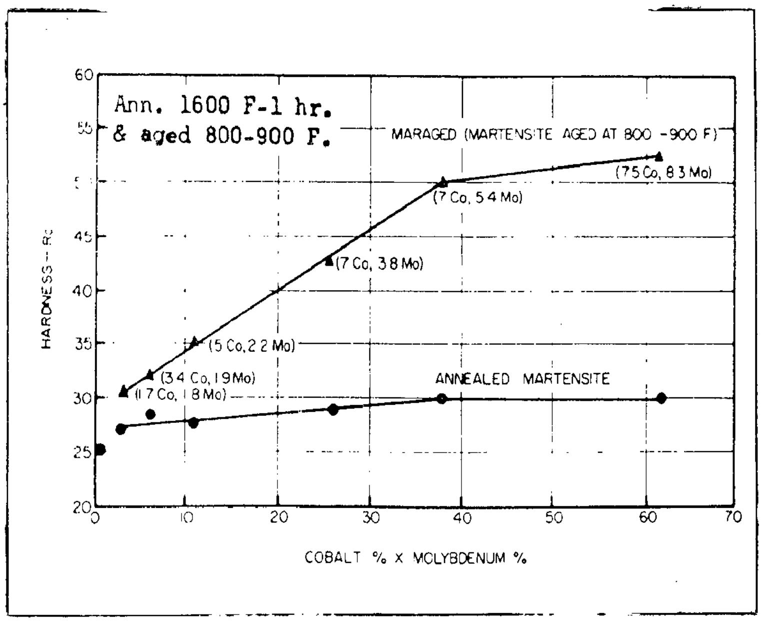


Fig.12. Influence of cobalt-molybdenum product on maximum hardness of Fe-18Ni maraging steels.[14]

marine environments have demonstrated that maraging steels are much less prone to failure than conventional ultra-high strength steels of similar yield strength.

The Fe-18Ni maraging steels[1,3,4] are sensitive to stress corrosion cracking in many environments, and the sensitivity seems to increase appreciably with increasing temperature. According to one report, cold reduction prior to aging increases resistance to stress corrosion in maraging steels. Welding, on the other hand, increases the susceptibility to stress corrosion cracking failure taking place in heat affected zone. Furthermore, maraging steels seem to have a very slow rate of stress-corrosion crack propogation with a large number of small cracks, rather than one large crack generally associated with normal high-strength low-alloy steels. The time to cracking of maraging steels is relatively longer than other conventional high strength steels heat treated to similar level. Since stress-corrosion cracking on microscale does occur in maraging steels, it is generally recommended that these steels, when used in corrosive environments, be protected by a coating.

It was concluded by Setterlund[23] that despite its high toughness, maraging steel will fail in a brittle manner when stressed and exposed to corrosive aqueous solutions, such as distilled-water, tap-water, or salt-water. These alloys will also fail when exposed in stressed condition to corrosive industrial or sea-coast atmospheres or when exposed for long periods to trichloroethylene. The time to failure of Fe-18Ni maraging steel can be decreased by -

(i) Increasing strength level
(ii) Increasing applied-stress level
(iii) Welding and
(iv) Increasing environmental temperatures.

Prior cold reduction increased the resistance of both Fe-18Ni and Fe-20Ni grades of maraging steels to stress corrosion cracking, although a reduction in fracture toughness and bend ductility was observed.

2.5 Fabricability :

2.5.1 Hot-Working :

Maraging steels are readily hot worked by any conventional forming operation and possess better hot plasticity than 18-8 chromium-nickel stainless steels. The hot-working range is wide, ranging from 1250 - 800°C. The maraging steels do not exhibit hot shortness at temperatures of 1250°C and cracking is not a problem even when the steels are finished below 820°C. Heat absorption is also faster than in austenitic steels, and a heating time of 15 minutes per inch of section is, therefore, suggested. Finishing operations are performed within the temperature range, 800 - 900°C. Careful control[4,19] of the finishing operation is essential, both to ensure a fine austenite grain size and to develop the best strength and ductility, particularly in large sections.

2.5.2 Cold-Forming Characteristics :

Although solution-annealed 18Ni/Co/Mo steels are reasonably hard, they exhibit an extremely low rate of work hardening and can be given cold reductions of over 90 per cent without re-annealing. The low work-hardening rate facilitates production of sheet, strip and wire. It also helps to simplify production procedures and to reduce manufacturing costs of finished components. Deep drawing operations have also been successfully carried out; for example, light-weight gas bottles have been produced from flat circular blanks.

The austenitic structure of the annealed Fe-25Ni-Ti-Al steel possesses[4] a lower hardness and slightly better ductility than the martensitic structures of other maraging steels. These properties have an advantage in reducing pressures and in ensuring more uniformity of deformation in complex cold-forming operations such as deep drawing. Although cold work has little effect on the hardness of solution-annealed martensite, it gives a pronounced strengthening effect after subsequent maraging. Cold work, if applied homogeneously across a section, can increase tensile strength by 2-4 tons/in.^{2} (3.6 Kg/mm.^{2}) for each 10 per cent of cold reduction.

2.5.3 Welding Characteristics of Maraging Steels :

Maraging steels exhibit good weldability and joints have been successfully made by such processes as coated electrode, submerged-arc, argon-shielded metal-arc, and argon-shielded tungsten-arc, without modifying the normal procedures[24]. Preliminary indications are that other processes, such as fine-wire, electron-beam and spot welding, can also be used successfully. Unlike medium-carbon steels sound welds can be produced in the maraging steels without the use of preheat. Both the weld metal and the heat-affected zone of as welded material are soft and have hardness of annealed alloys. The mechanical properties can be restored, however, in the Fe-18Ni-Co-Mo and Fe-20Ni-Ti-Al steels by simply applying the low temperature maraging treatment. Ausaging, in addition to maraging, must be applied to welds made in the Fe-25Ni-Ti-Al steels in order to obtain hardening. Argon-shielded metal-arc and argon - shielded tungsten arc processess have been found to be particularly suitable for the welding of Fe-18Ni maraging steel using a filler wire of composition[4,19] which is essentially that of the parent alloy. With reasonable welding precautions, the loss of strength will not normally exceed 5 per cent and this decrease will be accompanied by an increase in toughness, since unlike carbon high strength steels, no brittle phase can be formed in the heat-affected zone.

2.5.4 Machining Characteristics and Dimensional Stability:

Maraging steels have machining characteristics similar or superior to those of medium-carbon low-alloy steels of similar strength. Unlike conventional steels, the strength developed by maraging steel is independent of mass and rate of cooling. Because the gross volume change associated with martensite formation is completed during solution-annealing and dimensional changes during maraging are very small (0.0 to 0.04 per cent contraction), maraging steels can be finish-machined in the soft condition before hardening[4,25]. As maraging is conducted at a comparatively low temperature, gross oxidation can easily be prevented and there is no problem of decarburization. Also, the negligible volume changes and the very low hardening temperatures employed minimize or avoid the need of over-size allowances made on conventional steel to accommodate distortion, volume change and decarburization during hardening.

Present investigations are that 18 per cent Ni-Co-Mo maraging steels may be slightly easier to machine than the 20 or 25 per cent nickel grade steels in the maraged condition. The smaller number of operations involved in the machining and hardening of maraging steel can greatly reduce production costs in comparison with conventional ultra-high strength steels.

2.6 Major Applications of Maraging Steels :

The various outstanding characteristics of the maraging steels offer to the engineer and designer, the possibility of stronger, lighter and more reliable constructions combined with ease of fabrication[4].

The ultra-high-tensile properties[19,26] and outstanding notched toughness of the 18Ni/Co/Mo steels have together justified the use of these steels in applications where weight saving is essential. Such as rocket and missile cases, air-craft-structural parts, light-weight weapons and portable-structure. In the form of plate these steels have potential applications as hull plates in marine engineering, and as high pressure containers. Fe-18Ni-Co-Mo types of steel are attractive for cryogenic applications. Whilst these steels will be considerably more expensive than the low-alloy steels, the price difference must be viewed in relation to the simplified process procedures and considerably higher margin of safety against brittle failure offered by the maraging steels.

In many other applications[4], both existing and potential, the comparatively high price of these steels is off-set by production savings resulting from other attractive features, such as freedom from distortion, simple heat-treatment, good-machinability and the ability to weld without difficulty. In this connection the steels are in use or are being considered for use in, for example, gears, fasteners, precision machine parts, shafts, springs, compressor parts, dies for injection moulding of metal and plastics, extrusion dies and tools for hot and cold forming of metals.

CHAPTER - III

EXPERIMENTAL DETAILS

3.1 Composition of Maraging Steels :

The composition of the maraging steels that were used in the present investigation are shown in the Table-IV. The steel bars of 1.8 cm. diameter were received in the hot-forged condition, by the courtesy of Internationa Nickel Company.

Table - IV

Composition of the Maraging Steels

Steel	Weight Percentage						
	Ni	Co	Mo	Ti	Al	Nb	C
1	18	7	5.0	0.4	-	-	-
2	19	-	-	1.4	0.25	0.4	-
3	25	-	-	1.4	0.25	0.4	0.05

3.2 Preparation of Specimens :

Cylindrical specimens of 7 mm. to 9 mm. height were prepared from the forged section for solution-treatment, hardness measurement and metallographic studies. The specimens were polished, etched (in 5 per cent nital solution) and examined under the optical microscope (Model MIM 7). The hardness values of the various maraging steel specimens were also taken in the as received condition.

3.3 Thermal and Mechanical Treatments :

The specimens from each steels were solution treated in the muffle furnace with a temperature control of ± 5°C at temperature 820°C for 1 hour. After solution treatment the specimens were air-cooled and thus allowed to transform to martensite or to semi-austenitic condition depending upon the composition of the steel. The specimens were polished, etched and examined under the optical microscope. The hardness values of the various steel specimens were also taken.

Steel specimens of various compositions were compressed on 100 Ton Universal Testing Machine, with a cold deformation varying from zero to 47 per cent. Cold deformation was calculated as:

$$\text{Pct. Cold deformation} = \frac{\text{Change in height of the specimen} \times 1}{\text{Original length of the specimen.}}$$

Hardness measurements after the cold-deformation(marforming) of the steel specimens were carried out and some of them were polished, etched and studied under the optical microscope.

The specimens were halved into the semi-circular shape. One part of the cut specimens of different compositions after varying extent of cold deformations were aged at 450°C and the rest half at 520°C. The aging treatment was carried out for different lengths of time, viz., 1 hour, 3 hours, 5 hours, 7 hours, 9 hours, 11 hours and 15 hours, after which the specimens were air-cooled. The specimens were polished and hardness values were measured. The specimens were afterwards examined under the optical microscope.

A similar aging treatment was also done at 400°C for various lengths of time varying from 1 hour to 20 hours.

3.4 Hardness Measurements :

The hardness tests were performed in the Vicker's hardness tester using a load of 30 kg. An average of the three readings was taken as the hardness value of the specimen.

3.5 Metallographic Studies :

The structures were examined at different magnifications, the maximum being about X 500. Photographs of some typical micro-structures were taken at a magnification of X 450.

CHAPTER - IV

RESULTS

4.1 Effect of Maraging on Hardness :

(a) Aging Period :

The plot of aging time versus hardness with varying cold deformation for Fe-18Ni, Fe-19Ni and Fe-25Ni maraging steels at 450°C and 520°C aging temperatures are shown in figures 13-18. The aging curves are similar to those of typical age-hardening type of alloys. For both the temperatures the hardness value increases with increasing aging time, reaches a peak value and then drops continuously. The behaviour of all the three steels is very similar. Initially the hardness increases very rapidly, reaches a peak and then decreases slowly. The maximum hardness, 680 VPN, is achieved for Fe-19Ni maraging steel aged at 450°C for 7 hours when 46 per cent cold deformation i.e., marforming was imparted. The Fe-25Ni maraging steel shows a maximum hardness of 587 VPN, when aged at temperature of 450°C for 6 hours and with 47 per cent cold deformation. The variation of hardness for Fe-18Ni maraging steel stands in between the other two types of maraging steels i.e., Fe-19Ni and Fe-25Ni steels with a peak value of 618 VPN when aged at temperature of 450°C for 8 hours and with 47 per cent cold-deformation.

(b) Aging Temperature :

A comparison of the hardness peaks with maraging temperature for different steels at various cold-deformations is shown in figures 25-29. It is evident that the peak hardness values are attained in shorter time for higher temperatures of aging and percentage of cold deformation. At 400°C the hardness increases slowly and reaches a peak in 16 hours of aging time for the Fe-18Ni and Fe-19Ni maraging steels, while in the case of Fe-25Ni maraging steel peak is observed at about 12 hours of aging time (figure 25A).

4.2 Effect of Mar-forming on Hardness :

Figures 19-24 show the effect of mar-forming followed by maraging on hardness at 450°C and 520°C for Fe-18Ni, Fe-19Ni, and Fe-25Ni maraging steels. In

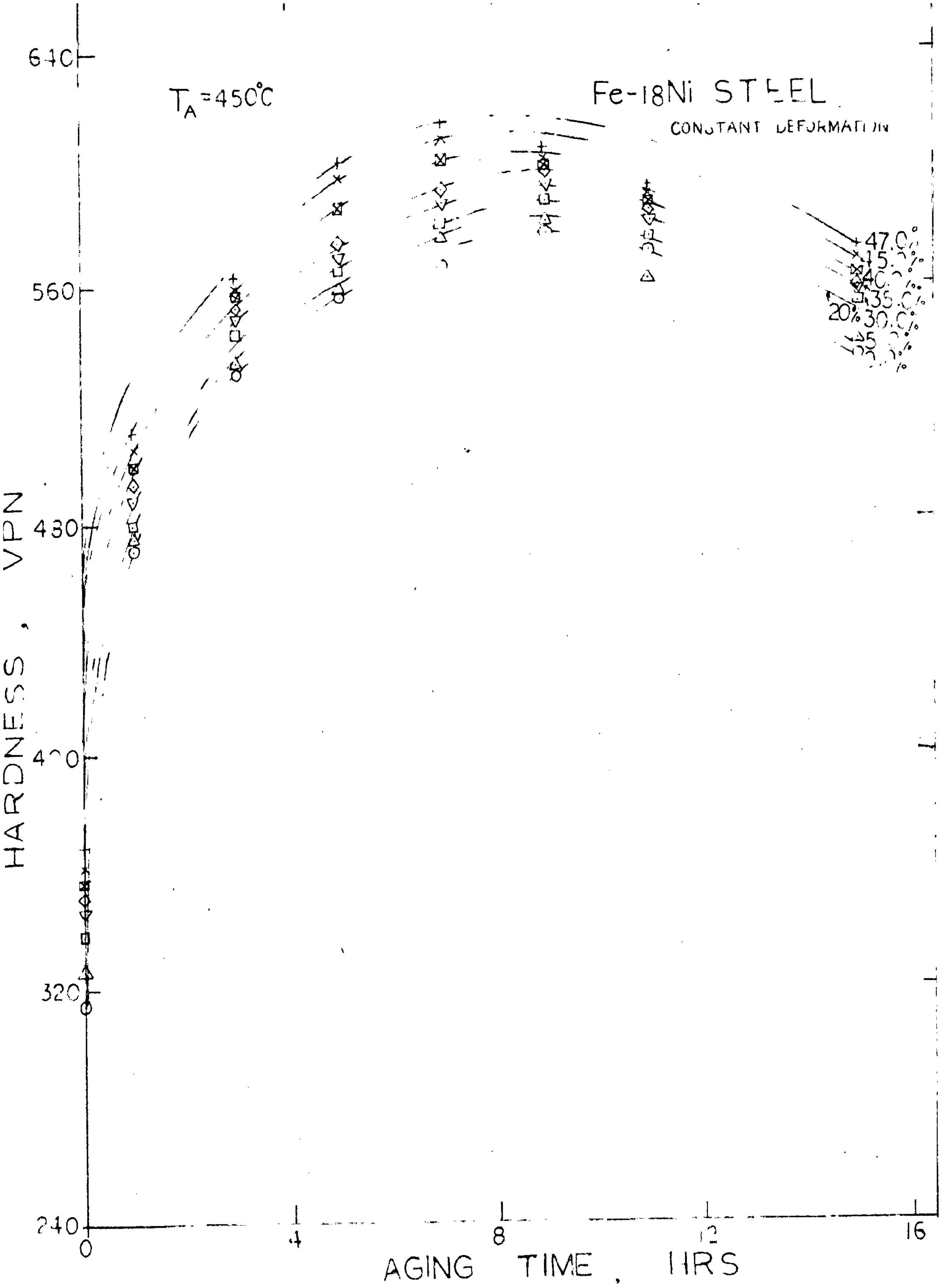


FIG.13 VARIATION OF HARDNESS WITH AGING TIME FOR Fe-18Ni MARAGING STEEL; AGING TEMPERATURE 450°C; FOR CONSTANT DEFORMATION DURING MARFORMING.

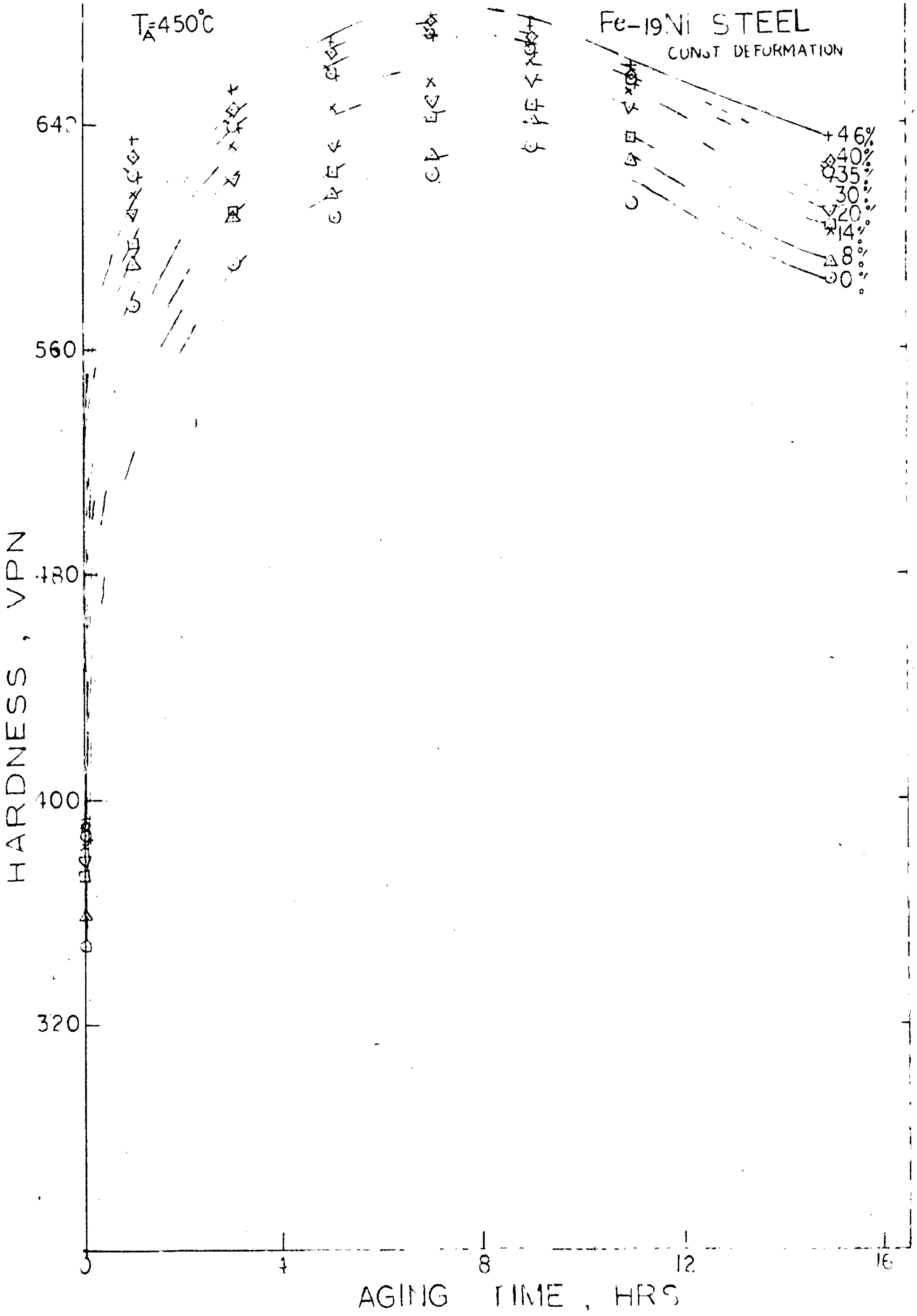


FIG.1[illegible] VARIATION OF HARDNESS WITH AGING TIME FOR Fe-19Ni [illegible] [illegible] [illegible] FOR [illegible]

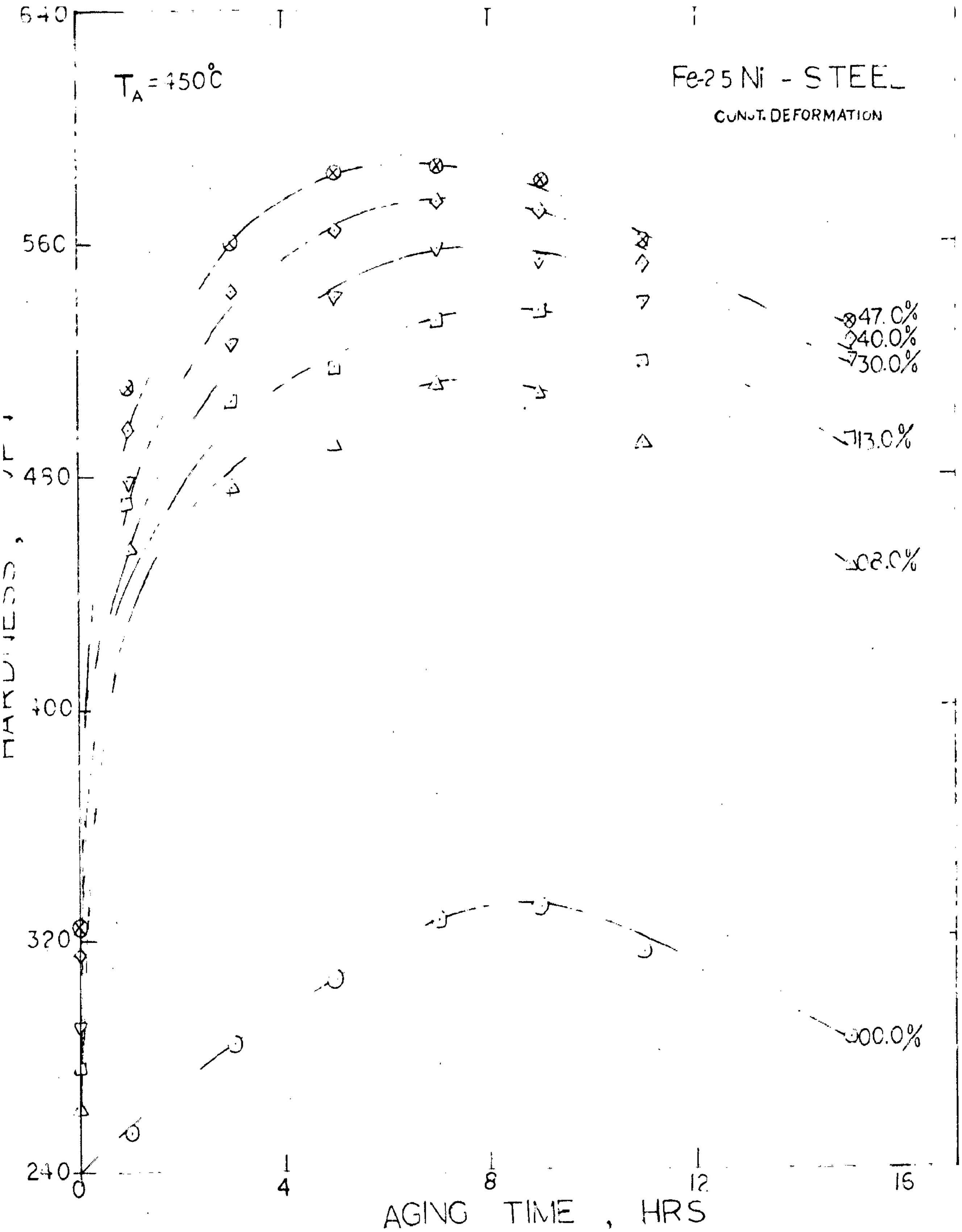


FIG.15 VARIATION OF HARDNESS WITH AGING TIME FOR Fe-25Ni MARAGING STEEL, AGING TEMPERATURE 450°C; FOR CONSTANT DEFORMATION PERCENT OF DEFORMING.

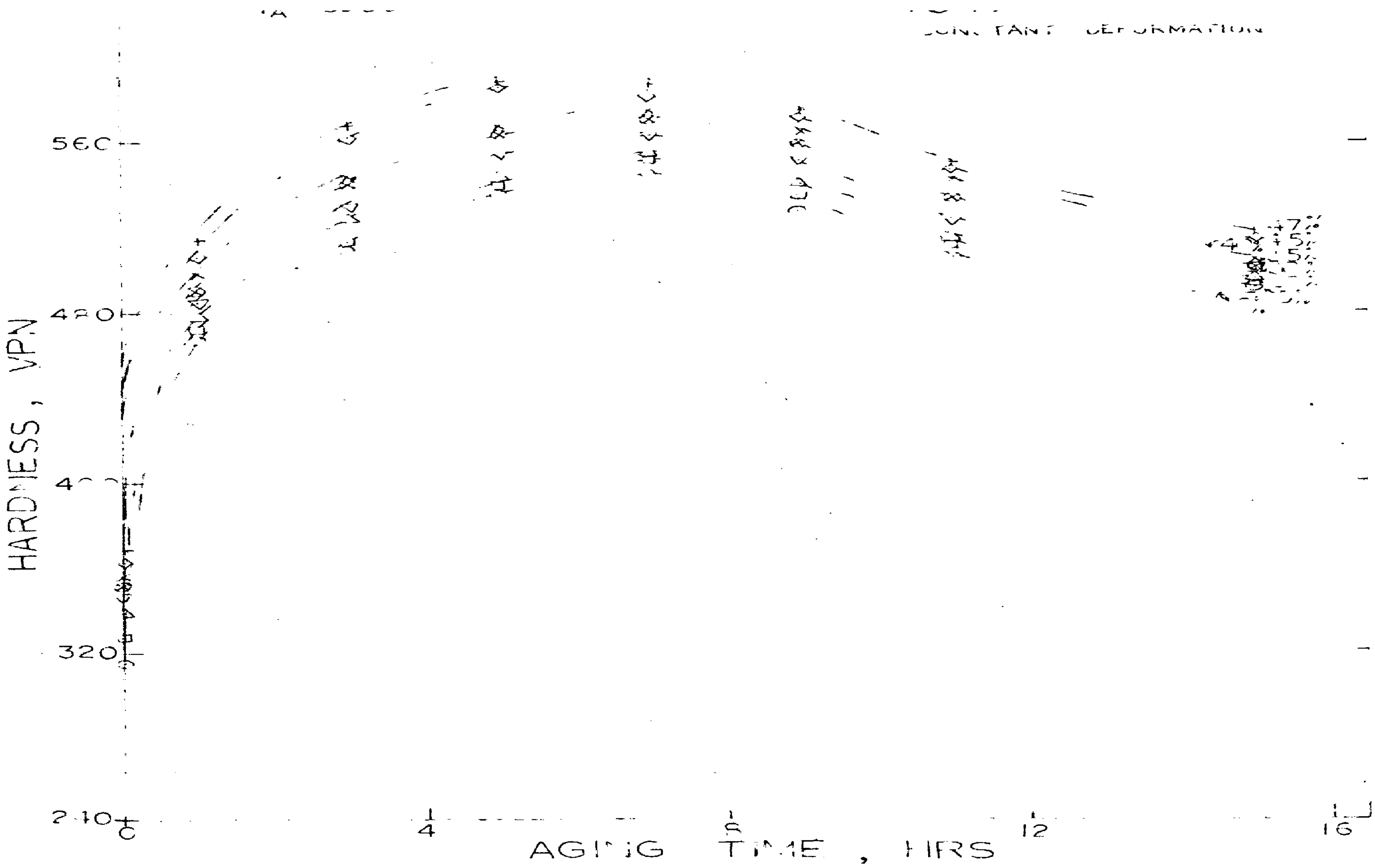
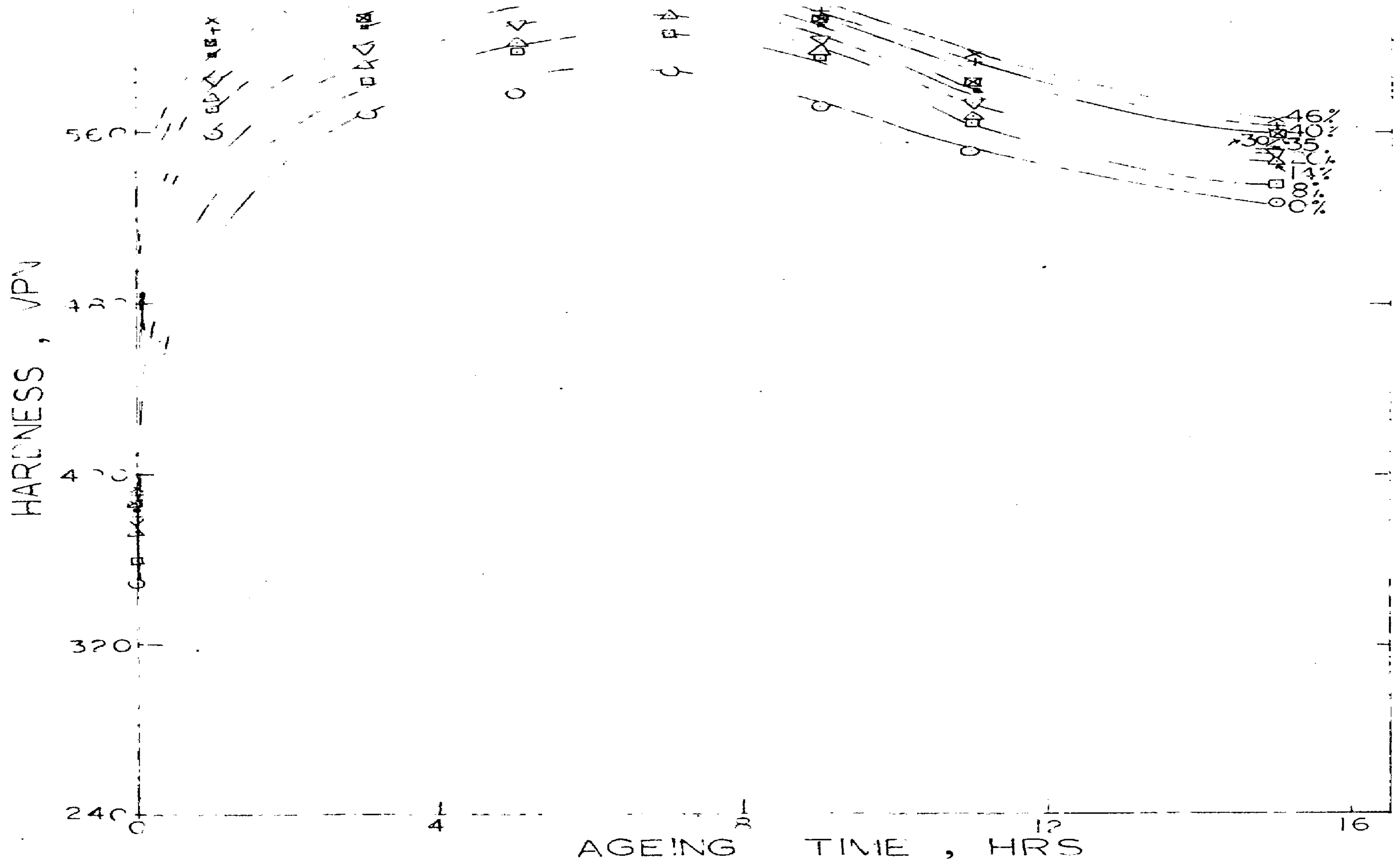
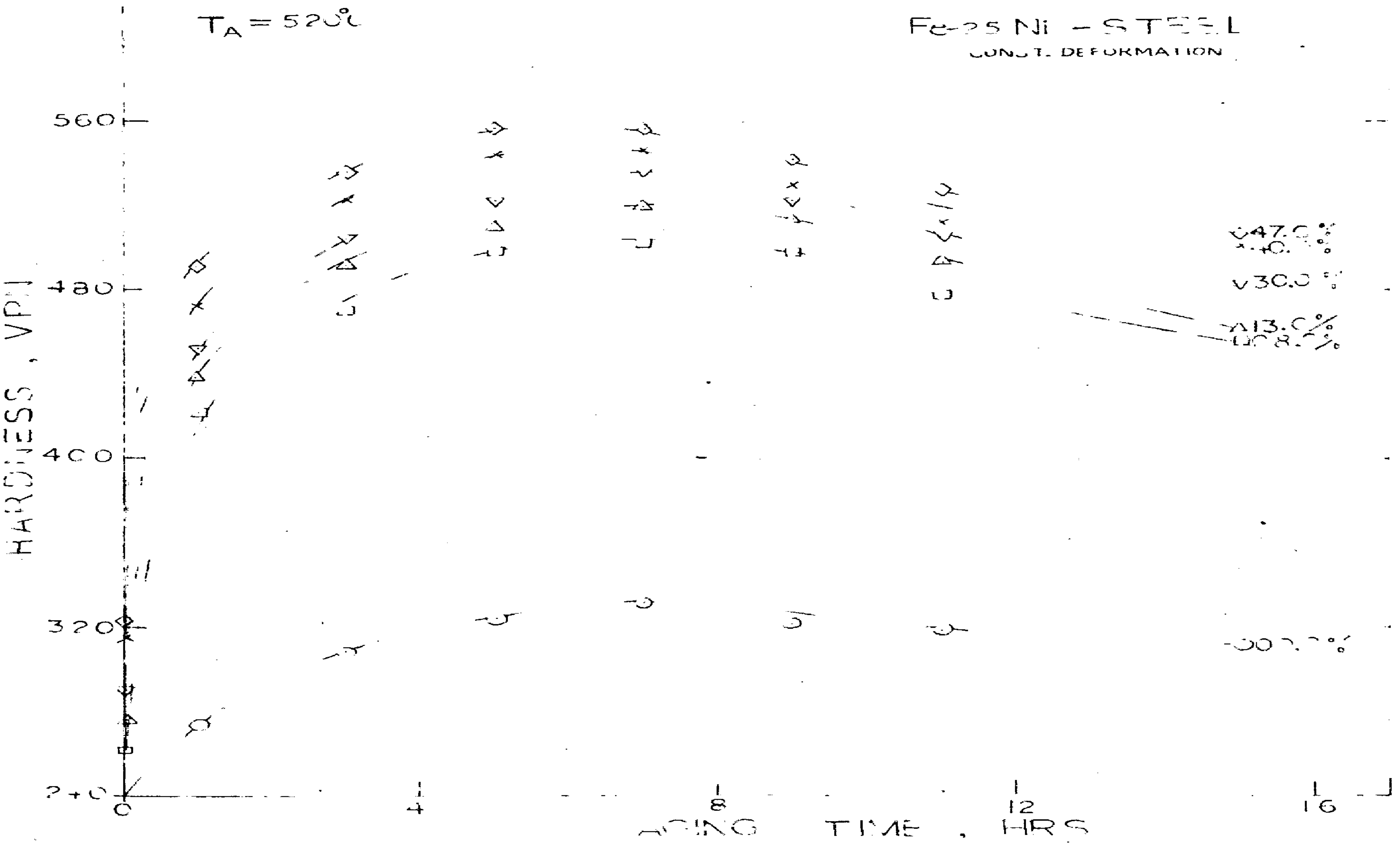
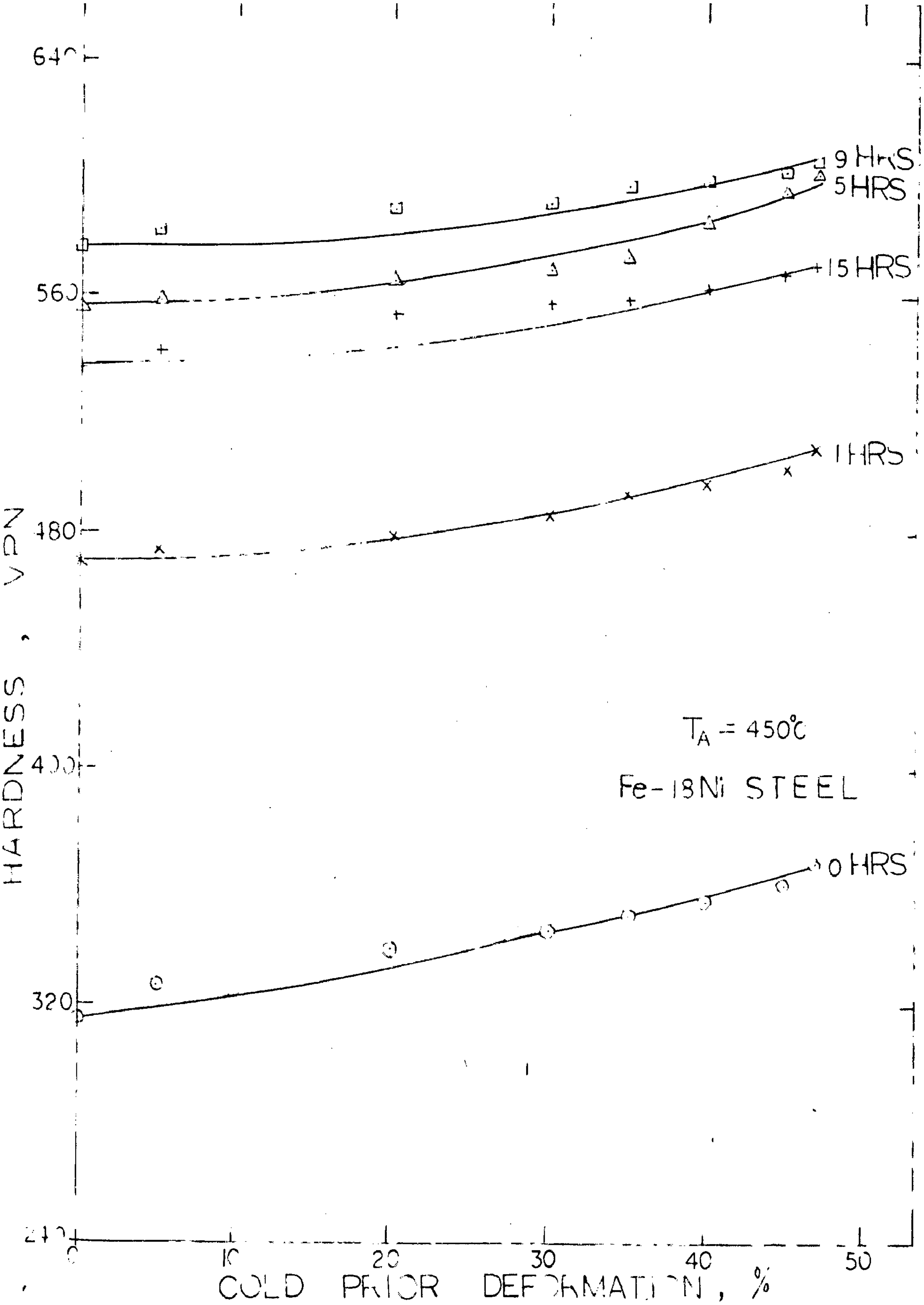
CONSTANT DEFORMATION
HARDNESS, VPN
560
480
400
320
240
0
4
8
12
16
AGING TIME, HRS
7
5
5
4

FIG.13 [illegible]


HARDNESS , VPN
560
480
400
320
240
0
4
8
12
16
AGEING TIME , HRS
46%
40%
35%
30%
20%
14%
8%
0%

[illegible]


T_A = 520°C
Fe-25Ni - STEEL
CONST. DEFORMATION
47.0%
40.0%
30.0%
13.0%
08.0%
00.0%
HARDNESS , VPN
560
480
400
320
240
0
4
8
12
16
AGING TIME , HRS



1.19 VARIATION OF HARDNESS WITH PRIOR COLD DEFORMATION DURING MARFORMING FOR Fe-18Ni MARAGING STEEL; AGING TEMPERATURE 450°C; FOR CONSTANT MARAGING PERIOD.

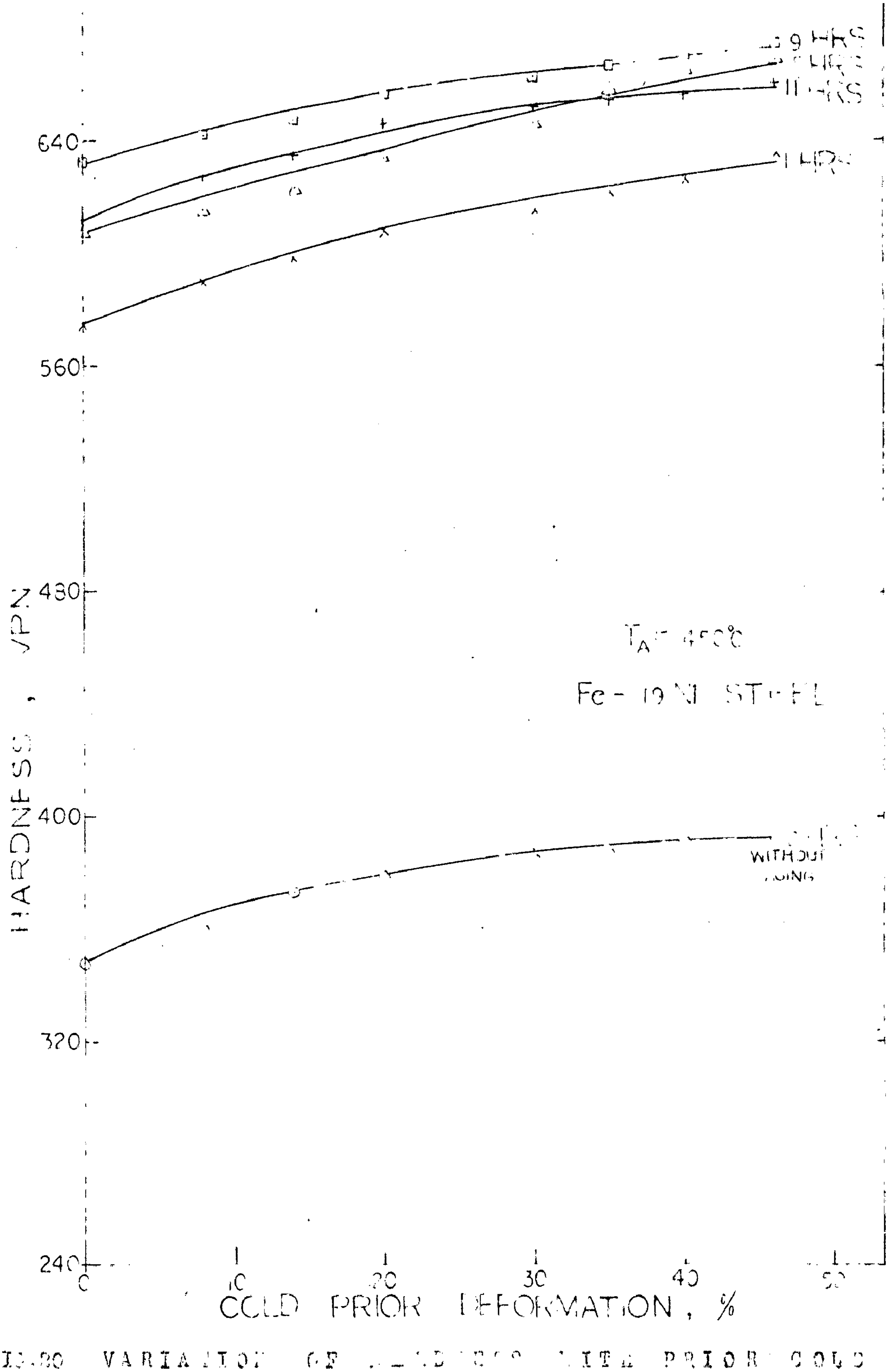
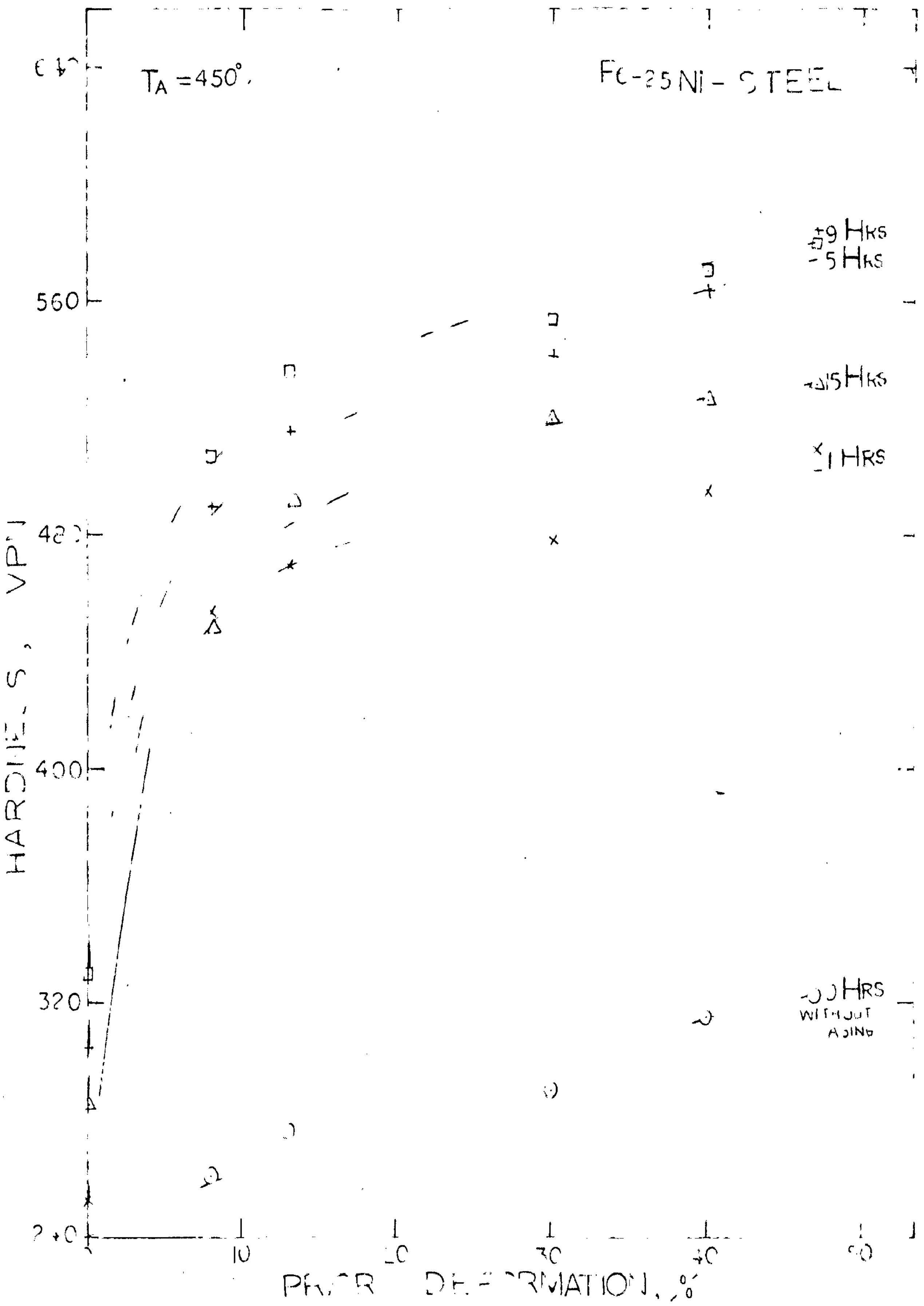


FIG.20 VARIATION OF HARDNESS WITH PRIOR COLD DEFORMATION DURING MARFORMING FOR Fe-19Ni MARAGING STEEL; AGING TEMPERATURE 450°C, FOR CONSTANT AGEING PERIOD.


T_A = 450°
Fe-25 Ni - STEEL
9 HRS
5 HRS
15 HRS
1 HRS
0 HRS WITHOUT AGING
HARDNESS, VPN
640
560
480
400
320
240
0
10
20
30
40
50
PRIOR DEFORMATION, %

[illegible]

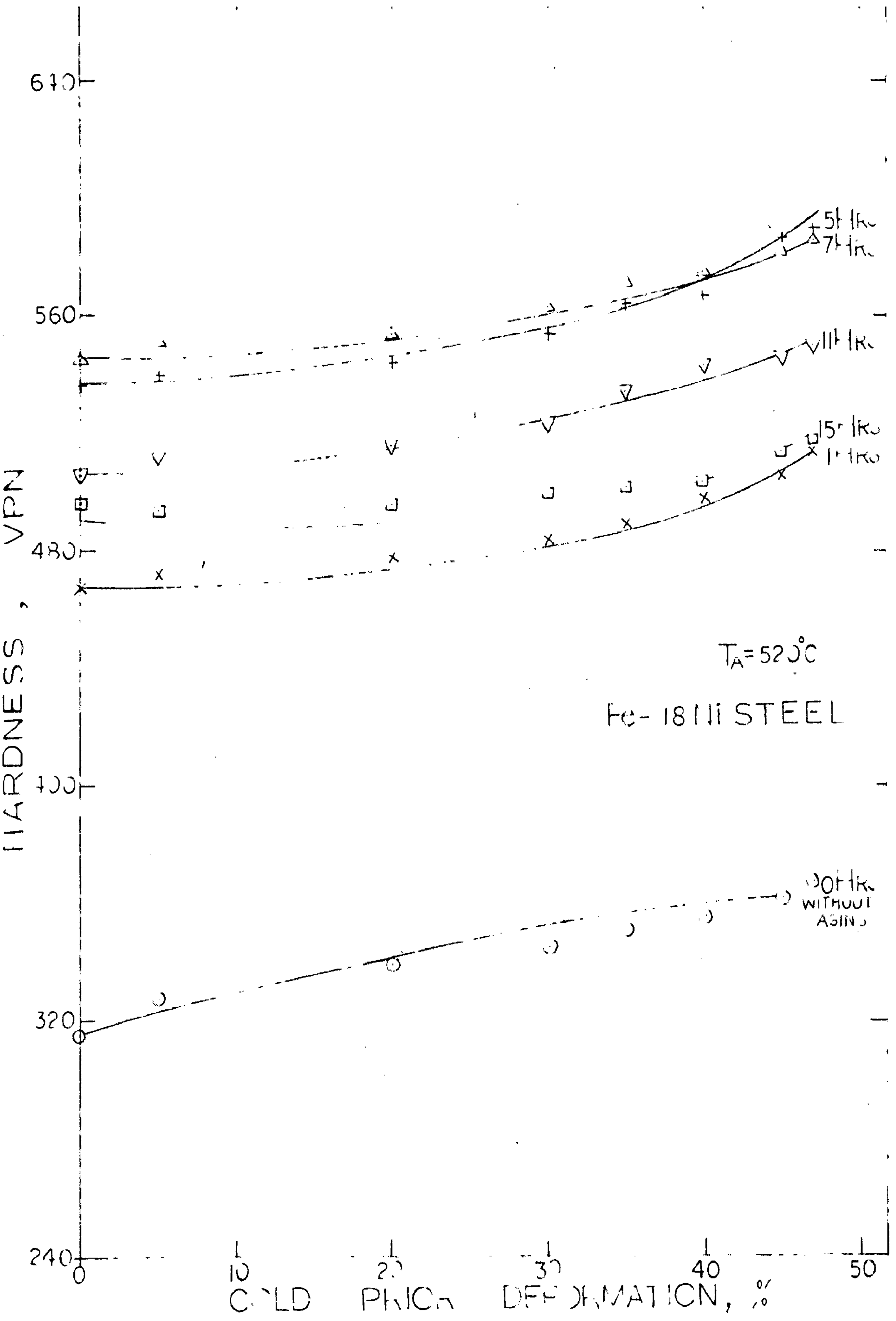


FIG.28 VARIATION OF HARDNESS WITH PRIOR COLD DEFORMATION DURING MARFORMING FOR Fe-18 Ni MARAGING STEEL; AGEING TEMPERATURE 520°C, FOR CONSTANT MARAGING PERIOD.

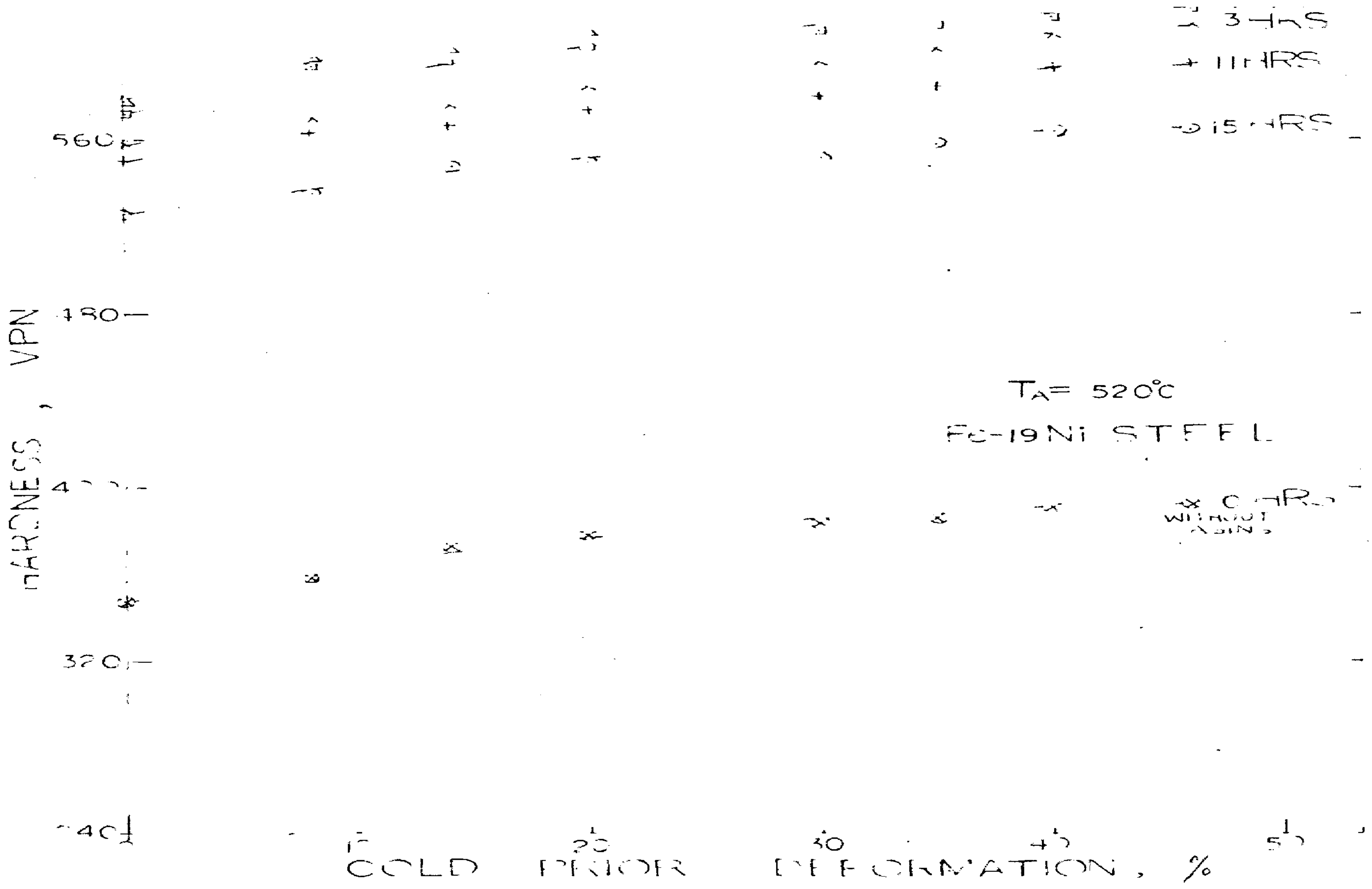
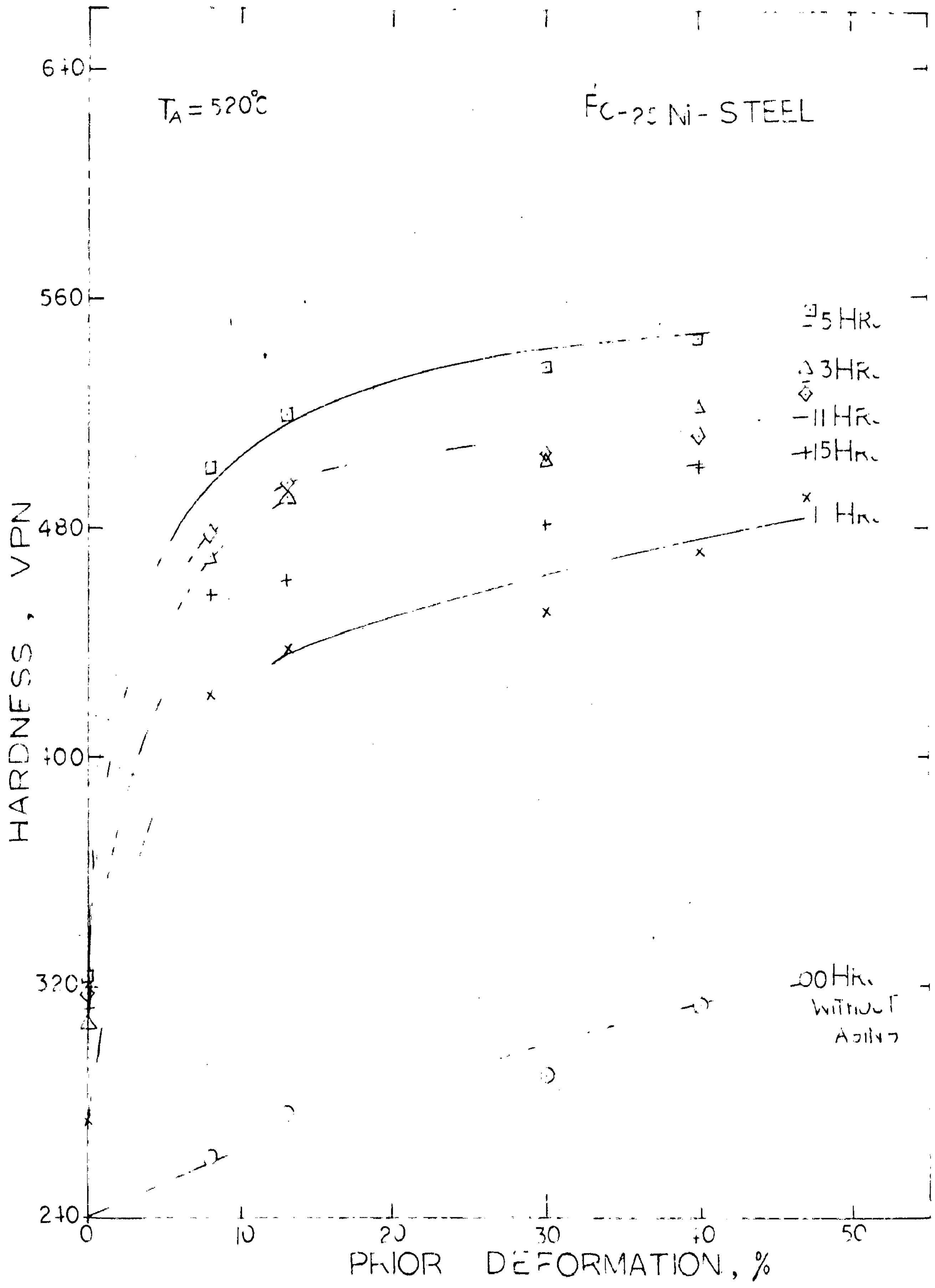


FIG 23 VARIATION OF [illegible] WITH PRIOR COLD DEFORMATION [illegible] FOR Fe-19Ni MARAGING STEEL [illegible] TEMPERATURE 520°C FOR CONSTANT [illegible] PERIOD.



FI. [illegible] VARIATION OF [illegible] PRIOR COLD DEFORMATION DUR[illegible] FOR Fe-25Ni [illegible] TEMPERATURE [illegible]°C [illegible] PERIOD

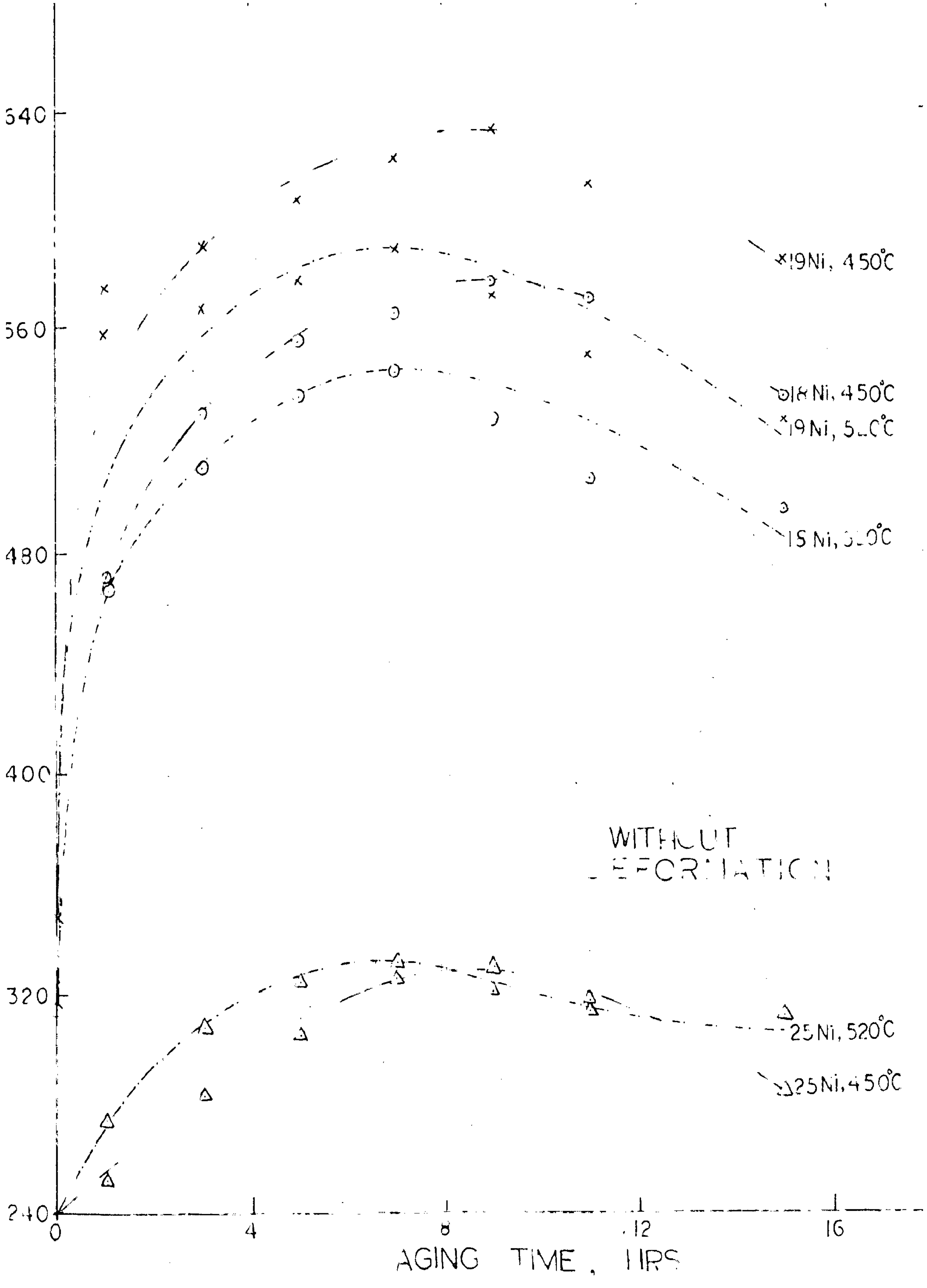


FIG.5 COMPARISON OF HARDNESS VARIATION OF DIFFERENT MARAGING STEELS WITH AGING PERIOD AT 450 AND 520°C RESPECTIVELY, WITHOUT DEFORMATION

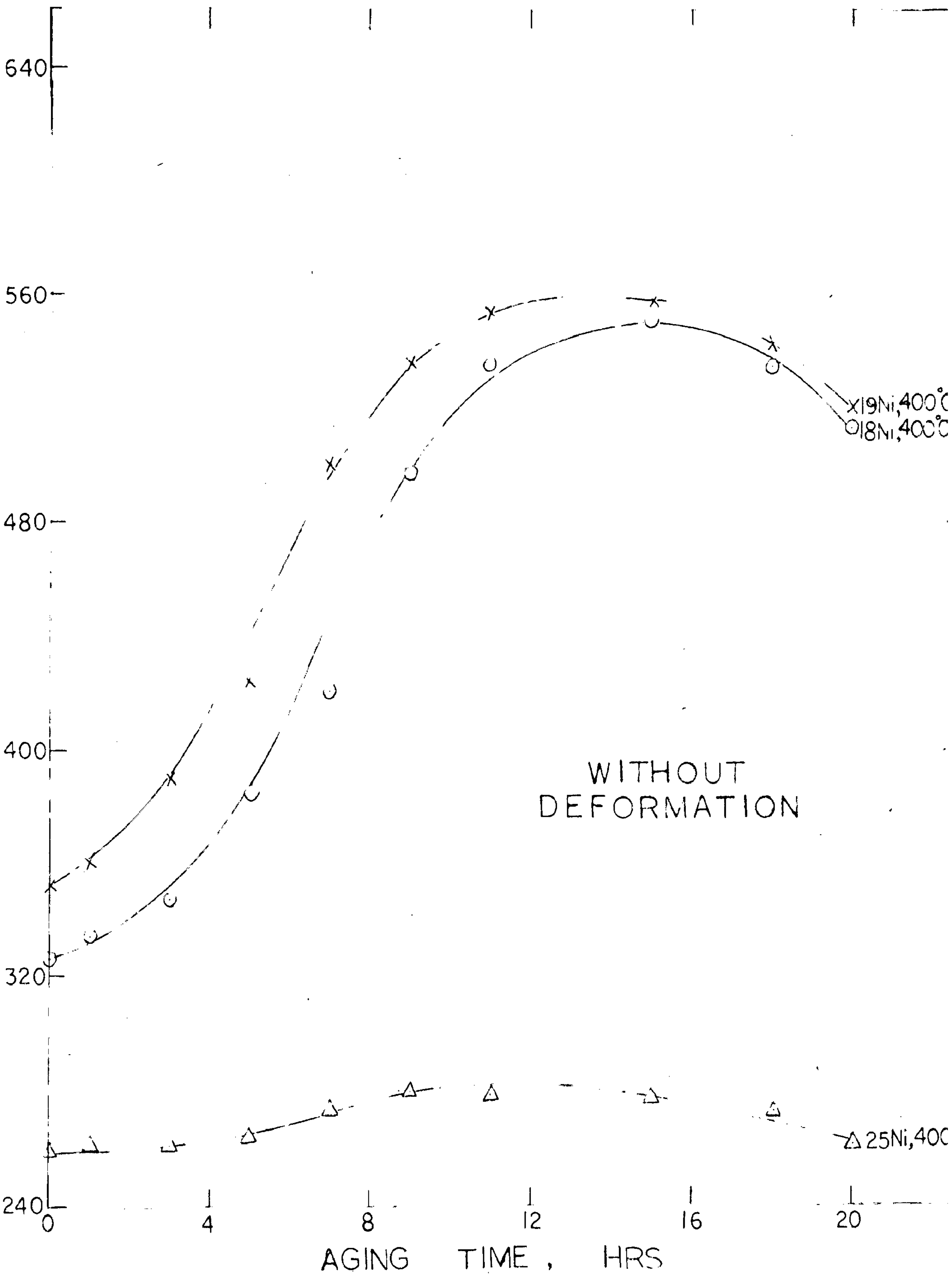


FIG.25(a) COMPARISON OF HARDNESS VARIATION OF DIFFERENT STEELS WITH AGING DURATION AT 400°C [illegible]

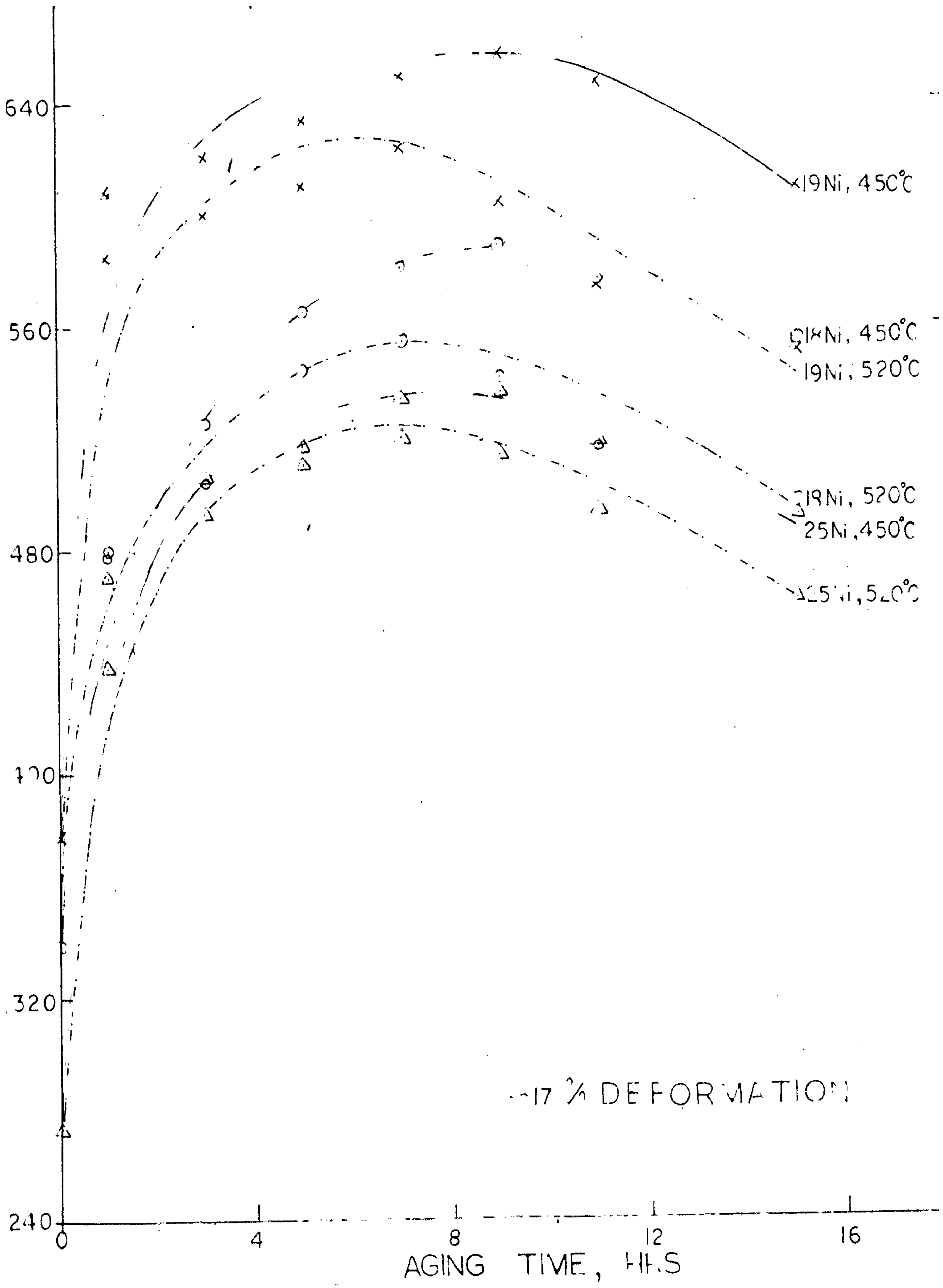
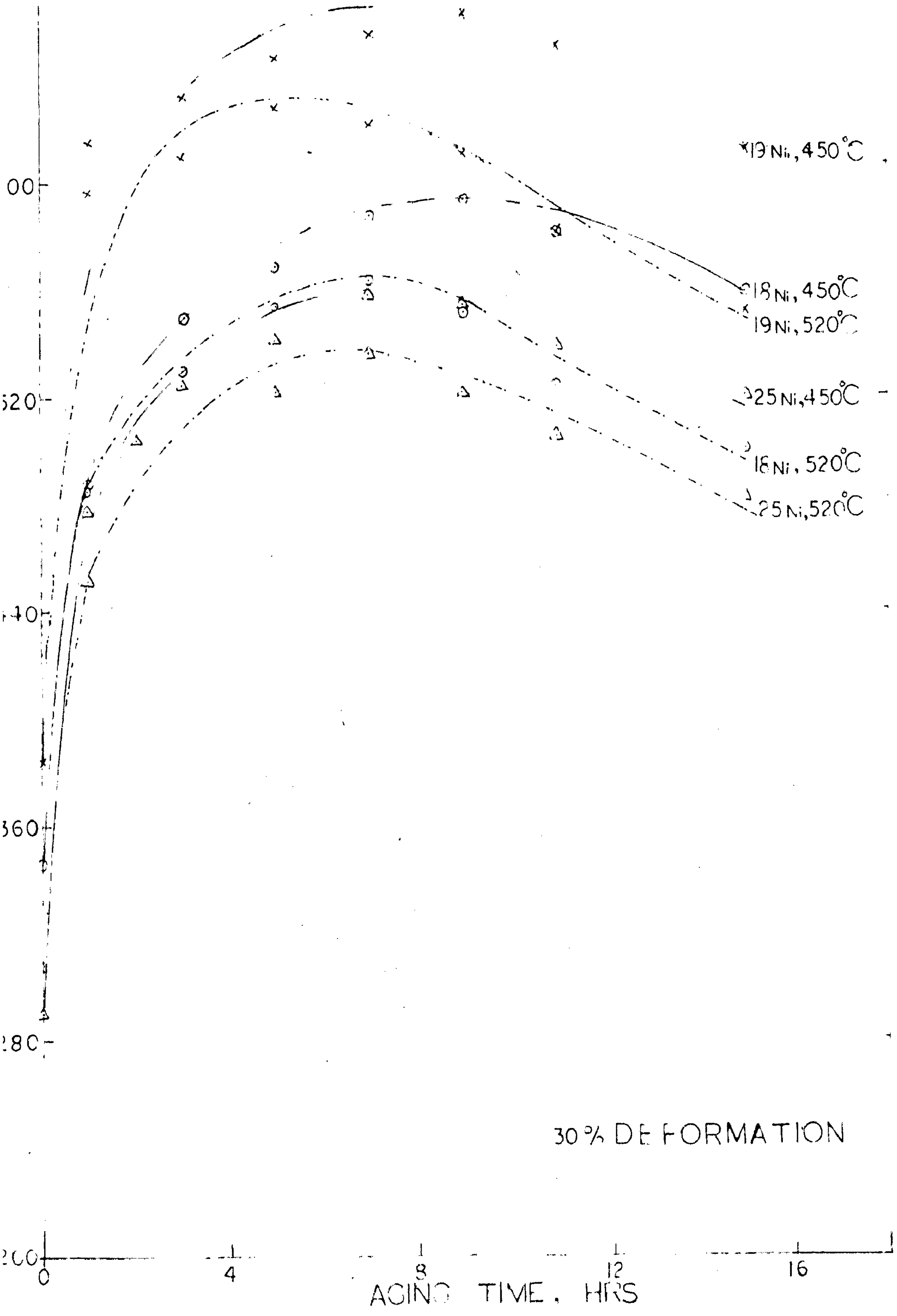
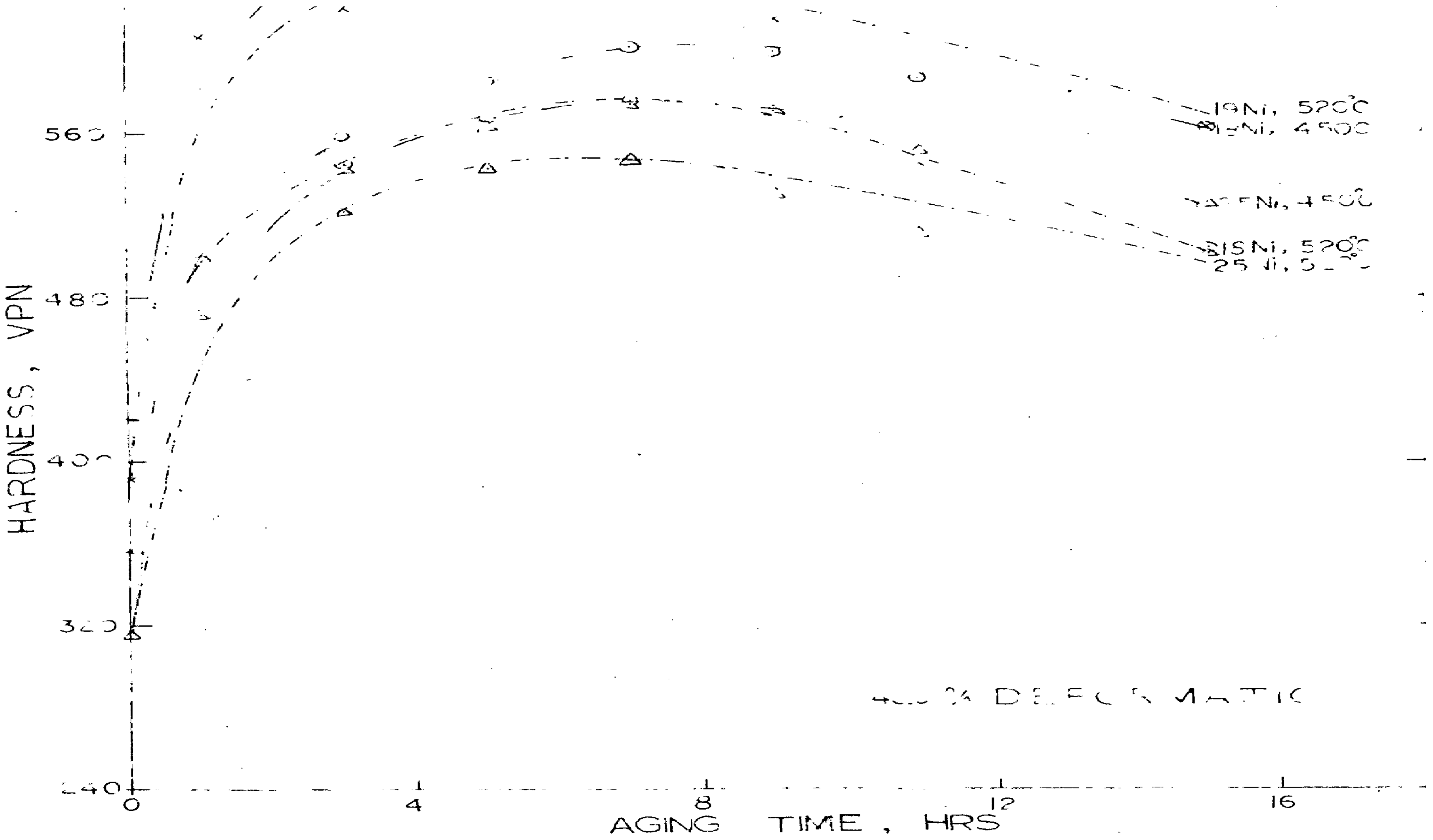


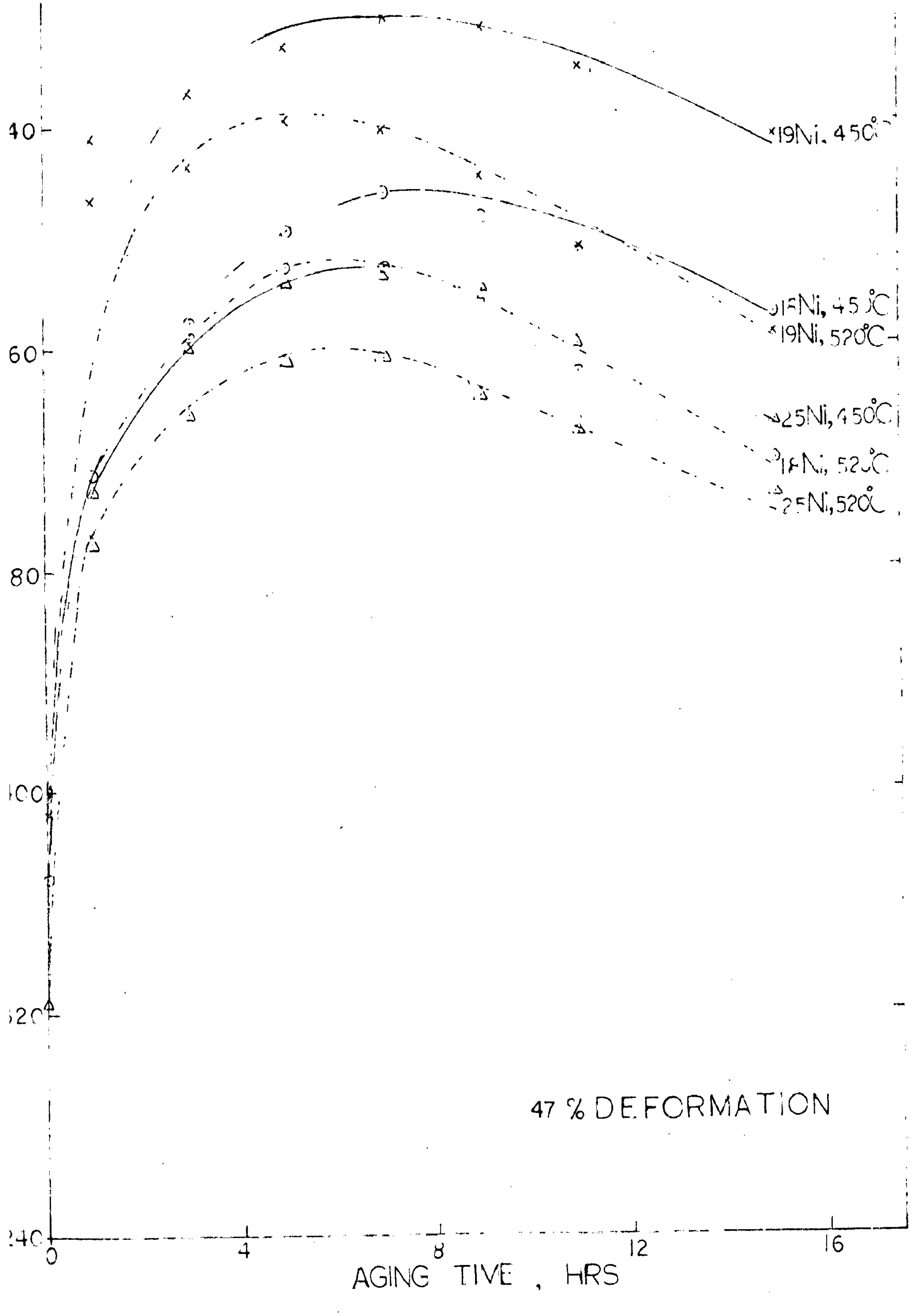
FIG. 19 [illegible] OF
[illegible] AGING
[illegible] SPECIMENS,
[illegible]


00
520
440
360
280
200
0
4
8
12
16
AGING TIME, HRS
19 Ni, 450°C
18 Ni, 450°C
19 Ni, 520°C
25 Ni, 450°C
18 Ni, 520°C
25 Ni, 520°C
30 % DEFORMATION

[illegible]


HARDNESS, VPN
560
480
400
320
240
0
4
8
12
16
AGING TIME, HRS
19Ni, 520°C
Ni, 450°C
Ni, 450°C
15Ni, 520°C
25 Ni, 520°C
% DEFORMATI

[illegible]


40
60
80
100
120
140
0
4
8
12
16
AGING TIVE , HRS
19Ni, 450C
18Ni, 450C
19Ni, 520C
25Ni, 450C
18Ni, 520C
25Ni, 520C
47 % DEFORMATION

[illegible]

Fe-18Ni and Fe-19Ni steels the hardness increases continuously with cold-deformation for constant aging period, while Fe-25Ni steel shows discontinuity in this linearity (figures 21 and 24). The nature of the curves is almost the same at 450°C and 520°C aging temperature for all the three maraging steels.

4.3 Study of Micro-structures :

Optical micrographs of the air-quenched Fe-18Ni, Fe-19Ni maraging steels after solution treatment show almost 100 per cent martensite (figures 31A and 31B). However, micro-structures of the quenched Fe-25Ni steel show martensite as well as some retained austenite (Fig.31C). In the micro-structures of the aged samples for all the maraging steels it was observed that two distinct phases- the dark etching martensite and the bright austenitic areas are present. A careful study of all the maraging steels under investigation aged at different temperatures for different periods of time clearly shows that the amount of austenite gradually increases with continued aging. This shows that reversion to austenite from martensite takes

[A] Fe-18Ni steel

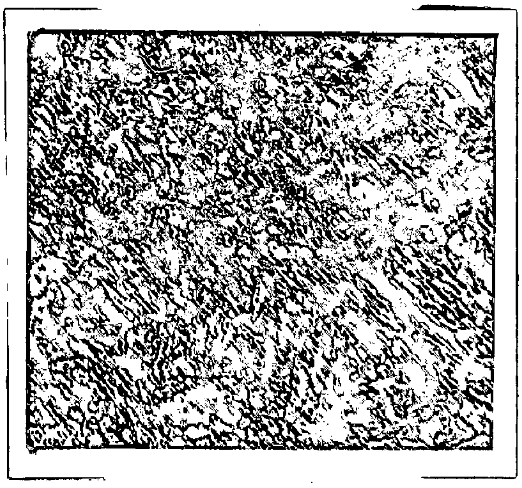
[B] Fe-19Ni steel

[C] Fe-25Ni steel

Fig.30. Micro-structures of Various Maraging Steels in the as-received condition (X450)

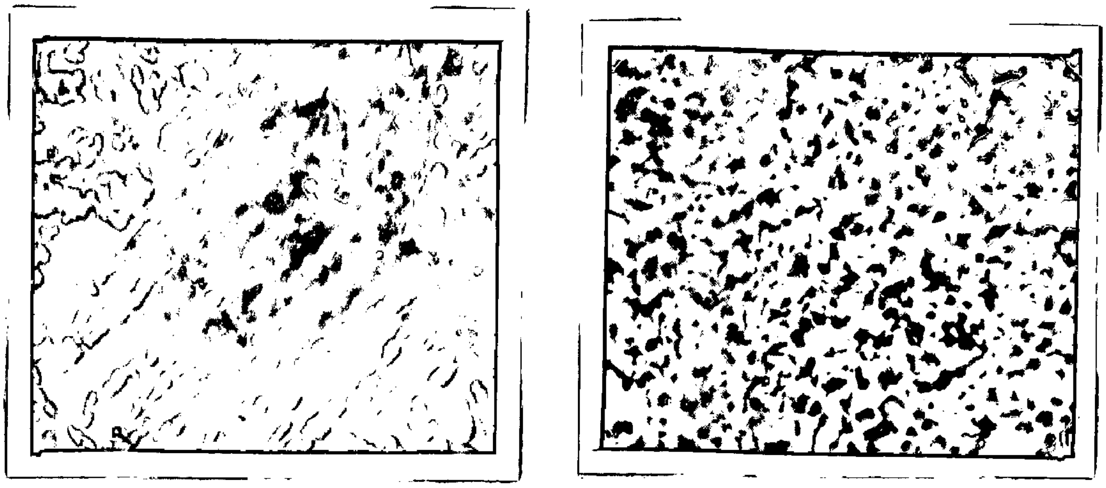
[A] Fe-18Ni Steel.

[B] Fe-19Ni Steel.



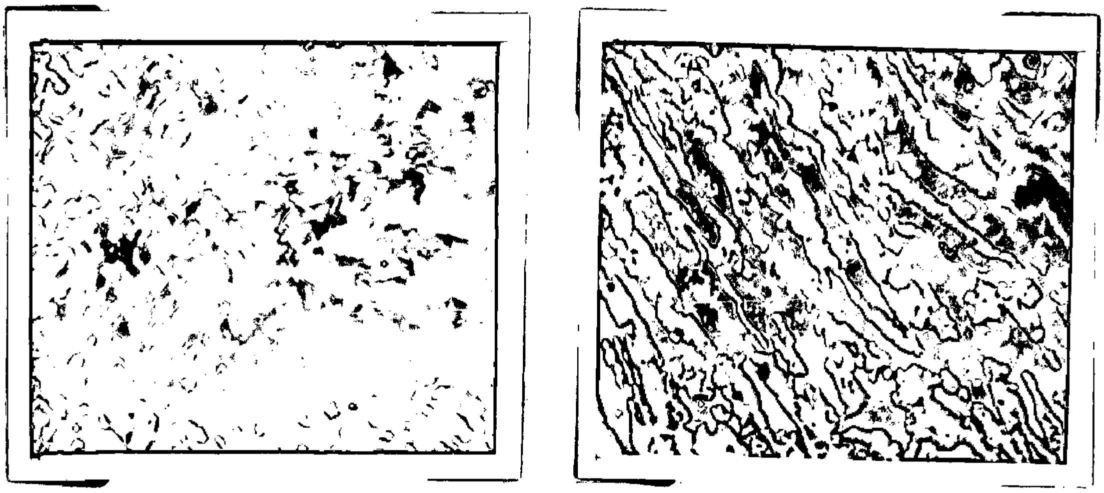
[C] Fe-25Ni Steel.

Fig.31. Micro-structures of Air-quenched Maraging Steels.
(X450)



[A] After 30 pct. deformation, without aging.

[B] 30 pct. deformation, aged at 450°C for 8 hours.



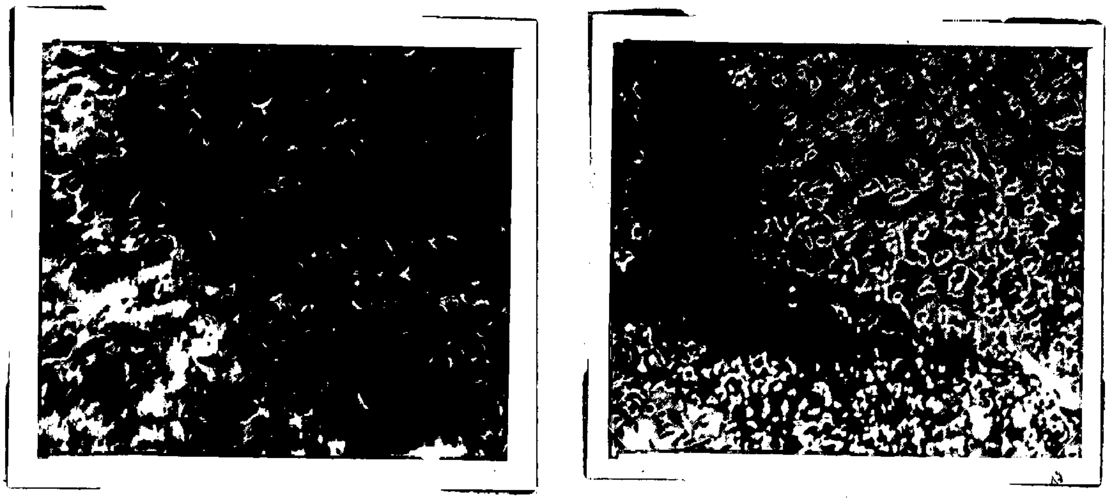
[C] 30 pct. deformation, aged at 520°C for 9 hours.

[D] 35 pct. deformation, aged at 450°C for 15 hours.

Fig.32. Micro-structures of Fe-18Ni Maraging Steel (X450)

[A] After 30 pct. deformation, without aging.

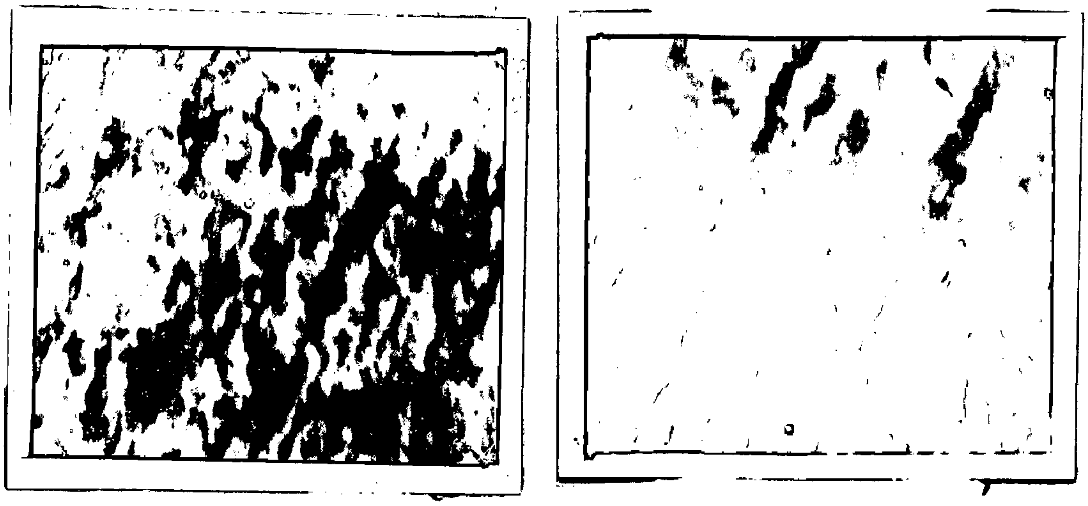
[B] 30 pct. deformation, aged at 450°C for 9 hours.



[C] 30 pct. deformation, aged at 450°C for 11 hours.

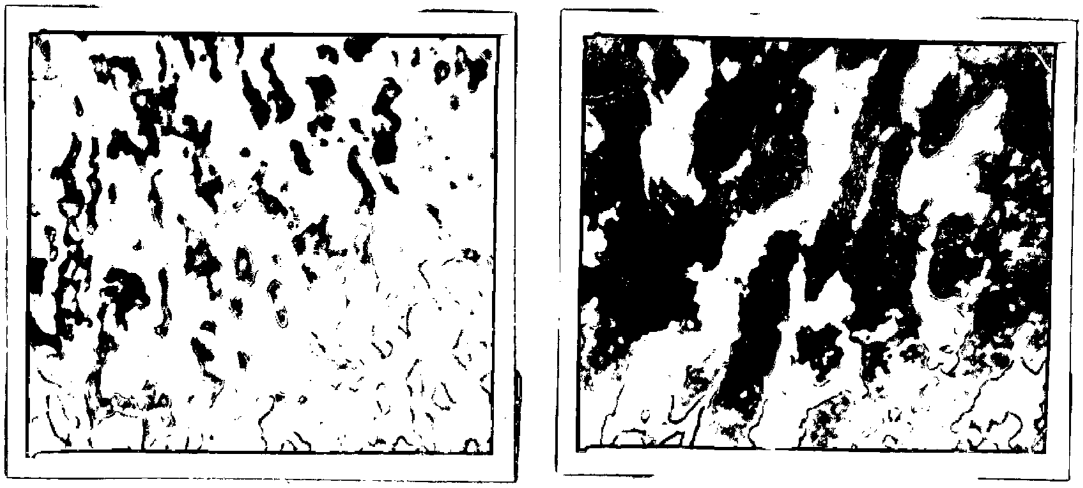
[D] 40 pct. deformation, aged at 450°C for 15 hours.

Fig.33. Micro-structures of Fe-19Ni Maraging Steel (X450)



[A] 8 pct. deformation,
aged at 520°C
for 5 hours.

[B] 13 pct. deformation,
aged at 520°C
for 9 hours.



[C] 30 pct. deformation,
aged at 450°C
for 7 hours.

[D] 30 pct. deformation,
aged at 450°C
for 9 hours.

Fig. 34. Micro-structures of Fe-25Ni Maraging Steel
(X450)

place along with the aging reaction. However it may be emphasized that in optical metallography very fine precipitates could not be resolved.

The micro-structure (figures 32D, 33C, 33D, and 34D) of the specimen aged for longer period shows presence of large precipitates, which are presumably due to coarsening of the fine precipitates detected earlier at the initial stage of aging.

CHAPTER - V

DISCUSSION.

An essential feature of the maraging steels is a martensitic transformation from γ to α with the resultant production of supersaturated b.c.c. solid solution. This solution decomposes to form precipitates during a subsequent aging treatment. The strength level is achieved through a combination of solid solution hardening[38] and the precipitation hardening[39], the latter being most important.

The investigation shows that the maraging reaction in all the three experimental alloys is an interplay of two phenomena, namely, (i) Precipitation in the martensitic matrix (ii) Reversion of martensite to austenite.

From the hardness curves it is seen that the hardness of all the three steels increases very rapidly initially and then slowly until some peak hardness value is reached beyond which the hardness drops indicating overaging. It was reported by Speich and Swann[40] that structures of the air-quenched Fe-18Ni and Fe-19Ni maraging steel consists of bundles of martensite needles with very high dislocation density similar for low-carbon martensites in plain carbon steel; however, the structure of Fe-25Ni maraging steel shows some retained austenite along with martensite. The rapid increase in hardness has been attributed to the dislocation nucleated fine precipitation at the very early stage of maraging. During the aging-treatment some re-arrangement of dislocations takes place in the martensitic matrix and simultaneously precipitation starts without any incubation period by the heterogenous nucleation at dislocations. Because of the high density of dislocation, ($\sim 10^{11}/cm^2$), a fine dispersion of the precipitate is obtained.

In the Fe-18Ni maraging steel the precipitates in solution treated and aged conditions are acicular and evenly distributed. This type of precipitate has been identified by Miller and Mitchell[41] as Ni_3Ti. A disc shaped precipitate identified as Fe_2Mo has also been reported[42]. A conflicting identification of the precipitates has been reported by Chilton and Barton[43] in Fe-18Ni maraging steels. These authors reported that one precipitate had the composition Ni_3Mo while the other was designated as σ (Fe-Ti). They reported that Ni_3Mo precipitate had a rod or ribbon shaped morphology and the σ precipitate was spherical. The work of Chilton and Barton appears to be definite. It has been reported that a disc shaped precipitate frequently forms on dislocations and there is a strong relationship between dislocation density and precipitation distribution[44].

Hardening of Fe-19Ni martensites containing titanium is accomplished by the formation of very fine dispersion of Ni_3Ti precipitate. As reported by Speich[13], the first phase that appears is stable in the Ni-Ti binary, but not in the iron-rich corner of the Fe-Ni-Ti ternary system. Possibly, this is associated with easier nucleation of the more complex close packed AB_3 type compounds, such as Ni_3Ti, from the b.c.c. lattice compared to the nucleation of the structurally more complex $MgZn_2$-type laves phase such as $(Fe, Ni)_2Ti$. The hardening precipitate in the Fe-25Ni maraging steel has been identified as $(Fe,Ni)_3$ (Ti,Al).

In our observations it is seen that the hardness for Fe-19Ni maraging steel is ~~much~~ ~~less~~ more in the quenched and as well as in the aged condition at any temperature. This can be attributed to the fact that in Fe-19Ni maraging steel large volume fraction of precipitate is formed due to higher solute-content i.e., nickel and resulting in finer dispersion of precipitate particle. In the case of Fe-25Ni maraging steel some retained austenite is present after quenching. This fact is also supported by optical metallography.

The high strength of maraging steels is the consequence of fine dispersion of the precipitate,which often results in an inter-particle spacing of the order of 200 and 300 A°. It has been customary to apply the theory of Orowan to explain the strength of maraging steels. This model certainly requires some modifications, when the particle distance becomes small. For such condition Ansell has derived a model[44] in which the strength of the particles are as important as the spacing between the particles. During the initial stage of precipitation process when the particles are very small, the yield strength, σ_y , of the alloy is a function of the volume fraction 'f' of the precipitation and the shear strength τ_p of the particles. Ansell derived the equation :

$$\sigma_y = \frac{\tau_p}{4} \frac{f^{1/3}}{0.83 - f^{1/3}}$$

When the size of the particles passes a certain critical diameter, dc, the yield strength can be written :

$$\sigma_y = \sqrt{\frac{Gb \ \tau_p}{2\lambda}}$$

where G = shear modulus ; b = Burgers Vector of the matrix; λ= interparticle spacing. Since the yield strength is now also a function of the interparticle distance, particle coarsening will cause a decrease of yield strength. The maximum yield strength is obtained when the particles have grown to the critical diameter, dc, which is determined by the volume fraction of the precipitate and by the strength of the particles. The critical diameter, dc, of the precipitate particle can be written as:

$$dc = \frac{8Gb}{\tau_p} \frac{0.83 - f^{1/3}}{f^{1/3}}$$

This consideration demonstrates that the high strength in maraging steel is not only due to the very fine interparticle spacing but also due to the very high shear strength of the precipitate particles.

From the graphs it is observed that with over-aging, there is progressive decrease in hardness with increasing time and temperature. The overaging of these maraging steels, as already indicated, is due to the combination of the two processes occurring simultaneously, viz; growth of the precipitated particles and the reversion of the austenite at higher aging temperatures. The overaged micro-structures of all the three steels aged at 450°C and 520°C show large precipitates which are presumably due to coarsening of fine precipitates present at the initial stage of aging (figures 32D, 33C, 33D, and 34D). The amount of austenite formed increases with aging time, although it does not appear in significant quantities in the alloys that undergo precipitation hardening until the aging peak is reached. Austenite appears to nucleate at the martensite needle boundaries as thin film which then thickens, resulting finally in alternate plates of ferrite and austenite[13]. The lower rate of austenite formation with titanium, aluminium, or molybdenum additions may be a result either of the effect of the alloying element in shifting the equilibrium relations between the ferrite and austenite so that ferrite becomes relatively more stable with respect to austenite, or of the rapid formation of nickel rich compound e.g., Ni_3Ti, which drain nickel from the ferrite before the austenite can form and thus increases the stability of the ferrite with respect to austenite.

Increasing the temperature of aging in all the three maraging steels decreases the time required to reach peak hardness for any constant deformation(figures 25-29). It may be attributed due to the fact that at higher temperatures faster diffusion of atoms takes place. It is also observed that the peak hardness attained did not vary much with temperature. This could be due to constant density of nucleation sites present within the martensitic needles.

Cold deformation after solution treatment of the given steels improves the hardness obtained during subsequent aging. This improvement is a result of a change in precipitate distribution and the morphology as function of the increased dislocation generation and their interaction accompanying the cold deformation. Cold deformation increases the density of dislocations, dislocation tangles, and dislocation debris. Bush[29] proposed that the dislocation distribution produced by thermo-mechanical process controlled the precipitate dispersion during the subsequent aging treatment. The dislocations or dislocation debris may serve as nucleation sites, or as channels for more rapid diffusion of elements participitating in the aging reaction, or both. So the increase in dislocation density in cold-worked material leads to an increase in density of precipitate in the aged material and hence the increase in hardness.

The rate at which aging proceeds increases with increase in prior cold-deformation for the given maraging steels (figures 13-18). This can be attributed to the fact that more tangles are present in specimens heavily deformed, which leads to an increase in the density of precipitates and thus results in higher hardness.

It is observed that for a fixed aging period the hardness of Fe-18Ni and Fe-19Ni steels increases linearly with increase in the prior cold-deformation, (figures 19, 20, 22, and 23), but in case of Fe-25Ni steel (figures 21 and 24) the increase in hardness is not a continuous one, and exhibits discontinuity in the region of 10 per cent cold-reduction. The increase in hardness of the Fe-25Ni-Ti-Al steel during the initial stages of cold reduction is perhaps associated with the work-hardening of the martensite and retained austenite accompanied with precipitation from martensite. The slow increase in hardening on further cold reduction appears to be related with the decomposition of the retained austenite into martensite. It is striking to note that the absence of maraging does not reveal this subtle hardening difference.

It is interesting to investigate the peak-hardness increment with the extent of cold-deformation for

Table - V

Difference in peak hardness of Fe-18Ni
Thermo-mechanically tested Marging Steel.

omposition	Temperature	Hardness	Amount of prior cold deformation, per cent				
	C°	VPN	0	17	30	40	47
e-18Ni	450	Peak Value	579	588	593	604	616
		Pct.increment in peak value x 10^{-2}	Nil	155	242	432	639
	520	Peak value	546	554	564	576	592
		Pct.increment in peak value x 10^{-2}	Nil	146	330	550	841

Table - VI

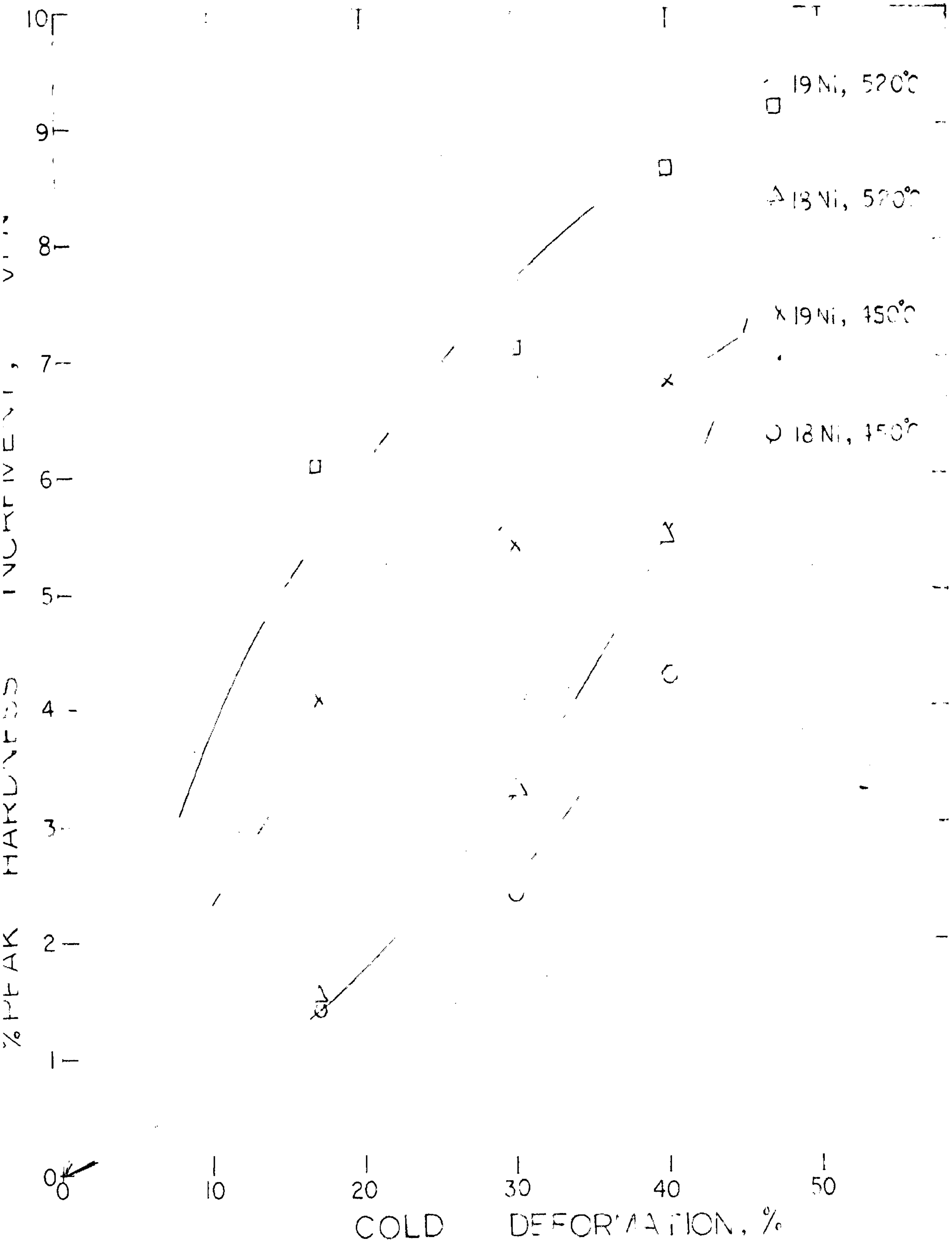
Difference in peak hardness of Fe-19Ni
Thermo-mechanically tested Maraging Steel.

mposition	Temperature	Hardness	Amount of prior cold deformation, per cent				
	C^0	VPN	0	17	30	40	47
-19Ni	450	Peak value	632	658	666	675	678
		Pct.increment in peak value x 10^{-2}	Nil	411	538	681	728
	520	Peak value	590	626	632	641	576
		Pct.increment in peak value x 10^{-2}	Nil	611	712	865	915

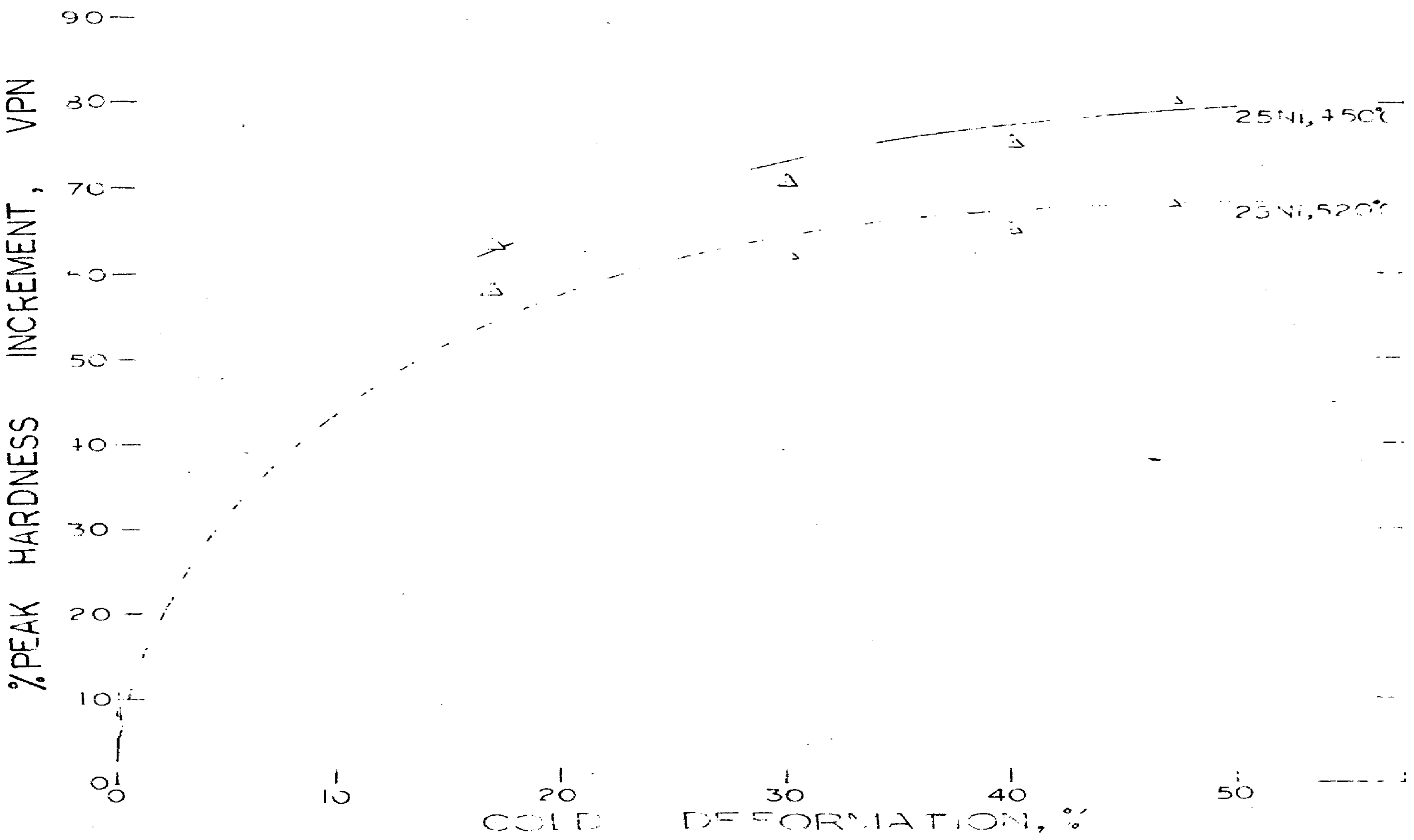
Table - VII

Difference in peak hardness of Fe-25Ni
Thermo-mechanically tested Maraging Steel.

omposition	Temperature	Hardness	Amount of prior cold deformation, per cent				
	C°	VPN	0	17	30	40	47
e-25Ni	450	Peak Value	328	536	560	576	591
		Pct. increment in Peak Value x 10^{-1}	Nil	634	707	756	803
	520	Peak Value	332	524	538	548	560
		Pct. increment in Peak Value x 10^{-1}	Nil	578	620	651	686


% PEAK HARDNESS INCREMENT, VHN
10
9
8
7
6
5
4
3
2
1
0
0
10
20
30
40
50
COLD DEFORMATION, %
□ 19 Ni, 520°C
△ 18 Ni, 520°C
× 19 Ni, 450°C
○ 18 Ni, 450°C

[illegible]


%PEAK HARDNESS INCREMENT, VPN
90
80
70
60
50
40
30
20
10
0
0
10
20
30
40
50
COLD DEFORMATION, %
25Ni, 450°C
25Ni, 520°C

all the three maraging steels (figures 35 and 36). Tables V-VII show the data of such increments for all the three steels calculated from the figures 25-29. For all the maraging steels it is noted that the variations of peak hardness increment is not linear one. In the case of Fe-19Ni and Fe-25Ni maraging steels, in early stage of deformation the variation is a rapid one, while for Fe-18Ni maraging steel the picture is reversed. For both the steels i.e., Fe-18Ni and Fe-19Ni, with increase of aging temperature the peak hardness increment is increased. However, in the case of Fe-25Ni maraging steel, the trend is reversed. This appears to be related to the austenite reversion at elevated temperatures for such steel composition. At higher degree of prior cold deformation, say, 45 per cent the picture is not consistent as in case of lesser degree of deformations. For example, the peak hardness increment of Fe-18Ni steel at 520°C maraging temperature is more than Fe-19Ni steel at 450°C.

CHAPTER - VI

CONCLUSIONS.

1. Hardness value of solution treated and air-cooled specimens of Fe-19Ni steel is higher than that of Fe-18Ni maraging steel. However, hardness value of Fe-25Ni maraging steel is lesser than those of either composition.
2. A plot of hardness with aging period reflects maxima for all the three maraging steels investigated.
3. For all the steels investigated with increase in prior cold deformation, the hardness for any period of aging increases.
4. For each maraging steel it is observed that an increase in the prior cold-deformation shifts the hardness peak towards lesser aging period.
5. The variation of hardness with aging time for any fixed aging temperature also shows a maxima, which shifts towards lesser aging period, when temperature is increased.

6. For a fixed aging period the hardness of Fe-18Ni and Fe-19Ni maraging steels increases linearly with increase of prior cold deformation. But in case of Fe-25Ni steel there is a discontinuity in this linearity of such curves. In this case upto 8 per cent cold-deformation the hardness increase is rapid which gets decreased with further increase of cold-deformation.

7. For no prior cold-deformation it is observed that the hardness peak for constant maraging temperatures of 450 and 520°C and for any steel composition investigated occurs at the same aging period, while at 400°C the hardness peak shifts towards higher aging time. Prior cold-deformation upto 17 per cent, the peak hardness remains unaltered. However, with further increase in prior cold-deformation i.e., 40 per cent there is a progressive shift of the peak hardness period towards lower values. But a still higher prior deformation i.e. 47 per cent causes no change in comparison with those having 40 per cent prior cold deformation.

8. The peak hardness increment variation with the extent of cold deformation for all the three maraging steels is not linear one. In case of Fe-19Ni and Fe-25Ni maraging steels in early stage of deformation the variation is rapid one, while for Fe-18Ni maraging steel the picture is reversed.

CHAPTER - VII

SUGGESTIONS FOR FURTHER STUDIES

On the basis of the experimental results already obtained it is evident that scope of thermo-mechanical treatment of maraging steel is very extensive. However, a number of parameters are still necessary to understand the picture completely and give a clear cut base . In this regard the following types of work may be further extended.

1. A systematic study of phase identification by electron-microscopy technique, not only at room temperature but also at elevated temperatures.
2. Magnetic measurements could very well be extended to quantitatively estimate the pressure of retained austenite.
3. A detailed micro-hardness study is also desirable in order to evaluate the possible presence of different micro-constituents.

4. Various investigations have revealed that substitution of manganese for nickel has not been found of much significance because of embrittling behaviour. A useful research could be directed in this field in involving Fe-Mn maraging steel by studying in details the precipitation process and their kinetics.

These above techniques will be of great significance in understanding some non-linear variations of properties as obtained by us in terms of complex precipitate.

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Certified that the attached Thesis/Dissertation on Thermo Mechanical Treatment of Maraging steels

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