

**EFFECTS OF HEAT TREATMENT AND CHEMICAL COMPOSITION
ON MICROSTRUCTURE AND MECHANICAL PROPERTIES OF
HADFIELD STEELS**

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SERHAT ALYAZ

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Approval of the Graduate School of Natural and Applied Sciences

Prof. Dr. Canan ÖZGEN

Director

I certify that this thesis satisfies all the requirements as a thesis for the degree of Master of Science.

Prof. Dr. Bilgehan ÖGEL

Head of Department

This is to certify that we have read this thesis and that in our opinion it is fully adequate, in scope and quality, as a thesis for the degree of Master of Science.

Assoc. Prof. Dr. C. Hakan GÜR

Supervisor

Examining Committee Members

Prof. Dr. Haluk ATALA

Prof. Dr. Bülent DOYUM

Prof. Dr. Rıza GÜRBÜZ

Assoc. Prof. Dr. Cevdet KAYNAK

Assoc Prof. Dr. C. Hakan GÜR

ABSTRACT

EFFECTS OF HEAT TREATMENT AND CHEMICAL COMPOSITION ON MICROSTRUCTURE AND MECHANICAL PROPERTIES OF HADFIELD STEELS

Alyaz, Serhat

M.S., Department of Metallurgical and Materials Engineering

Supervisor: Assoc. Prof. Dr. C. Hakan Gür

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The aim of this thesis is to investigate the effects of Mn content and alloying additions such as Cr and Mo, and various heat treatment procedures on both microstructure and mechanical properties of austenitic manganese (Hadfield) steels. For this purpose, steels with two different Mn content were considered (12-14 Mn, 16-18 Mn). First, five different heat treatment procedures were applied to the as-cast 12-14 Mn specimens to decide the procedure resulting the optimum tensile properties. Then, the specimens having various amounts of Mn, Cr and Mo were cast and heat-treated to investigate the effect of alloy modifications on austenitic manganese steels. Optical and scanning electron microscopies were used for microstructural investigation. To determine the mechanical properties, tensile tests and hardness tests were carried out. In addition to correlation between microstructure and mechanical properties, ultrasonic velocity measurements were also done. The results show that both composition and heat treatment affect the performance of hadfield steels extensively, and these changes also affect the propagation velocity of the ultrasonic waves.

Keywords: Austenitic manganese steel, mechanical property, ultrasound velocity

ÖZ

ISIL İŞLEM VE KOMPOZİSYONUN HADFIELD ÇELİKLERİN MİKROYAPISINA VE MEKANİK ÖZELLİKLERİNE OLAN ETKİLERİ

Alyaz, Serhat

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Bu tezin amacı bileşimdeki Mn miktarının veya bileşime alaşım olarak eklenebilen Cr veya Mo gibi elementlerin ve değişik ısıt işlemlerinin yüksek manganlı (Hadfield) östenitik çeliklerin mikro yapısında ve mekanik özelliklerinde yarattığı etkiyi incelemektir. Bu amaçla iki değişik Mn miktarına sahip (12-14 Mn, 16-18 Mn) yüksek manganlı çelikler incelemeye alındı. İlk olarak optimum çekme değerlerini veren ısıt işlem prosedürünü belirleyebilmek için 12-14 Mn çelik çubuklara beş değişik ısıt işlem uygulandı. Daha sonra kompozisyonun ve alaşım elementlerinin yüksek manganlı çeliklere etkisini inceleyebilmek için bileşiminde değişik oranlarda Mn, Cr, Mo bulunduran numune çubuklar döküldü ve ısıt işleme tabi tutuldu. Mikroyapı incelemeleri için optik ve tarama elektron mikroskopları kullanıldı. Mekanik özelliklerin ölçümü için çekme testleri ve sertlik testleri yapıldı. Mikroyapı ve mekanik özelliklerin korelasyonuna ek olarak numunelerde ultrasonik hız ölçümleri yapıldı. Elde edilen sonuçlar hem kompozisyonun hem de ısıt işlemin Hadfield çeliklerin performansını büyük ölçüde etkilediğini gösterdi. Bu değişimler yüksek manganlı çeliklerdeki ultrasonik dalgaların hızını da etkilemektedir.

Anahtar Kelimeler: Östenitik manganlı çelik, mekanik özellikler, ultrasonik hız

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CHAPTER I

INTRODUCTION

1.1 General

The original Austenitic manganese steel, containing about 1.2% C and 12% Mn, was invented by Sir Robert Hadfield in 1882. It was unique in that it combined high toughness and ductility with high work-hardening capacity and usually good resistance to wear.

Hadfield's austenitic manganese steel is still used extensively, with minor modifications in compositions and heat treatment. ASTM Standard A-128-64 [1] covering this steel allows composition ranges from 1.0 to 1.4% C and from 10 to 14% Mn. However, commercial alloys with manganese contents greater than 12 to 13% are seldom used because of cost. Moreover, work hardening in a 1.15% C alloy reaches a maximum at 13% Mn. Hadfield steel is usually austenitized to dissolve carbides and to produce homogeneous austenite, which is preserved by water quenching from above 1000°C. So it is a stable, single phase, austenitic alloy which is annealed and quenched before use to retain all the carbon in supersaturated solid solution. Typical properties are 0.2% offset yield strength 379 MPa, ultimate tensile strength 965 MPa, elongation in 50 mm 50%, reduction of area 40%, as- quenched hardness 190 HB, hardness, at fracture, 500 HB [2].

In gouging abrasion tests, Hadfield steel performs better than wrought alloy steels, cast alloy steels, stainless steels, tool steels or high-chromium white irons [3]. To modify Hadfield steels' properties, especially wear resistance, alloying elements are used. So the selection of right alloying element and its quantity and also required

heat treatment is critical. Results of mechanical tests should be supported by metallographic findings to make the phenomena more clear.

These combinations of properties make it useful in such diverse applications as crawler treads for tractors, grinding mill liners, crusher jaws and cones, impact hammers, dipper bucket teeth and nonmagnetic plates for electromagnets [4]. An important use is in railway trackwork, such as frogs, switches and crossings, where the multiple impacts at intersections are especially severe. Although austenitic manganese steel, by virtue of its toughness, wear resistance and nonmagnetic properties, finds use in many fields, its chief applications are in the industries of construction, mining, quarrying, oil-well drilling, steel making, manufacturing of cement and clay products, railroading, dredging, and lumbering. Austenitic manganese steel resists metal to metal wear; therefore it may be used in sprockets, pinions, gears, wheels, conveyor chain and various wearing plates, shoes or other contact members. Nonmagnetic parts, required for lifting-magnets, for induction furnaces and special electrical equipment, are an expanding field of usefulness.

As a result, as already known, the mechanical and microstructural properties of metals determine the range of usefulness of the metal and establish the service that can be expected. Mechanical and microstructural properties are also used to help specify and identify metals. So it is really important to study hadfield steels because of that it is not an ordinary steel. On the other hand it is clear that hadfield steels have a combination of desirable properties both for processing and use, which make them commercially attractive. If these properties could be combined with improvements like more resistance to flow with detailed understanding then these steels would probably become more popular.

1.2 Scope and Objective of the Thesis

Despite extensive applications of Hadfield manganese steel since its discovery more than a century ago, there is almost no documentation which presents the results of modifications in both composition and heat treatment together clearly.

In this scientific environment the findings should help the scientists, academicians, students and industrial producers to evaluate development alternatives in a logical and quantitative manner and then enhance the understanding through estimates of the effects of changes in Hadfield steel production from the point of composition and heat treatment. In this view, the scope of the study will include the points listed as follows:

- the effect of modifications in heat treatment on properties
 - the effect of solutionizing temperature
 - the effect of solutionizing time
- the effect of modifications in composition on properties
 - the effect of increase in Mn addition
 - the effect of Cr addition
 - the effect of Mo addition

More generally, the main objective of the study is to investigate these effects on both microstructural and mechanical properties of Hadfield steels by mechanical tests and microstructural examination. More specifically, the study aims at understanding the relationship between modifications in heat treatment and composition and steel's properties by investigating those points listed above

In chapter III, while mentioning about experimental procedure, approach of the thesis study will be dealt in detail. This document proceeds as follows: In chapter II general properties and features of Hadfield steels are presented. In the next section, chapter III, experimental procedure and so the approach of the study will be given. After presenting the results and then making discussion on these results in chapter IV, finally chapter V summaries the main conclusions.

CHAPTER II

AUSTENITIC MANGANESE STEELS

2.1 General

The nominal composition of the austenitic manganese steel introduced commercially was 1.2% carbon, 12.5% manganese and this became known by the name still applied to it today, Hadfield Manganese Steel (1883, British Patent No. 200 issued to Robert Hadfield). Until 1919, most manganese steel was made by mixing molten carbon steel with separately melted ferromanganese. Low phosphorus pig iron and steel scrap were melted in a cupola furnace, then blown in a Bessemer type converter and ferromanganese melted in crucibles on special furnaces, was mixed in a ladle with the blown steel. However, for the past years, most manganese steels have been made in electric arc furnaces to obtain the greater quality control inherent in electric melting.

The characteristics and important properties possessed by this steel in the water quenched condition, were exceptional toughness and ductility, the capacity for a thin surface layer to rapidly work harden to a hardness in the order of 500 Brinell, all the while maintaining a non-magnetic character.

Austenitic manganese steel has certain properties that restrict its use. It is difficult to machine and usually has a yield strength of only 345 to 415 MPa. Consequently, it is not well suited for parts that require close-tolerance machining or that must resist plastic deformation when highly stressed in service. However, hammering, pressing, cold rolling or explosion shocking of the surface raises the yield strength to provide a hard surface on a tough core structure.

To improve the wear resistance of austenitic manganese steels without, at the same time, seriously injuring their toughness, a logical approach appeared to lie in the production of the properly dispersed hard carbides in the austenitic matrix of the steel. Increasing the carbon in the solution in the austenite is also another approach. It has been observed however that in the conventional Hadfield manganese steel, an increase in the carbides, or the carbon in solution, was usually accompanied by the formation of embrittling-type carbide envelopes around grain boundaries or as plates along crystallographic planes. To avoid such embrittlement, the form in which the carbides occurred in the austenite would obviously have to be modified, either by addition of other alloying elements or by special thermal treatments.

2.2 Composition

In the normal composition, 1.2% C and 12-13% Mn are essential elements. Commercial alloys will usually vary within the range from 1.0-1.4% C and 10-14% Mn as established by ASTM-A128 and some other specifications. The most common of these compositions, as listed in ASTM-A128 are given in Table 2.1.

These compositions in Table 2.1 do not permit any austenite transformation when the alloys are water quenched from above the A_{cm} . However, this does not preclude lower ductility in heavy sections because of slower quenching rates. The effect is due to the formation of carbides along grain boundaries and other interdendritic areas and to some degree affects nearly all commercial castings except the very smallest. The A_{cm} temperature increases with increasing C wt%; for instance, for 13% Mn steels it is 700°C for 0.6% C, and increases up to 1100°C for 1.4% C.

Table 2.1 Standard composition ranges for austenitic manganese steel castings [1].

ASTM A128 Grade	Composition %						
	C	Mn	Cr	Mo	Ni	Si (max)	P (max)
A	1.05-1.35	11.0min	-	-	-	1.00	0.07
B-1	0.9-1.05	11.5-14	-	-	-	1.00	0.07
B-2	1.05-1.2	11.5-14	-	-	-	1.00	0.07
B-3	1.12-1.28	11.5-14	-	-	-	1.00	0.07
B-4	1.2-1.35	11.5-14	-	-	-	1.00	0.07
C	1.05-1.35	11.5-14	1.5-2.5	-	-	1.00	0.07
D	0.7-1.3	11.5-14	-	-	3.0-4.0	1.00	0.07
E-1	0.7-1.3	11.5-14	-	0.9-1.2	-	1.00	0.07
E-2	1.05-1.45	11.5-14	-	1.8-2.1	-	1.00	0.07
F	1.05-1.35	11.5-14	-	0.9-1.2	-	1.00	0.07

The mechanical properties of austenitic manganese steels vary with carbon and manganese content. There is a tendency to operate close to the midpoint carbon range and with 12-13% Mn since the lower level of the composition range is associated with somewhat inferior tensile properties and the upper extreme has no economic advantage. Figure 2.1.a and b indicate that carbon increases strength up to the range of ASTM A 128, grade A.

2.2.1 Carbon

Carbon has a slight but distinct effect on yield strength; reduction in carbon content causes reduction in yield strength. The effect of carbon content on other tensile properties is overshadowed by variables such as grain size but there is suggestive indication of optimum carbon content around 1.15%. Higher carbon contents than 1.25% percent usually tend to embrittle the steel by the formation of embrittling-type carbide envelopes around grain boundaries or as plates along

crystallographic planes. This means that as carbon is increased it becomes increasingly difficult to retain all of the carbon in solid solution, which may account for reductions in tensile strength and ductility. Carbides form in castings that are cooled slowly in molds. In fact, carbides form in practically all as-cast grades containing more than 1% C, regardless of mold cooling rates. They form in heavy section castings during heat treatment if quenching is ineffective in producing rapid cooling throughout the entire section thickness. Carbides can also form during welding or during service at temperatures above about 275°C. Higher carbon contents also may cause trouble in heat treatment or in the foundry. During cooling below the limit of solubility, low carbon content is helpful in avoiding the embrittling effect of carbide precipitation. For this reason,

- Low carbon content is generally employed in alloys to be used for welding rod and other modifications where the normal heat treatment, involving a water quench, is impractical.
- Highest level content is employed for wear resistant castings taking a depreciation ductility into account seriously.

2.2.2 Manganese

Manganese contributes a vital austenite stabilizing affect operating to delay transformation rather than to eliminate it. Thus with a simple steel that contains 1.1% Mn the beginning of isothermal transformation at 371°C may occur in about 15 seconds while with 13% Mn about two days may be required. Below 260°C phase change and carbide precipitation are so sluggish that for practical purposes they may be neglected in the absence of deformation if manganese exceeds 10%. Figure 2.2 shows the influence of manganese content on the strength and ductility of cast austenitic steel that has been solution treated and then water quenched.

Manganese within the limits of 10-14% has almost no effect on yield strength but it does benefit tensile strength and ductility. The difference between 10% and 13% manganese can be demonstrated although it requires careful control of other variables to make it apparent. Below 10% Mn the tensile properties decline rapidly

perhaps to half of their normal level at about 8% Mn. For critical requirements 11% Mn is desirable as a minimum although the improvement over 10% is slight. The maximum is rather arbitrary and probably depends more on the cost of alloy than on metallurgical results, since acceptable properties may be produced up to at least 20% Mn. Generally for commercial applications, a manganese-carbon ratio is about 10 to 1 or higher.

The lower manganese contents would provide better wear resistance due to partly to the better carbide dispersion and partly to the less stable austenite in the lower manganese steels. In the interests of obtaining improved wear resistance, the lower manganese steels with their lower toughness should be usable in many applications. However, the aim of producing these type steels is the high toughness. So the reducing manganese content is not useful.

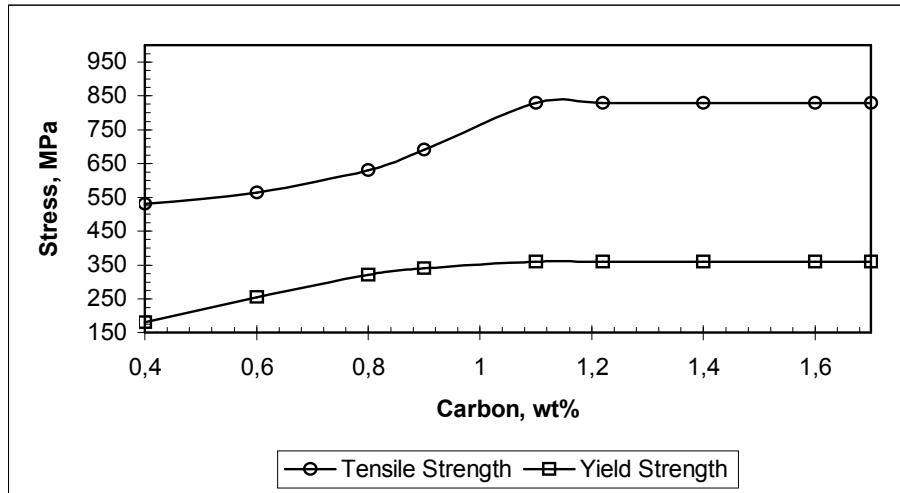
Also, if carbon and manganese are lowered together, for instance to 0.53% C with 8.3% Mn or 0.62% C and 8.1% Mn, the work-hardening rate is increased because of the formation of strain-induced α (body-centered-cubic, bcc) martensite.

2.2.3 Chromium, Nickel and Molybdenum

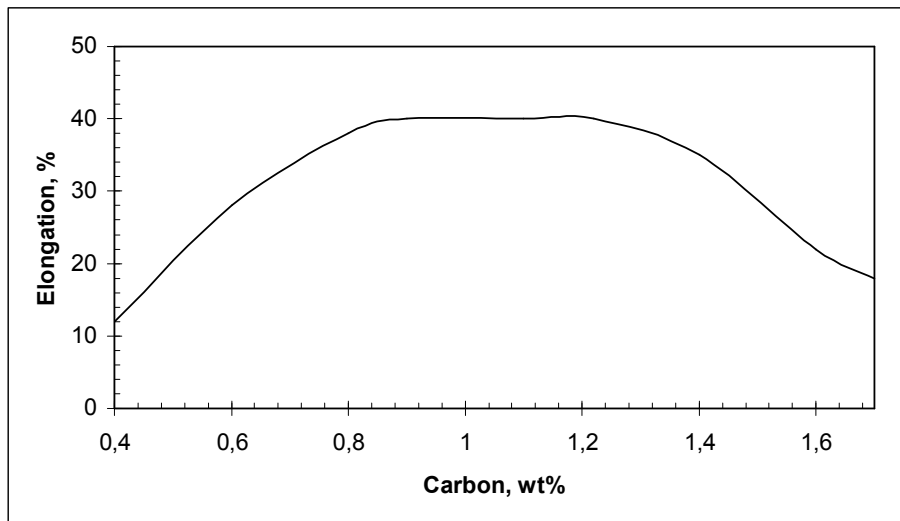
Chromium additions are less expensive for a given increase and chromium grades (ASTM A 128, grade C, for instance) are probably the most common modifications. ASTM A 128, grade B often contains some Cr also. The 2% Cr addition in grade C does not significantly lower toughness in light sections. However, in heavier sections its effect is similar to that of raising the carbon level; the result is a decrease in ductility due to an increase in the volume fraction of carbides in the microstructure.

Nickel and molybdenum additions are preferred for welding electrodes. Molybdenum additions, usually 0.5 to 2% are made to improve the toughness and resistance to cracking of castings in the as-cast condition and to raise the yield strength (and possibly toughness) of heavy section castings in the solution treated and quenched condition.

These effects occur because molybdenum in manganese steel is distributed partly in solution in the austenite and partly in primary carbides formed during solidification of the steel. The molybdenum in solution effectively suppresses the formation of both embrittling carbide precipitates and pearlite even when the austenite is exposed to temperatures above 275°C during welding or in service. The 1% Mo grades (ASTM A 128, grade E-1) are resistant to the reheating effect that limits the usefulness of the standard B-2, B-3, and B-4 grades. This is why grade E-1 is adapted to heavy-section castings used in roll and impact crushers that are frequently reheated during weld buildup and overlays. Grade E-2, which contains about 2% Mo, may be given a special heat treatment to develop a structure of finely dispersed carbides in austenite. This heat treatment entails a partial refinement by pearlitizing near 595°C for 12 hours and water quenching from 980°C. This type of microstructure will enhance abrasion resistance in crusher applications. Molybdenum when present in amounts over about 1.5% produces a globular type of carbide which forms from the melt in interdendritic sites and minimizes the development of grain boundary Fe_3C is an asset in heavy casting.

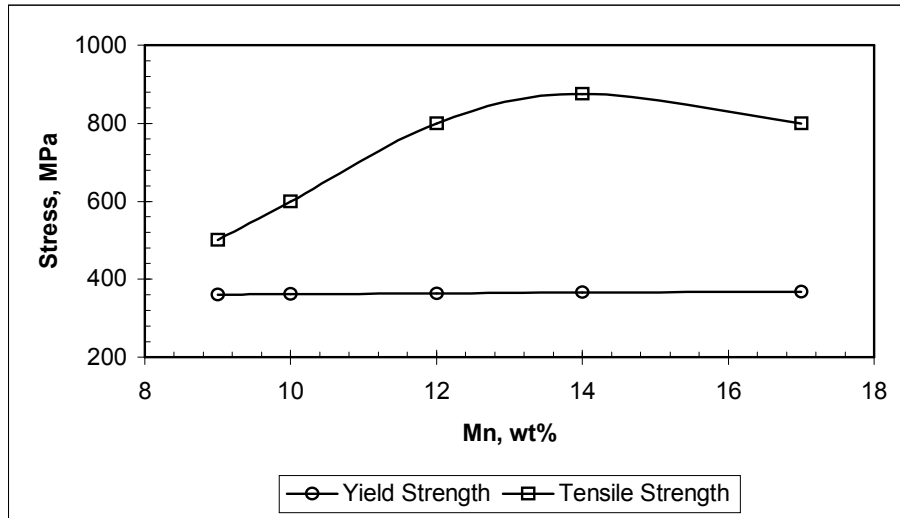


(a)

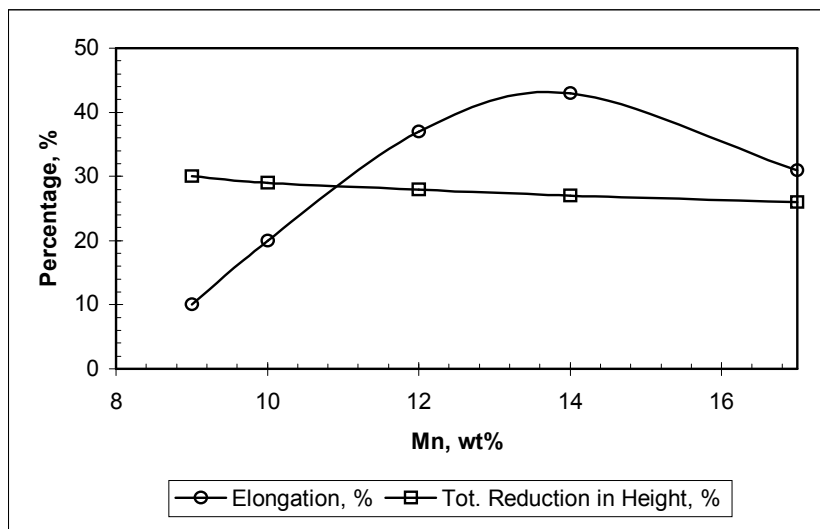


(b)

Fig. 2.1 Effect of carbon content on (a)yield and tensile strength, (b)ductility of the 12-14Mn Hadfield steels [1]

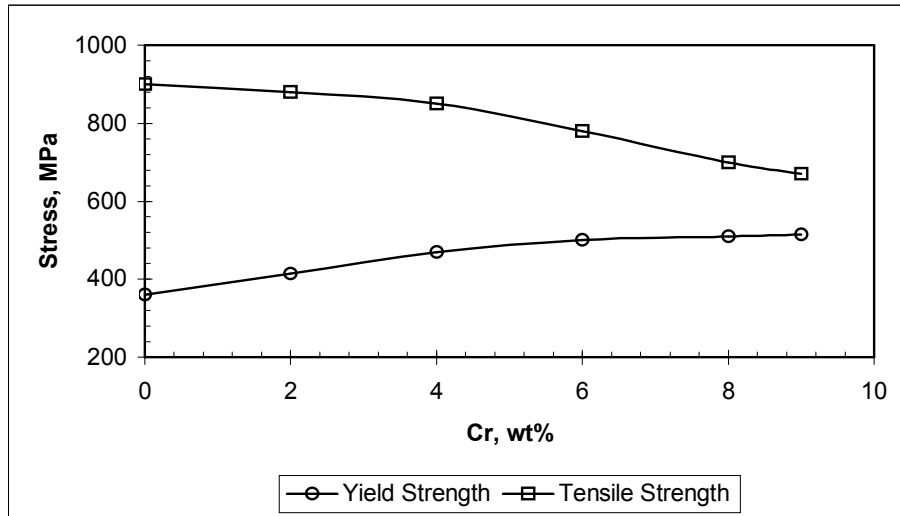


(a)

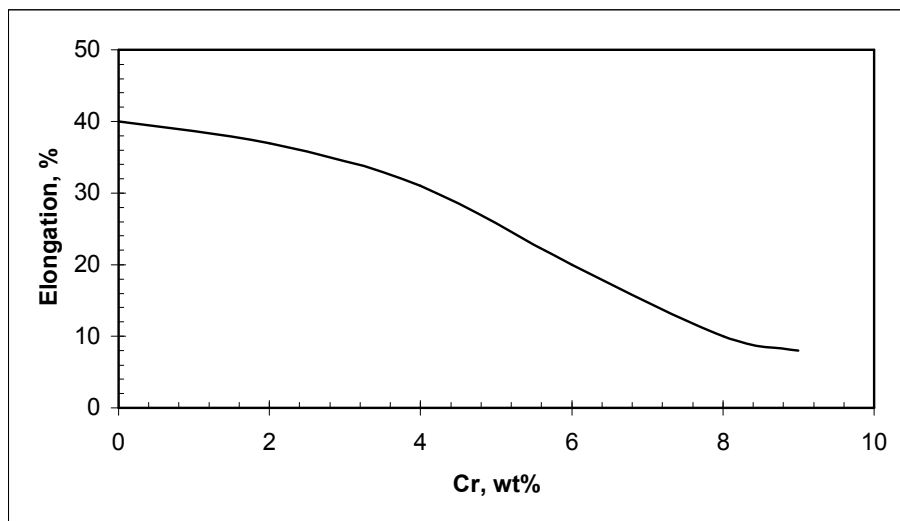


(b)

Fig. 2.2 Effect of Mn content on (a) tensile and yield strength, (b) elongation and total reduction in height of Hadfield steels [1]

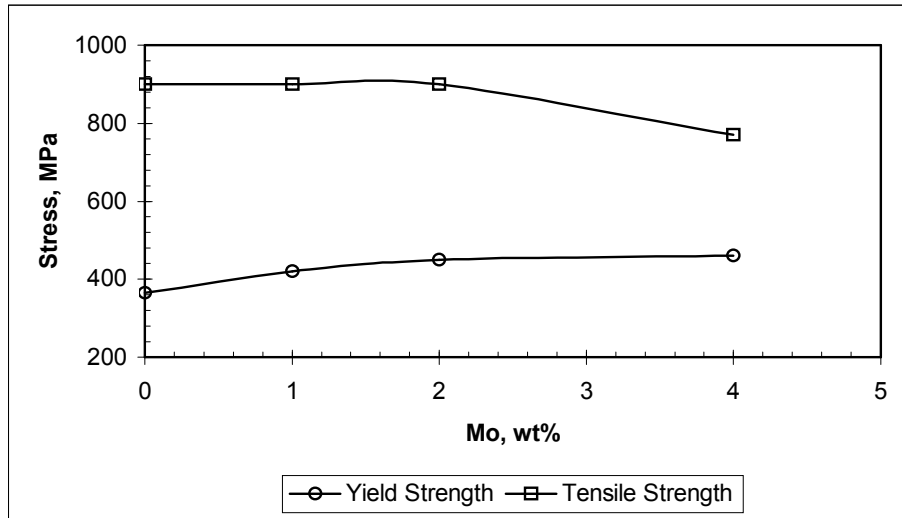


(a)

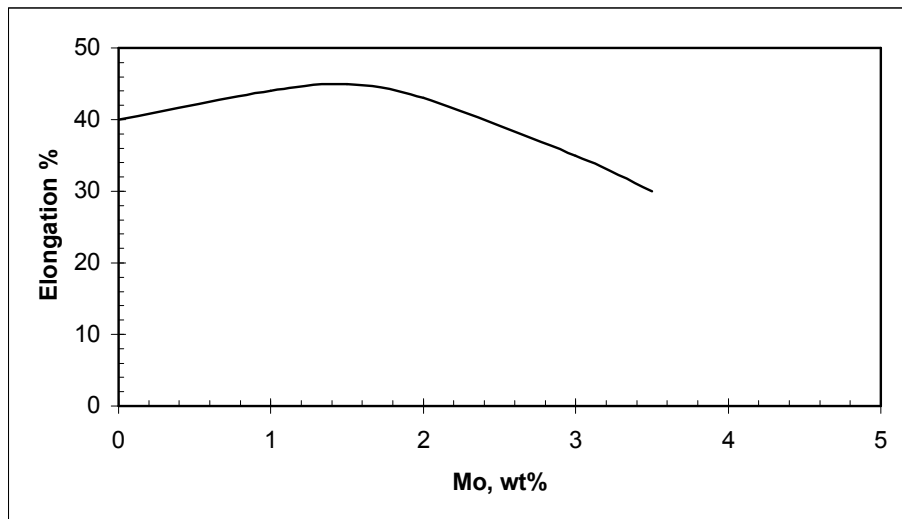


(b)

Fig. 2.3 Effect of Cr addition on (a) yield and tensile strength, (b) ductility of 12-14 Mn Hadfield steel [1]



(a)



(b)

Fig. 2.4 Effect of Mo addition on (a) yield and tensile strength, (b) ductility of 12-14 Mn Hadfield steel [1]

2.3 Heat Treatment

The as-cast structure of manganese steel contains carbides and other transformation products that produce marked brittleness by their continuity. In small test casting, as cast, the tensile strength will approximate 400-500 MPa with elongation values down to less than 1%. Although austenitic manganese steels in the as-cast condition are generally considered too brittle for normal use, lowering carbon content to less than 1.1% and/or adding about 1% Mo or about 3.5% Ni results in commercially acceptable ductilities in light and moderate section thicknesses.

Heat treatment strengthens austenitic manganese steel so that it can be used safely and reliably in a wide variety of engineering applications. The standard toughening heat treatment involving solutionizing and water quenching produces the normal mechanical properties. The solutionizing temperature should be high enough to assure complete solution of carbon. This is achieved by choosing the temperature 30 to 50°C higher than A_{cm} . The time at this temperature is not critical, since above 1010°C equilibrium is probably established within 20-30 minutes. An allowance is required for lack in heat transfer in heavy sections.

Variations of this treatment can be used to enhance specific desired properties such as yield strength and abrasion resistance. Usually a fully austenitic structure, essentially free of carbides and reasonably homogeneous with respect to C and Mn, is desired in the as-quenched condition, although this is not always attainable in heavy sections or in steels containing carbide-forming elements such as Cr, Mo, V or Ti. If carbides exist in the as-quenched structure, it is desirable for them to be present as relatively innocuous particles or nodules within austenite grains rather than as continuous envelopes at grain boundaries.

The quenching rate is important although difficult to accelerate beyond the rate fixed by absorption from a surface cooled by acetated water. This results in lower mechanical properties at the center of the heavy sections. Residual stresses

from quenching coupled with the lower properties of the heavy section have operated to establish a practical maximum of 12.5-15 cm for the thickness of commercial casting. Stresses that develop during cooling in the mould operate on a much more brittle structure and are likely to produce cracks in heavy castings before heat treatment.

The relatively high solutionizing temperature in combination with high carbon content causes marked surface decarburization by furnace gases and some loss of Mn. The skin may thus be partially martensitic at times and is usually weaker than underlying metal. Tensile deformation in service sometimes produces numerous cracks in this inferior skin, which terminate where the tough austenite of normal composition is reached. Service performance is not seriously affected unless critical fatigue conditions or very light sections are involved; in such instances premature failure may result. Under certain conditions reducing the effect of decarbideizing atmospheres used in heat treatment may protect sections such as rod sheets with covers, metal envelopes or organic and inorganic coatings, there.

The desired objective of producing fine carbide dispersions in the regular Hadfield type or specially alloyed austenitic manganese steels does not appear to be feasible with the conventional solution treatment. However, a consideration of the phase diagrams for high-C steels containing in excess of 1.5% Mo indicates that there should be a good possibility of producing the desired carbide dispersions in austenitic manganese steels by combining a 2% Mo addition with modification in thermal treatment as noted before.

It was determined that fine carbide dispersions could be produced and retained in 2% Mo austenitic manganese steels by a special heat treatment which involved first a transformation of part of the austenite to pearlite, followed by temperature controlled re-solutionizing treatment. This dissolved most of the globular carbides and part of the carbides in the pearlite, so the remainder of the carbides formed a fine dispersion of spheroidized carbides in the austenite.

2.4 Mechanical Properties

Representative tensile properties are listed in Table 2.2. The true tensile characteristics of manganese steel are better revealed by the stress-strain curves in Fig. 2.5, which compare manganese steel with gray iron and with a heat-treated, high strength, low-alloy steel of about the same nominal tensile strength.

The low yield strength is significant and may prevent the selection of this alloy where slight or moderate deformation is undesirable unless the usefulness of the parts in question can be restored by grinding. Tensile strength and ductility are affected somewhat by composition by heat treatment and considerably by grain size; the finer grain specimens exhibit greater strength and elongation. The difference may be as much as 30%. It should be noted that the values sometimes quoted for cast bars may reflect the presence of internal defects such as shrinkage cavities. Aside from the minor influence of directional properties, the chief differences between cast and wrought manganese steel are the results of difference in grain size. The midrange values of 120000 psi tensile strength and 40% elongation apply to sound, medium grain size cast specimens that have been properly heat treated. Wrought products are usually fine grained.

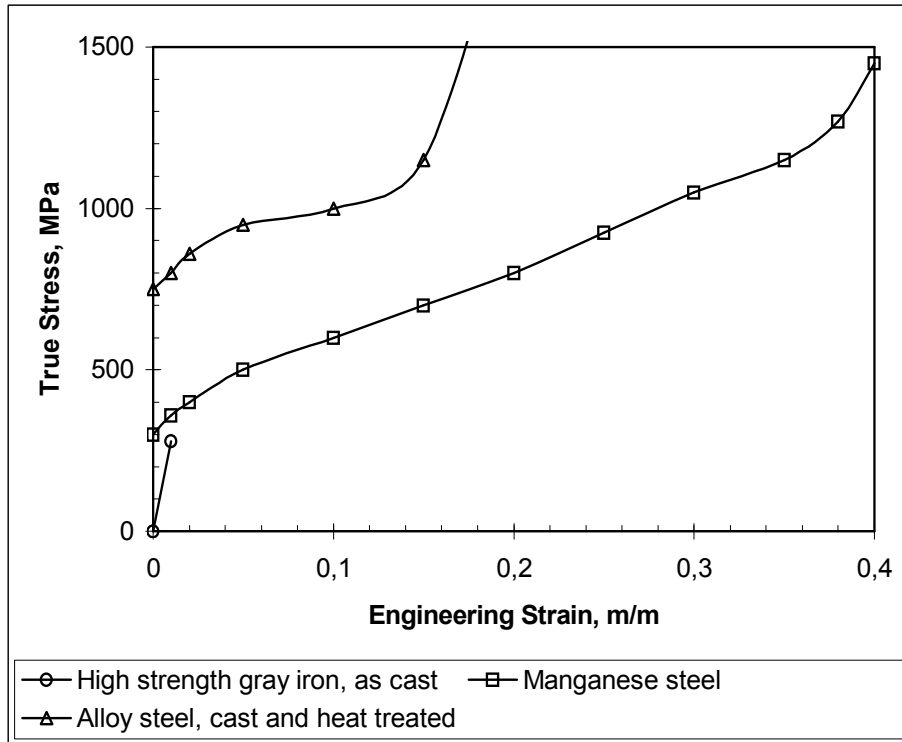
Hardness is about 200 BHN after toughening, but this value has little significance for estimating machinability or resistance to wear. The hardness will increase so rapidly from deformation that austenitic manganese steel must be evaluated on a distinctive basis.

Like tensile properties, impact resistance is influenced by grain size and heat treatment. The alloy remains tough at subzero temperatures. The austenitic alloys are apparently immune to hydrogen embrittlement, although with low carbon (0.02% +/-) and high manganese contents, this embrittlement has been produced. Resistance to crack propagation is high and is associated with very sluggish progressive failures, permitting periodic observation of fatigue cracks, for example, and removal from service before complete failure occurs like in railway track work.

Table 2.2 Mechanical and Physical Properties of Austenitic Manganese Steels [1]

FORM	SIZE (cm)	COMPOSITION				0.2% Yield Str. (Mpa)	Tensile Str. (MPa)	Elongation %	Reductio n in Area %	Brinell Hardness
		C	Mn	Si	Other					
Standard Manganese Steel										
As cast(a)	1(b)	1.11	12.7	0.54	--	360	448	4	--	--
Cast HT	1(b)	1-1.4	10-14	0.2-1.0	--	345-393	690-1000	30-65	30-40	185-210
Rolled HT	1(b)	1.1-1.4	11-14	0.2-0.6	--	296-462	903-1089	40-63	35-50	170-200
2.0% Cr Manganese Steel										
Cast HT	1(b)	1.1-1.25	12.5-13.5	0.4-1.0	1.8-2.1C	400-470	661-1013	27-59	26-38	205-215
Cast HT(a)	4	1.17	13.0	0.5	2.0C	365	565	31	29	--
Cast HT(a)	6	1.17	13.0	0.5	2.0C	385	558	20	19	--

1.0% Mo Manganese Steel										
As cast(a)	1(b)	0.83	11.6	0.38	0.96Mo	50	101	30	29	163
Cast HT	1(b)	0.75-0.98	12.1-14.1	0.4-0.7	0.9-1.1Mo	50-59	106-137	37-67	30-39	179-207
Cast HT	8	0.75-1.0	12.1-14.2	0.4-0.7	0.9-1.3Mo	42-55	82-133	27-61	26-60	--
As rolled	1(c)	0.72	13.0	--	1.0Mo	53L; 54T	140L; 137T	49L; 46T	44L; 45T	187
Rolled HT(a)	1(b)	0.72	13.0	--	1.0Mo	54L; 53T	147L; 145T	72L;60T	49L; 43T	187
As cast	1(b)	1.16	13.6	0.6	1.1Mo	58	81	13	15	185
Cast HT	1(b)	1.0-1.2	13-14	0.4-0.6	0.9-1.1Mo	52-62	110-135	40-50	31-41	180-210
Cast HT(a)	8	1.16	13.6-14.3	0.4-0.6	1.0-1.1Mo	50-56	76-77	16-33	12-29	--
(a): specimen properties, (b): in diameter, (c): plate; HT: heat treated, L: longitudinal properties, T: transverse properties, These various properties represent the tough austenitic condition.										



Alloy	Composition				
	C	Mn	Si	Cr	Other
Alloy Steel, Q and T	0.29	1.30	0.52	0.37	0.36 Mo
Manganese Steel	1.22	13.08	0.33	0.09	0.05 Al
Gray Iron	2.79	0.75	1.32	0.10	---
Q and T, quenched and tempered					

Fig. 2.5 True Stress versus engineering Strain for Manganese Steel, Cast Alloy Steel (quenched and tempered) of similar tensile strength and a high-strength Gray Iron

2.5 Work Hardening

The approximate ranges of tensile properties produced in other alloy steels by heat treatment are developed in manganese steel by work hardening. Thus in a tension test, yielding signifies the beginning of work hardening and elongation is associated with its progress. There is little or no marked reduction of area by necking, because work hardening is greatest at the point of greatest deformation; the increased strength from working stops elongation and deformation than occurs elsewhere until the hardening and reduction of area substantially equalized throughout the specimen. This type of behaviour is often compared to that exhibited by transformation-induced plasticity (TRIP) steels. Elongation thus occurs uniformly and without flow stress saturation, until failure [1].

An investigation showed that fracture occurs because of a combination of microvoid coalescence (without shear localization) and surface cracking within regions of localized plastic flow [8]. The nucleation of both voids and surface cracks was observed to be a function of carbides and nonmetallic inclusions in the steel. Plastic deformation is accompanied by the development of texture [9].

Various mechanisms have been to contribute to work hardening, depending on factors such as alloy composition (stacking fault energy, strain rate sensitivity), temperature, strain rate. These mechanisms include twinning or pseudotwinning [9,10], stacking fault formation [11], and dynamic strain aging [4,12]. However, it is well established that a deformation-induced transformation from austenite to α martensite (bcc) does not occur in ordinary hadfields steels. The role of such a transformation in work hardening is more significant only at lower carbon and manganese levels.

On a macroscopic scale, the work hardening rate has been observed to increase with increasing carbon content and decreasing grain size [13]. Work-

hardening rates of 1500 to 2500 MPa have been measured in austenitic manganese steels at nominal strain rates of 10^{-4} /s at room temperature.

Manganese steel exceeds even the austenitic stainless steels in ability to work harden and probably has no equal in this respect. The maximum hardness attainable in practice is about 550 BHN. Hardness on the wearing surface of a railway frog after service has ranged from 495-535 BHN. Work hardening is usually induced by impact as from hammer blows. Light blows even if they are of high velocity will cause shallow deformation with superficial hardening although the surface hardness may be high. Heavy impact produces deeper hardening usually with lower maximum values. Much energy is absorbed by work hardening. Most of the impact blows encountered through out industry are of low velocity and this material is suitable; it is the preferred choice where high shock resistance, toughness and absorption of energy are required.

The low yield strength of manganese steel is sometimes a disadvantage. Plastic deformation from impact increases the yield strength to levels more resistant to flow but the associated change in the dimensions is undesirable. Flow resistance and yield strength are intimately related and a number of methods for increasing them are available. Additions of alloying elements and preservice hardening may be employed; the latter is more successful. Additions of vanadium, chromium, silicon and molybdenum are effected; however vanadium and chromium reduce ductility. In some applications a dimensional allowance for flow may be required. The preferred method of increasing resistance to flow under impact is prehardening by deformation. Special equipment for hammering or pressing is usually employed to induce deep seated hardening. The zone affected usually ranges up to 2.5cm in depth. The superficial hardening that can be produced by high velocity shot blasting is seldom satisfactory for service requirements.

2.6 Wear Resistance

The Hadfield steels are probably the best materials for applications where high toughness is required. Although 12% Mn steel is unquestionably the best metal for resisting certain types of wear, it is not universally applicable. When this steel is being considered for abrasive service, the determining factor in selection should be toughness not resistance to abrasion. Hadfield steels are usually less resistant to abrasion than are martensitic white irons or martensitic high-carbon steels, but are often more resistant than pearlitic white irons or pearlitic steels. So for example, if impact and shock are absent, as in a pipe carrying sand laden water, a martensitic cast iron is a much better choice. If light or moderate impact is involved, the specification of a hardened steel may be justified. But if heavy impact is expected or a large safety factor is required, Hadfield steel is the logical choice, and the large annual tonnage goes chiefly into such uses.

The type of wear that is sustained has a major influence on the performance of manganese steels. They have

- excellent resistance to metal-to-metal wear, as in sheave wheels, crane wheels and car wheels;
- good resistance to gouging abrasion, as in equipment for handling or crushing rock;
- intermediate resistance to high-stress (grinding) abrasion, as in ball mill and rod mill liners;
- relatively low resistance to low-stress abrasion, as in equipment for handling loose sand or sand slurries [1].

For the high manganese austenitic steels, the wear properties are also a very important factor for determining the service life. There are two basic approaches available for improving the wear resistance.

- The carbide dispersions in the austenite were developed by means of special alloy additions and modifications in heat treatment.

- Less stable and more wear-resistant types of austenite were developed by the use of lean alloy, high carbon compositions.

To improve the wear resistance of austenitic manganese steels without, at the same time, seriously injuring their toughness, a logical approach appeared to lie in the production of properly dispersed hard carbides in the austenitic matrix of the steel. First of all, composition modification effect is going to be considered by giving separate elements:

- In general, for wear resistant castings, it is desirable to hold the carbon content at the highest level possible without seriously injuring the ductility of the steel. For the conventional Hadfield Steel, it is usually in a range of 1.10 to 1.25%. Higher carbon contents tend to embrittle the steel by forming envelopes of $(\text{Fe,Mn})_3\text{C}$ type carbides around the grain boundaries, or by forming plate- type carbide precipitates along crystallographic planes. This is the problem occurs in the conventional Hadfield steel.
- To retain a fully austenitic structure, the manganese content of an austenitized and quenched high carbon steel must be above certain minimum levels. The development of high ductility and toughness in the austenite generally requires in excess of 10%Mn. But as the high manganese steels as Hadfield steels contain more than that no problem occurs in that respect.
- The embrittlement is aggravated by chromium additions. Molybdenum on the other hand, when present in amounts over about 1.5%, produces a globular type of carbide, which forms from the melt in interdendritic sites and minimizes the development of grain boundary Fe_3C type carbides. Additions of chromium which tend to accentuate the formation of carbide networks around grain boundaries, are probably responsible for the reduced ductility of austenitic manganese steels containing over about 1% Cr. In spite of the embrittling effect of chromium, an addition of about 2% is frequently used in the belief that it improves resistance to wear in service. The industrial observations show that, under some conditions, Cr additions do improve the wear resistance, although similar or greater improvement may be obtained by

lowering the manganese content of chromium free steel with less loss in ductility.

- Silicon is normally added only in the amounts required for good deoxidization of austenitic manganese steel heats. But it is also noted that the higher silicon contents tended to throw carbon out of solution in the austenite by precipitating the carbon either as rather massive carbides or as pearlite. Presumably, where high carbon content in solution in austenite is required for good wear resistance, the effect of higher than normal silicon contents would be harmful.
- Phosphorus is probably particularly harmful in heavy section castings, due to segregation effect. The ASTM specification (A128-33) for manganese steel castings limits phosphorus to a maximum of 0.10%. But phosphorus content of not over 0.06% and preferably under 0.05% is now specified on all of the austenitic steel castings used in the mining and milling operations. Because over 0.06% P content reduces the hot strength and ductility.

CHAPTER III

EXPERIMENTAL PROCEDURE

3.1 Material

Austenitic steels having different compositions were produced by melting the steel in an induction furnace. Then, the samples of 400 mm long and 50 mm diameter were obtained by casting into sand moulds. The identification number and corresponding steel compositions obtained by spectrometric analysis are given in Table 3.1.

Table 3.1 Identification and compositions of steels

No	Identification	C%	Mn%	Si%	S%	P%	Cr%	Mo%
1	12-14 Mn	1.092	12.400	0.447	0.020	0.026	0.256	0.037
2	12-14 Mn 1.5 Cr	1.116	12.833	0.427	0.015	0.026	1.486	0.040
3	16-18 Mn	1.286	16.564	0.609	0.02	0.025	0.220	0.047
4	16-18 Mn 2 Cr	1.256	16.039	0.381	0.015	0.025	2.007	0.058
5	16-18 Mn 2 Mo	1.281	15.442	0.560	0.018	0.025	0.263	1.729

There is no need to try to find effect of increase or decrease in C percentage because at 1% of C maximum elongation, yield strength and true fracture strength values are obtained. Also more addition of C does not have any improvement on these values and may injure toughness by lowering ductility by separating along grain boundaries and crystallographic planes. Thus, commercially C percentage is always kept at this percentage.

3.2 Heat Treatment

In order to investigate the effect of heat treatment on mechanical properties, *five different heat treatment procedures* were applied to as cast rods of *12-14 Mn* as given in Table 3.2.

Table 3.2 Applied heat-treatment procedures for 12-14 Mn austenitic steel

No	Furnace Temperature (°C)	Soaking Period (minute)
HT1	950	70
HT2	1050	35
HT3	1050	70
HT4	1050	140
HT5	1150	70

In order to investigate the effect of composition on mechanical and microstructural properties of Hadfield steels, the as-cast rods of steels having *different composition* were heated to 1050°C with a rate of 150°C/hr in order to dissolve carbides. The specimens were water-quenched after holding them in the furnace for 70 minutes. Quenching bath was refreshed for each specimen. The resulting microstructure is completely austenitic.

3.3 Mechanical Tests

For tensile test, the specimens with 13 mm diameter were machined from the heat-treated rods according to ASTM standards. Final dimensions were obtained by fine grinding in order to minimize the formation of a surface hardened layer. Tensile testing was performed on a serve-hydraulic machine (ALŞA) under load-control (10^4

N/min) at ambient temperature employing an average of two specimens for each heat and composition (Fig. 3.1).

For hardness test, round cylindrical specimens of 3 cm diameter and 3 cm height were machined from rods. The test was performed using Heckert hardness tester employing an average of three measurements for each heat and composition. During the test a ball with a diameter of 2.5mm and a load of 62.5 kg were used (Fig. 3.2). At first, hardness values were so high and unexpected that specimens were prepared again by removing a layer of 3 mm by grinding for second hardness test.

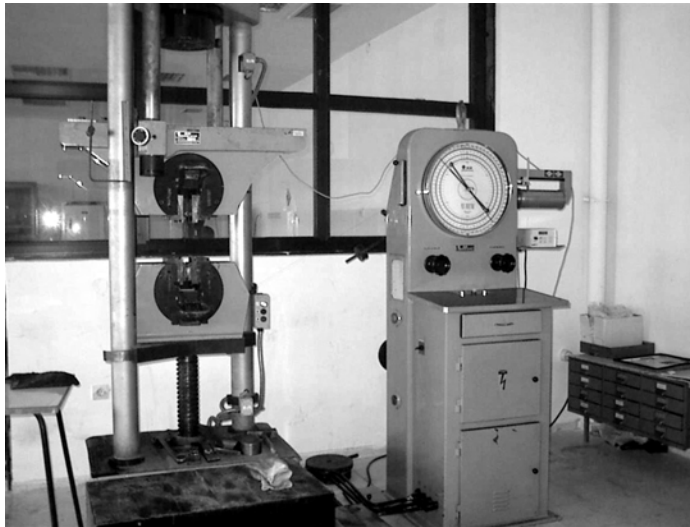


Fig. 3.1 Tensile test machine



Fig. 3.2 Hardness test machine

3.4 Metallographic investigation

Preparation of specimens for critical microscopic examination is difficult. Great care is required to avoid cold work and disturbed surface layers. Cold worked scratches from early stages may be flowed over and concealed during fine polishing, only to become pronounced after etching. Similar flow may obscure grain boundaries whose character is an important criterion of the quality of heat treatment. Spurious structures may also result from tarnishing and corrosion caused by the atmosphere.

For metallographic investigations round cylindrical specimens of 3 cm diameter and 2 cm height were machined from rods. Then, usual metallographic specimen preparation procedure was carried out. Finally, specimens were etched with 5% Nital for 20 seconds. However because of martensite structures which were noted during microstructural investigation, 3 mm of layer was removed from surfaces of specimens by grinding and metallographic specimen preparation and etching were carried out again.

All specimens were examined under optical microscope (Nikon Optihot-100, Fig. 3.3) and scanning electron microscope (JEOL JSM-6400, Fig. 3.4). By means of

scanning electron microscope spot analysis and X-ray mapping using EDS analysis were also done at several points on the specimens.



Fig. 3.3 Optical microscope

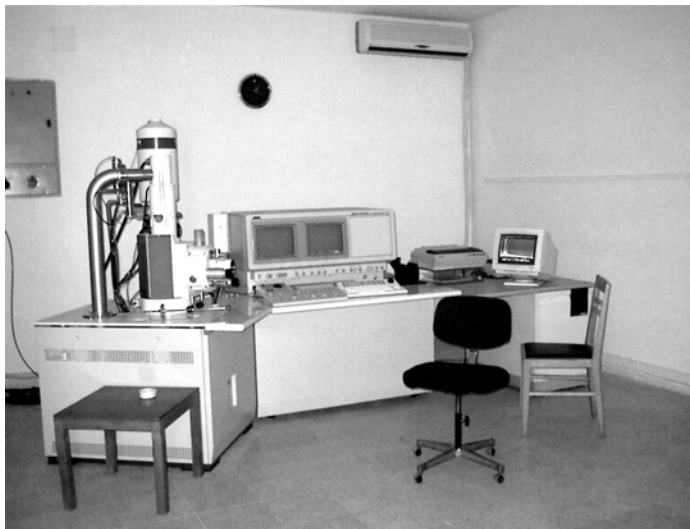


Fig. 3.4 Scanning electron microscope

3.5 Ultrasonic velocity measurements

Heat-treated specimens were ground to obtain round cylindrical specimens of 15-20 mm diameter and 8-10 mm height. Finally, the surfaces of the specimens were ground finely to improve the coupling condition for the ultrasonic measurements.

The propagation velocities of both longitudinal waves were determined by using Panametrics ultrasonic analyzer 5052UAX50 combined with Philips digital storage oscilloscope PM 3365A. During the measurements, the time of flight between two echoes was measured, and then, the ultrasonic velocity (m/s) was calculated by dividing the twice thickness of the specimen with time-of-flight. The measurements were performed by using 1, 2 and 5 MHz probes. Since 2 and 5 MHz probes did not give clear echoes due to noise effect, only the results of the measurements done by 1 MHz probe were considered. Oil was used as the coupling agent between the transducer and the specimen surface.

CHAPTER IV

RESULTS & DISCUSSION

4.1 Results of Microstructural Investigation

After the surfaces of all specimens were ground to remove approximately a 3 mm layer affected by machining, all of the specimens were investigated under optical microscope. Then, detailed SEM investigations were done on the selected specimens.

4.1.1 Microstructural changes in 12-14Mn Steel due to various Heat Treatments

Microstructure of 950°C/70min specimen includes dendritic structures around grain boundaries (Fig. 4.1). Rod type and spherical type carbides also exist. These carbides are seen as white under scanning electron microscope. EDS analysis showed that compositions of these carbides differ slightly (Table 4.1).

Table 4.1 Results of EDS analysis for 950°C/70min specimen

Element	Spherical carbides		Rod type carbides		Matrix	
	<i>Atom%</i>	<i>Weight%</i>	<i>Atom%</i>	<i>Weight%</i>	<i>Atom%</i>	<i>Weight%</i>
<i>Cr</i>	2.23	2.09	2.20	2.06	0.40	0.37
<i>Mn</i>	27.99	27.71	23.98	23.74	12.73	12.60
<i>Fe</i>	69.64	70.20	73.61	74.20	86.34	87.03

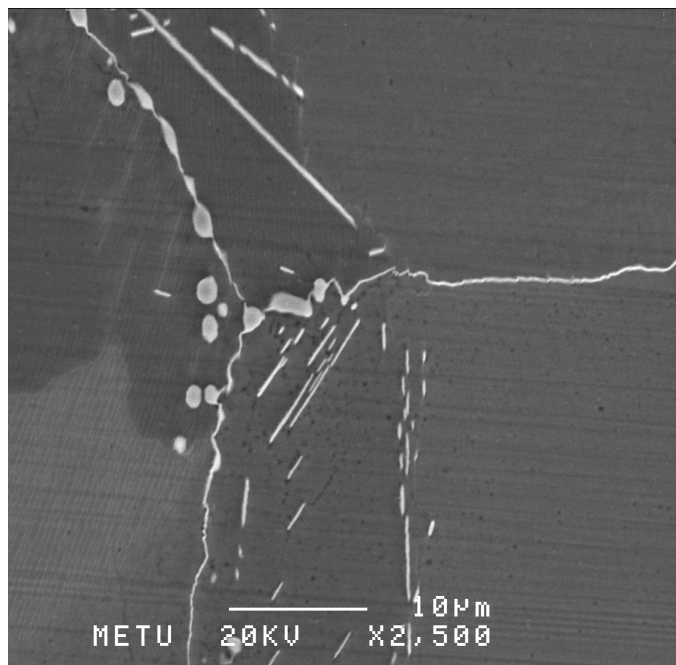
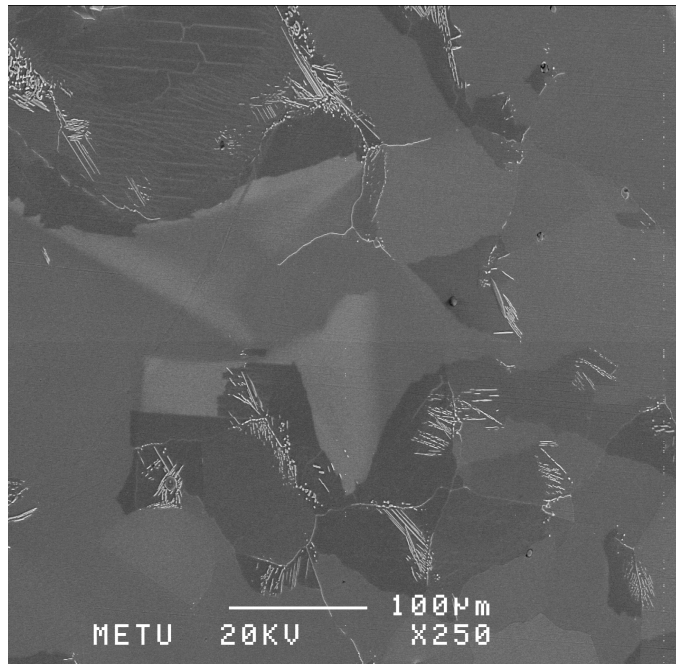


Fig. 4.1 Photos of microstructure of 950°C/70min specimen (12-14Mn)

There are carbides (Table 4.2) along and also near grain boundaries of the 1050°C/35min specimen (Fig 4.2). As soaking time increased, a corresponding increase in the average grain size was observed, such that 140µm after 70min. and 190µm after 140min. All specimens also include few MnS inclusions (62%Mn, 38%S) (Fig. 4.2-Fig. 4.4). In 1050°C/140min and 1150°C/70min specimens, the amount of carbide along grain boundaries is also low, and these are not continuous. In the case of 1150°C/70min specimen, it is difficult to distinguish grains (Fig. 4.4).

Table 4.2 Result of EDS analysis for carbides in 1050°C/35min specimen (12-14Mn)

Element	Atom%	Weight%
Cr	2.40	2.25
Mn	23.80	23.56
Fe	73.60	74.19

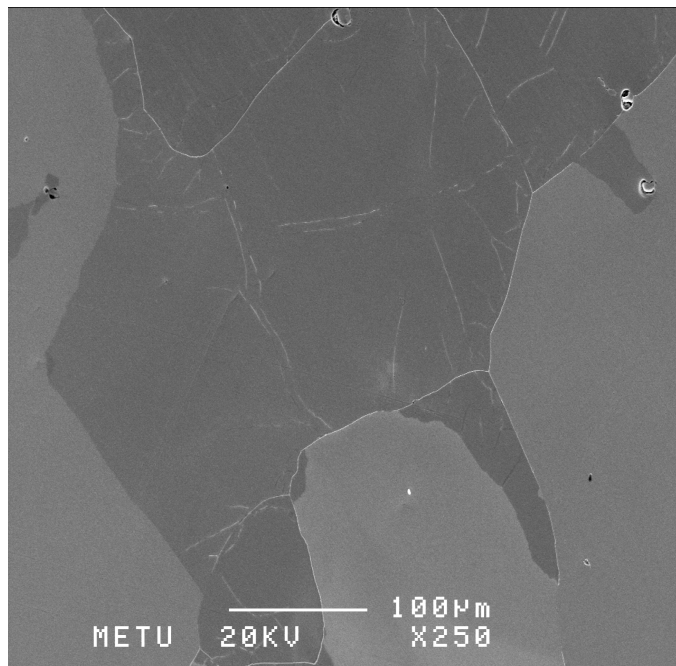


Fig. 4.2 Photo of microstructure of 1050°C/35min specimen (12-14Mn)

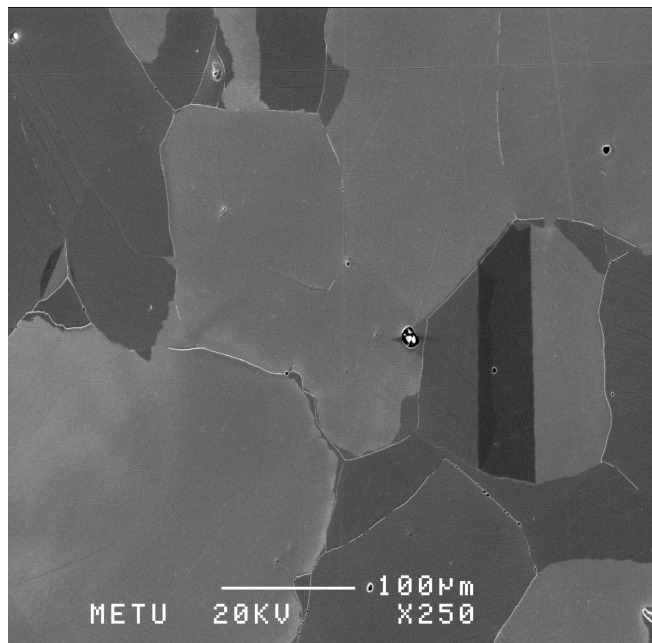


Fig. 4.3 Photo of microstructure of 1050°C/70min specimen (12-14Mn)

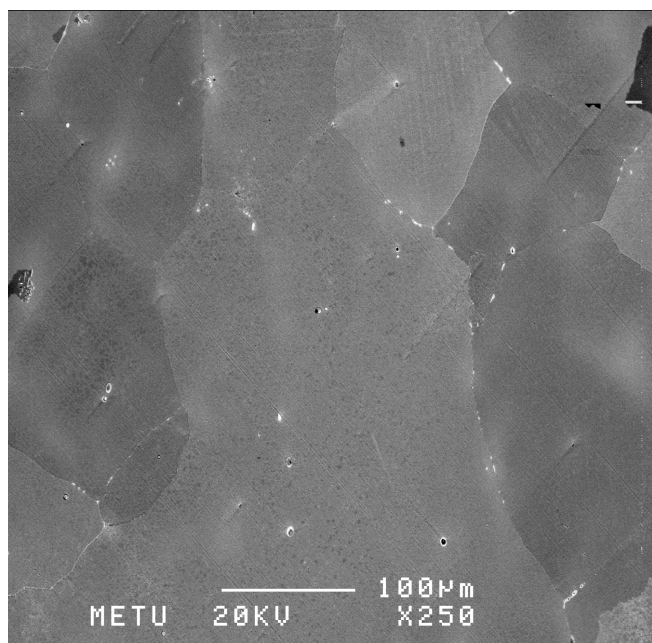


Fig. 4.4 Photo of microstructure of 1150°C/70min specimen (12-14Mn)

4.1.2 Microstructure of Hadfield Steels having Different Chemical Composition

All of these specimens were heat treated according to the usual procedure which includes heating to 1050°C, holding for 70min. and then quenching. The results for 12-14Mn specimen were already given in 4.1.1. The results of the remained specimens having different Mn (16-18Mn), Cr (12-14Mn 1.5Cr and 16-18Mn 2Cr), and Mo (16-18Mn 2Mo) content are given in this section.

In the 12-14Mn 1.5Cr specimen only few MnS (61%Mn, 38%S) particles exist in the grains, and some at the grain boundaries. Cr carbides which lie along the grain boundaries are almost not present, like in 12-14Mn specimen (Fig. 4.5).

The investigation of 16-18Mn specimen shows that grain boundaries of this specimen are more definite than 12-14Mn specimen and grains are coarser for 16-18Mn specimen as 165 μ m (Fig. 4.5). SEM analysis showed that there are carbides along grain boundaries (Table 4.3).

There are carbides (Table 4.4) distributed homogeneously within the grains of 16-18Mn 2Cr specimen. Unlike 12-14Mn 1.5Cr specimen, there exist spherical type (2.5-3.5 μ m) and rod type (2-4.5 μ m) carbides near grain boundaries.

In the case of 16-18Mn 2Mo specimen, the grain boundaries are not very clear. Because of Mo in composition there are globular types of carbides which probably form from the melt in interdendritic sites. However, this time there are no grain boundary carbides.

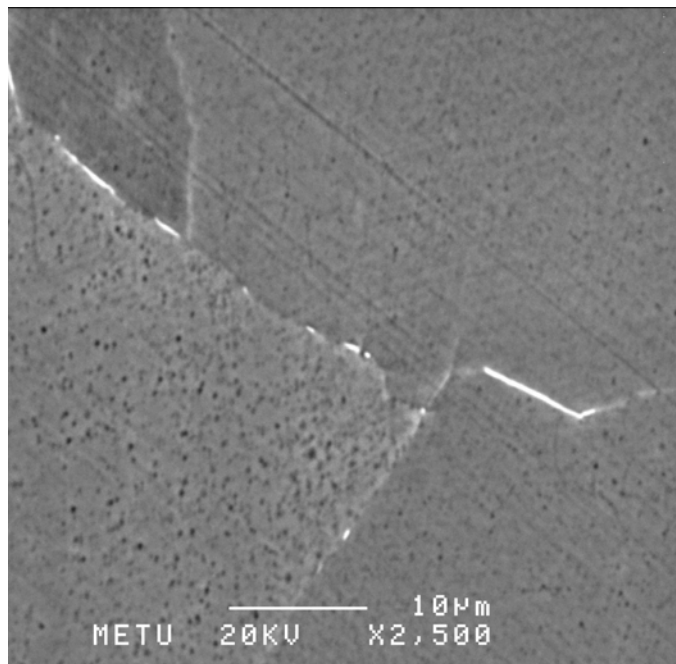
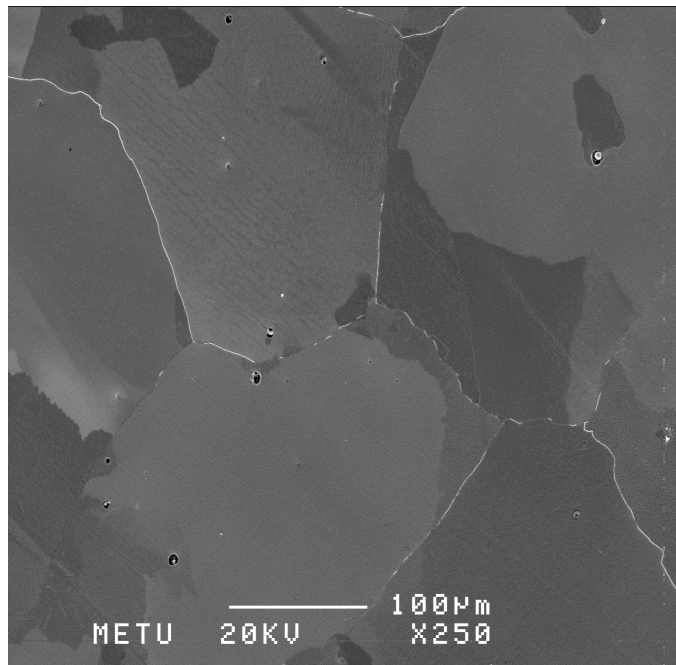


Fig. 4.5 Micrographs of 12-14Mn 1.5Cr specimen (1050°C/70min)

Table 4.3 Result of EDS analysis for grain boundary carbides in 16-18Mn specimen (1050°C/70min)

Element	Atom%	Weight%
Cr	2.26	2.12
Mn	23.90	23.66
Fe	73.63	74.22

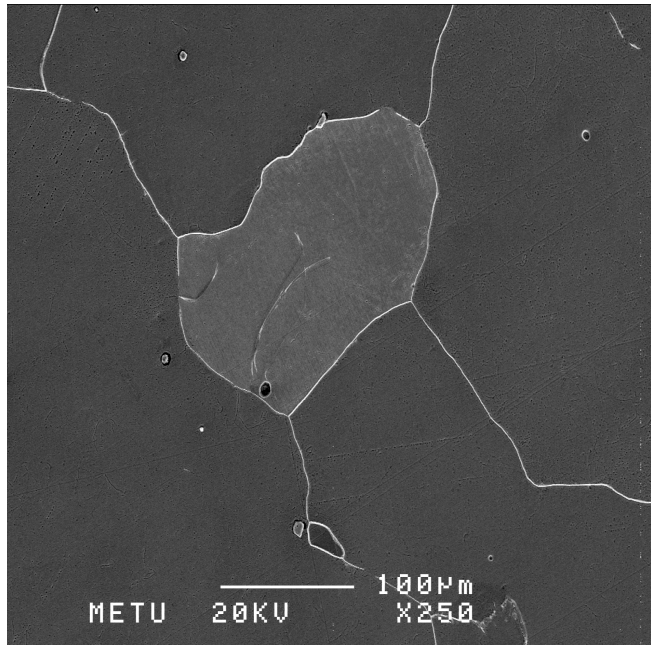


Fig. 4.6 Micrograph of 16-18Mn specimen (1050°C/70min)

Table 4.4 Results of EDS analysis for 16-18Mn 2Cr specimen (1050°C/70min)

Element	Spherical carbides		Rod type carbides	
	Atom%	Weight%	Atom%	Weight%
<i>Cr</i>	13.62	12.75	11.88	11.12
<i>Mn</i>	23.81	23.57	23.18	22.95
<i>Fe</i>	63.22	63.73	65.41	65.93

4.2 Results of Mechanical tests

For Hadfield steels, toughness is the quality most desired, which places a premium on ductility and strength together since one measure of toughness is the area under stress-strain curve. As approximation of this index, a parameter called ‘merit number’ is obtained by following formula [5]:

$$\text{Merit No} = (\text{conventional UTS}) \times (\text{elongation}) \dots \dots \dots (1)$$

The results of mechanical tests (yield strength, ductility and hardness) and calculated Merit numbers are given in Table 4.5. In calculations, instead of ultimate tensile strength (UTS) values true fracture strength (TFS) values were used because no necking is observed during tensile test.

4.2.1 Strength and Ductility

Macroscopic features as orange-peel formation, coarse slip bands and lack of tensile necking can characterize the tensile deformation of Hadfield steels (Fig. 4.7). Examination of the samples, during tensile loading and after rupture, shows disclosed numerous cracks on the surface of specimens. These cracks developed on planes almost perpendicular to the loading direction. The cracks are equally distributed along the gage of the specimen and they develop parallel to coarse slip bands.

The fracture surface of the specimens was noted to be macroscopically flat and perpendicular to tensile axis without marked shear slip. Fracture occurred without necking of specimens. This is why true fracture strength values were shown instead of ultimate tensile strength values in the table.

Table 4.5 Results of mechanical tests

Specimen	Composition	Heat-treatment condition	Yield strength (MPa)	True Fracture Strength* (MPa)	Elong. (%)	Merit No	Hardness (BH)
<i>HT1</i>	12-14 Mn	950°C - 70 min. + WQ**	425	646	16	103.4	167
<i>HT2</i>		1050°C - 35 min. + WQ	525	661	19	125.6	157
<i>HT3</i>		1050°C - 70 min. + WQ	470	736	34	250.2	158
<i>HT4</i>		1050°C - 140 min. + WQ	475	767	28	214.8	186
<i>HT5</i>		1150°C - 70 min. + WQ	468	704	24	169.0	166
<i>1</i>	12-14 Mn	1050°C - 70 min. + WQ	470	736	34	250.2	158
<i>2</i>	12-14 Mn 1.5 Cr		510	740	33	244.2	172
<i>3</i>	16-18 Mn		455	765	32	244.8	173
<i>4</i>	16-18 Mn 2 Cr		550	770	31	238.7	180
<i>5</i>	16-18 Mn 2 Mo		555	890	38	338.2	182
*As fracture occurs without necking, true fracture strength (TFS) is shown instead of ultimate tensile strength (UTS).							
**WQ: water quenched							



Fig. 4.7: Sample photographs of specimens after tensile test

When 1050°C/35min, 1050°C/70min, 1050°C/140min specimens are compared to see the effect of solutionizing time on tensile properties (Fig. 4.8), it is found that 1050°C/35min has the highest yield strength, and 1050°C/70min and 1050°C/140min gave almost the same value. However, the elongation of 1050°C/70min is remarkably higher than others (Fig. 4.9). True fracture strength of 1050°C/70min is 10% higher than that of 1050°C/35min, and 5% lower than that of 1050°C/140min.

When 950°C/70min, 1050°C/70min, 1150°C/70min specimens are compared to see the effect of solutionizing temperature on tensile properties (Fig. 4.10), it is found that at 1050°C maximum yield strength (470 MPa), true fracture strength (736 MPa) and ductility are obtained (Fig. 4.11). With increasing solutionizing temperature, true fracture strength increased slightly, however, the increase in the ductility was considerable.

When Mn percentage increased from 12.4 to 16.5, yield strength decreased slightly (4%), and a similar increase, i.e., from 736 MPa to 765 MPa, was observed in the true fracture strength. Ductility showed a slight decrease (Fig. 4.12 and Fig. 4.13).

When Cr is added into 12-14Mn or 16-18Mn steel up to 2%, tensile strength did not change or negligibly decreased. On the other hand, the yield strength of 16-18Mn 2Cr specimen is nearly 100 MPa higher than that of 16-18Mn specimen. True fracture strength and ductility of 16-18Mn 2Cr are 5% and 10% higher than those of 16-18Mn, respectively (Fig. 4.14 and Fig. 4.15).

Presence of 2% Mo resulted in an increase in yield strength and ductility, however, no change was observed in the true fracture strength. By adding 2% Mo to 16-18Mn the yield strength increased from 455 MPa to 555 MPa. In addition, true fracture strength increased 15%, and ductility increased 20% due to this addition (Fig. 4.16 and Fig. 4.17).

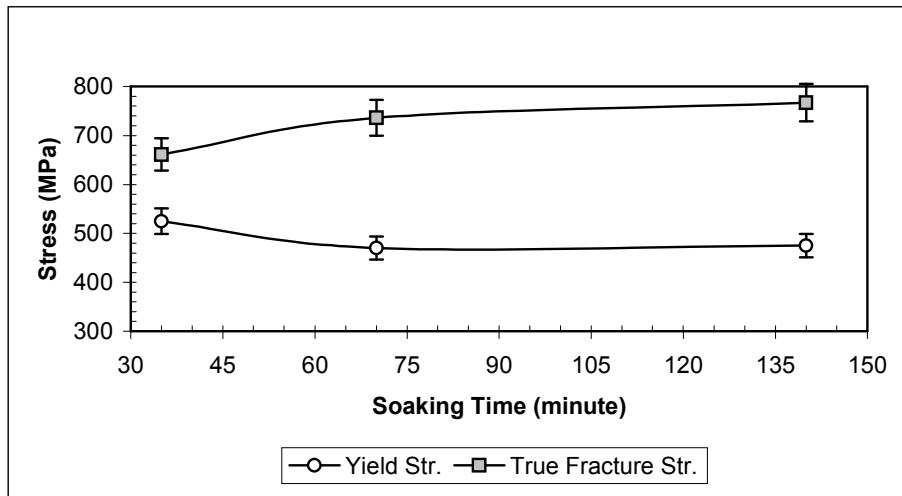


Fig. 4.8 Effect of solutionizing time at 1050°C on strength of 12-14Mn Hadfield steel

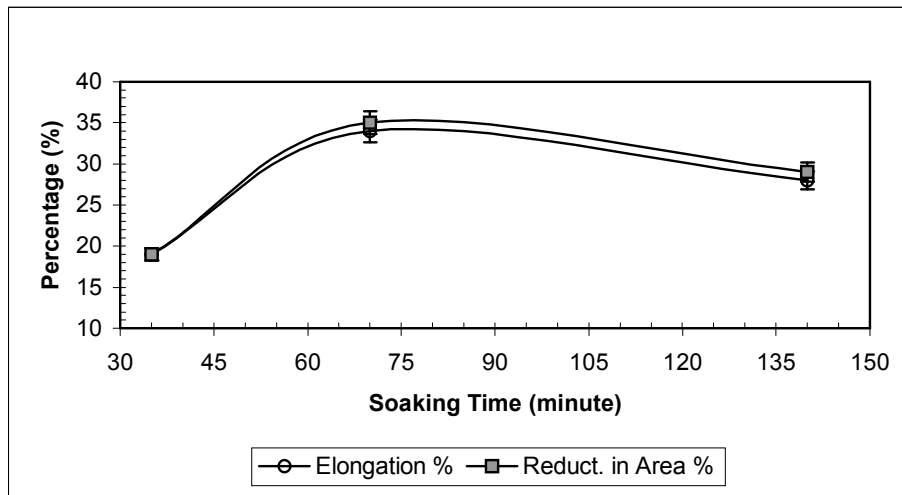


Fig. 4.9 Effect of solutionizing time at 1050°C on ductility of 12-14Mn Hadfield steel

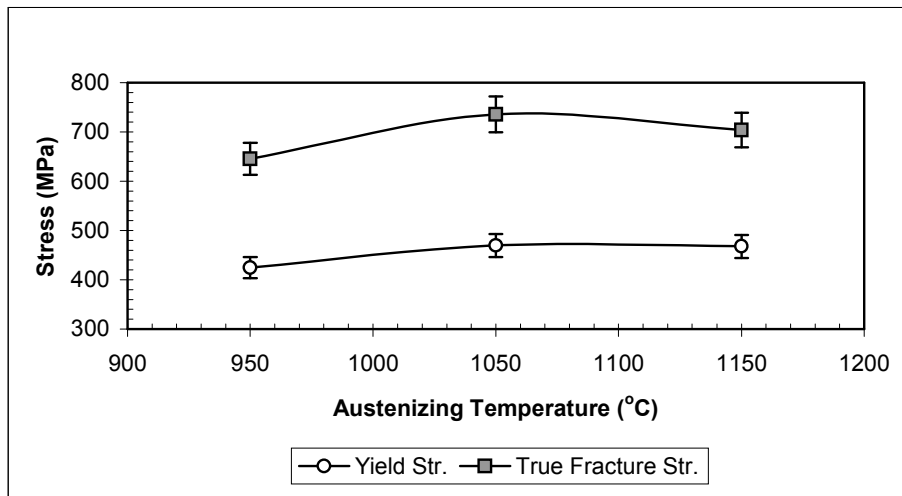


Fig. 4.10 Effect of solutionizing temperature on strength of 12-14Mn Hadfield steel (for 70 minutes solutionizing)

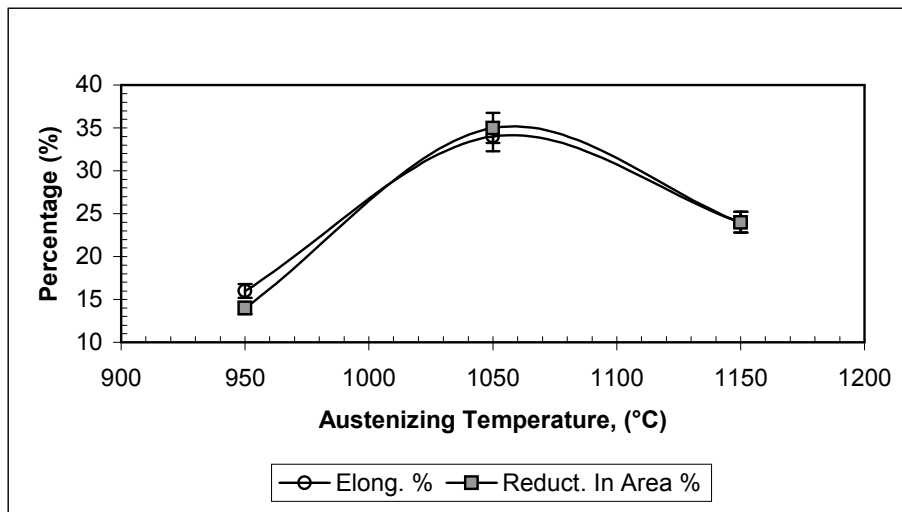


Fig. 4.11 Effect of solutionizing temperature on ductility of 12-14Mn Hadfield steel (for 70 minutes solutionizing)

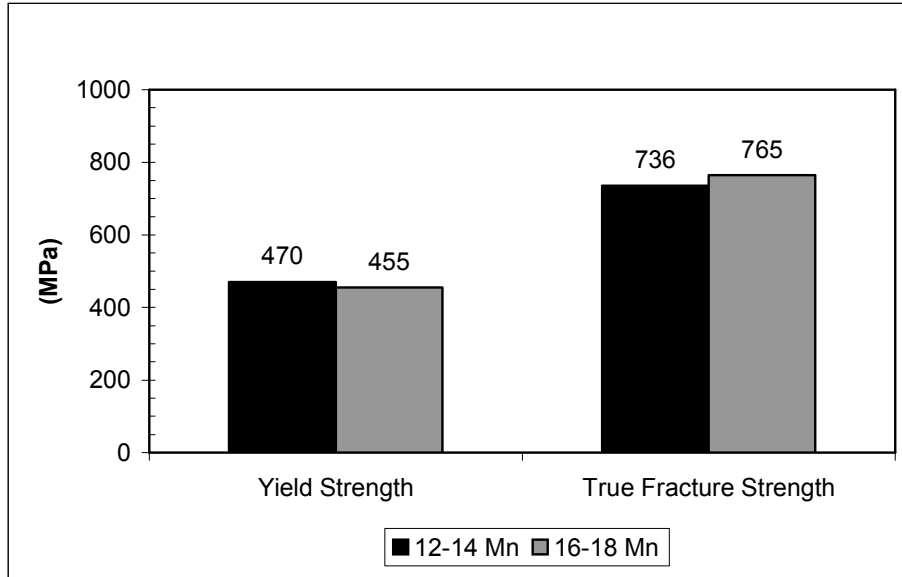


Fig. 4.12 Effect of Mn content on strength of Hadfield Steels (1050°C, 70min)

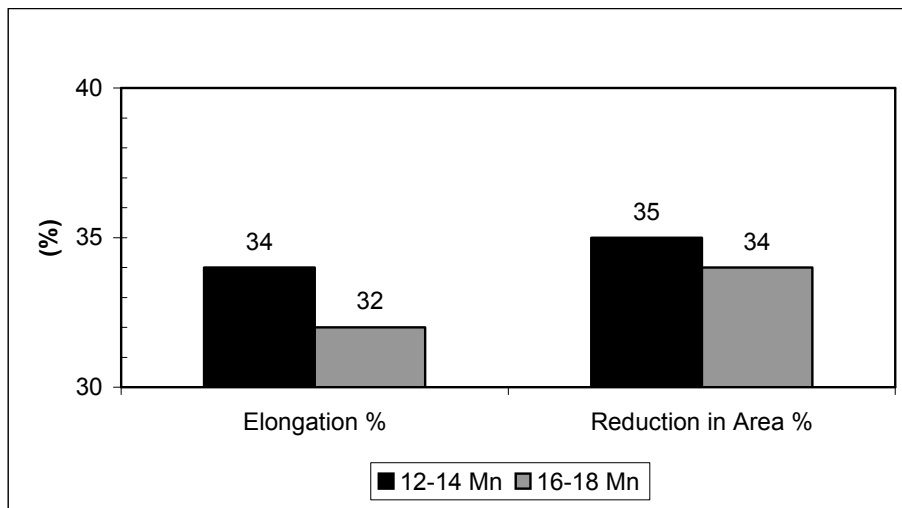


Fig. 4.13 Effect of Mn content on ductility of Hadfield Steels (1050°C, 70min)

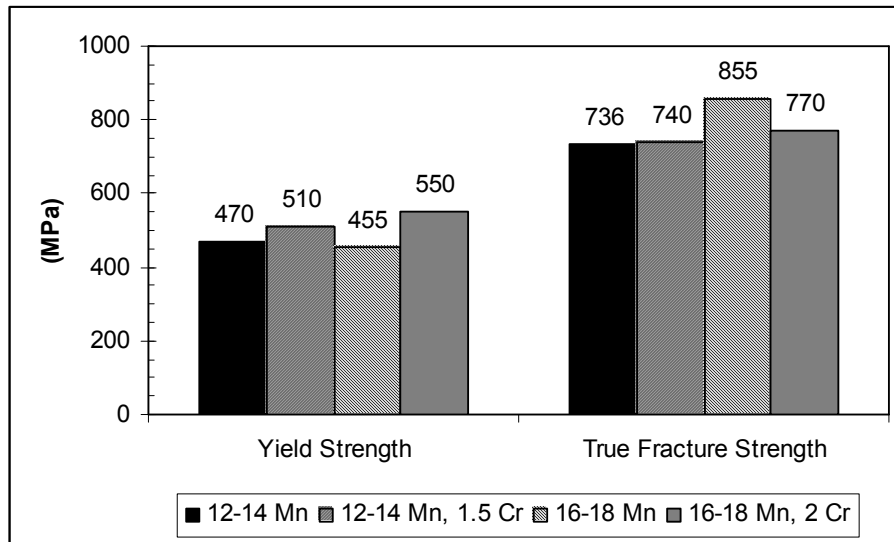


Fig. 4.14 Effect of Cr content on strength of Hadfield Steels (1050°C, 70min)

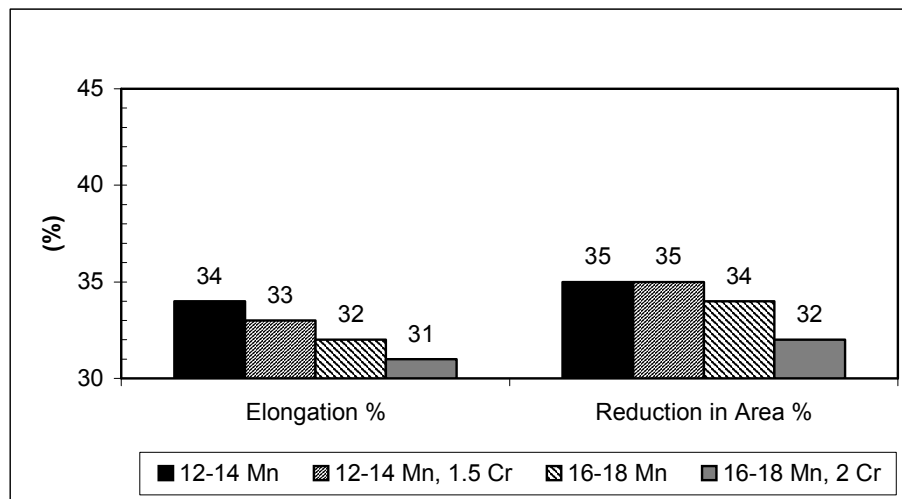


Fig. 4.15 Effect of Cr content on ductility of Hadfield Steels (1050°C, 70min)

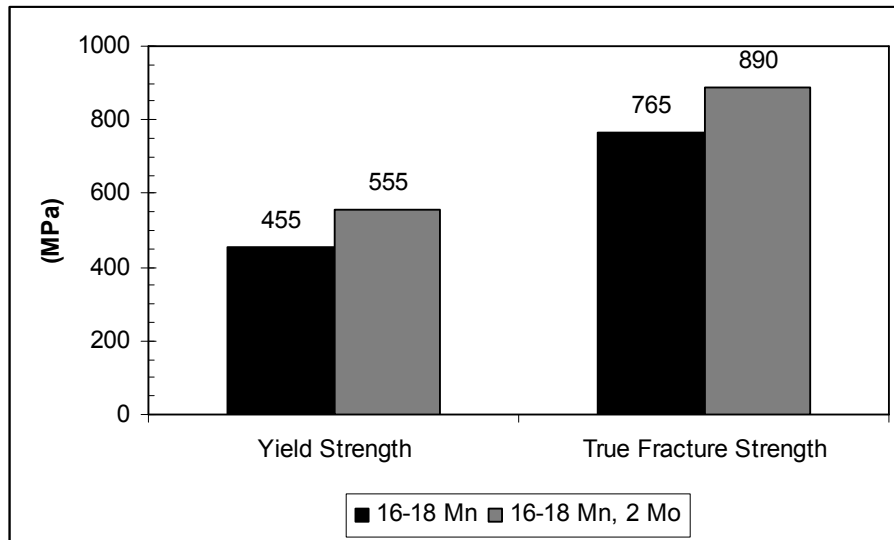


Fig. 4.16 Effect of Mo content on strength of 16-18Mn Hadfield steels (1050°C, 70min)

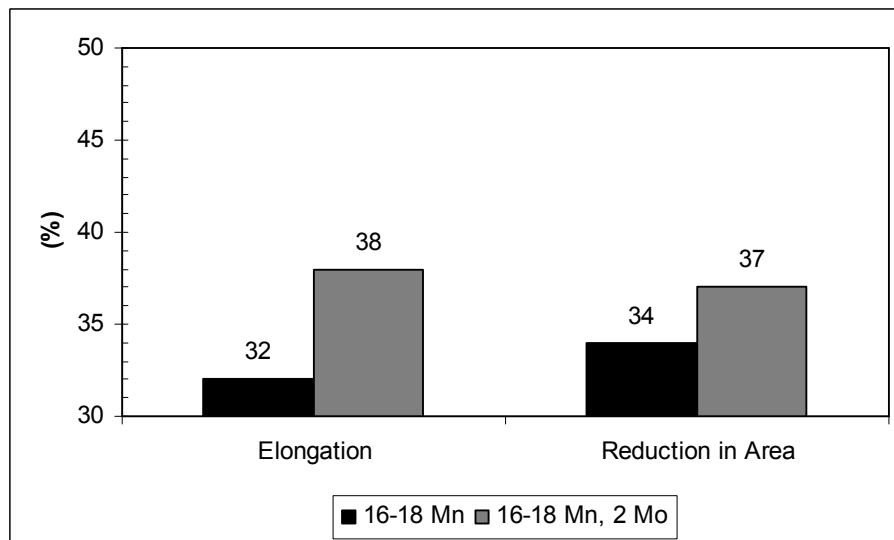


Fig. 4.17 Effect of Mo content on ductility of 16-18Mn Hadfield Steels (1050°C, 70min)

4.2.2 Hardness

In the case of 12-14Mn steel, Fig. 4.18 shows that as solutionizing time increased from 35 minutes to 140 minutes at 1050°C, a remarkable increase occurred from 160 to 190 HB after 70 minutes. Figure 4.19 shows that hardness changed slightly as a function of solutionizing temperature between 950 and 1150°C for a given solutionizing time of 70 minutes. On the other hand, if differently alloyed hadfield steels are compared, it is seen that hardness values are much higher for Cr or Mo added steels than 12-14Mn steel (Fig. 4.20).

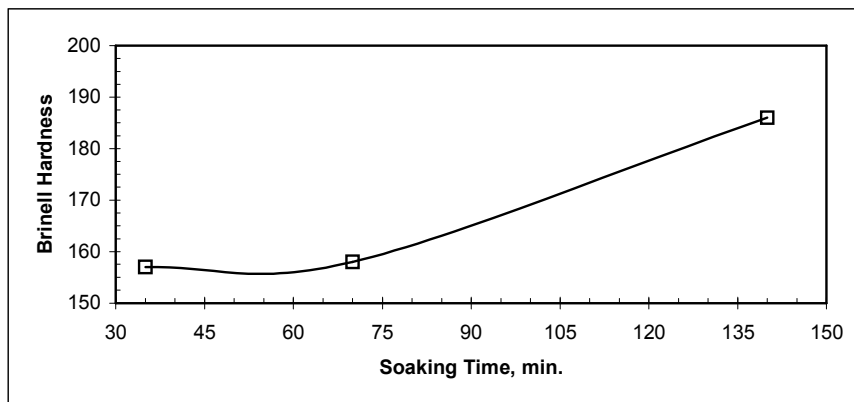


Fig. 4.18 Effect of solutionizing time on hardness of 12-14Mn steel at 1050°C

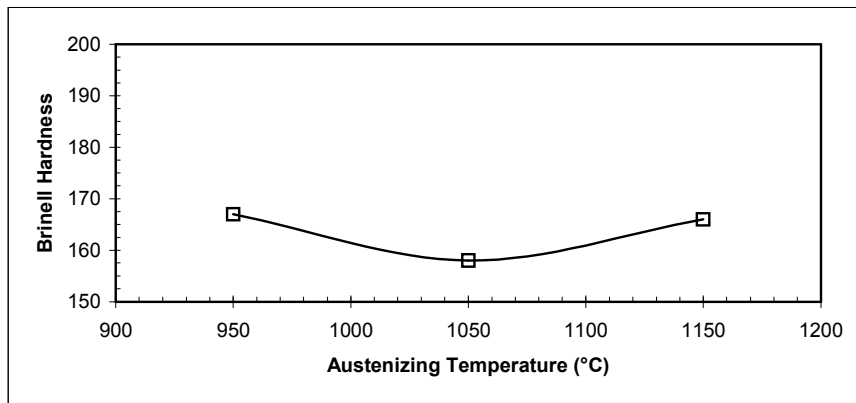


Fig. 4.19 Effect of solutionizing temperature on hardness of 12-14Mn Hadfield steel for 70 minutes solutionizing time

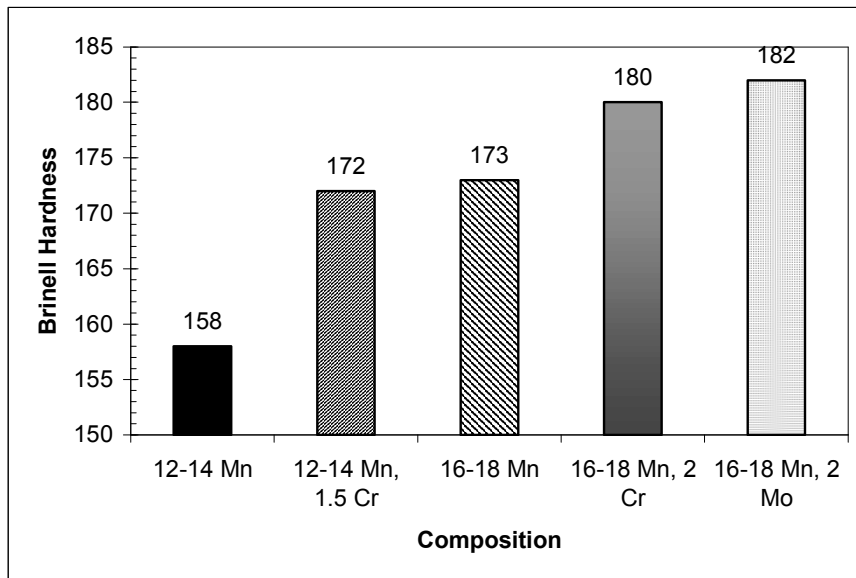


Fig. 4.20 Effect of Mn, Cr and Mo content on hardness of Hadfield steels after 70 minutes solutionizing at 1050°C

4.3 Results of Ultrasonic Velocity Measurements

The results of ultrasound velocity measurements for 12-14Mn steels are summarized in Fig. 4.21, and those for other steels are in Fig.4.22.

As seen in Fig. 4.21, for a given solutionizing period of 70 minutes, the effect of solutionizing temperature up to 1050°C on ultrasound velocity is negligible, however, a sudden increase from 5690 m/s to 5870 m/s was observed when the temperature was raised to 1150°C. Similarly, for a given solutionizing temperature of 1050°C, the solutionizing period up to 70 minutes resulted in no change in ultrasound velocity, but velocity value showed a significant increase after 140 minute-solutionizing (from 5690 m/s to above 5820 m/s).

Fig. 4.22 shows that Mn addition resulted in a reduction in ultrasound velocity (from 5680 m/s to 5540 m/s). For both 12-14Mn and 16-18Mn steels, ultrasound velocity increased remarkably due to Cr addition of 1,5% and 2%. Addition of 2% Mo to 16-18Mn steel gave similar result, however, the amount of increase in the ultrasound velocity is less than that having 2% Cr.

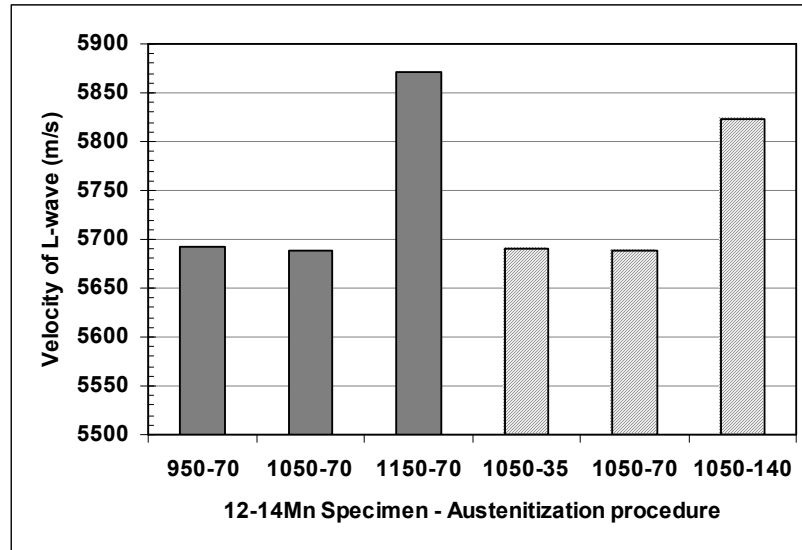


Fig. 4.21 Propagation velocity of ultrasonic longitudinal waves in 12-14Mn steels, quenched after solutionizing at different temperatures for different periods.

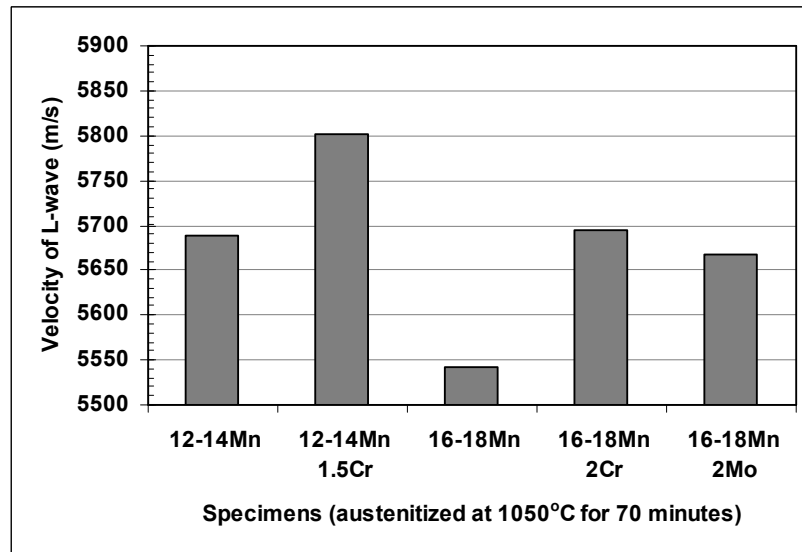


Fig. 4.22 Propagation velocity of ultrasonic longitudinal waves in various Hadfield steels, quenched after solutionizing at 1050°C for 70 minutes.

4.4 Discussion

4.4.1 General

Surfaces of the specimens were ground twice because of an unexpected structure like twins/martensite and very high hardness (see Chapter III). After removing about 3 mm layer by grinding, the expected microstructure and hardness values were achieved. The reason is supposed to be work hardening or heating which happened during the preparation of specimens. Since austenite is not entirely stable, it will reject some of the carbon at the intermediate temperatures or during deformation. This, in the form of manganese-iron carbides, occurs as fine particles or films at grain boundaries, as flat-brittle plates, and in the lamellae of pearlite. Carbide precipitation in any of these forms leads to increased hardness and brittleness. Deformation raises hardness most effectively with the least loss in toughness. Such carbide precipitation caused by slow cooling from the completely austenitic range or by reheating the tough structure is undesirable.

With its behavior of toughening after a water quench and embrittling after a tempering heat treatment, manganese steel appears as a paradox in contrast with conventional steels. The austenite is not homogenous in cast material, because carbon and manganese gradients result from the dendritic pattern of solidification. There are 3 types of carbides affecting the performance of Hadfield steels: carbides within matrix, especially $(Fe\ Mn)_3C$ type carbides; carbides along or around grain boundary, spherical or rod type; and, eutectic carbides. Grain boundary carbide precipitation is the primary cause of impaired properties associated with slow cooling. The mechanical properties of partially transformed austenite are poor particularly when carbides or other brittle constituents form in large flat plates parallel to crystallographic planes. The mechanical properties are low also when pearlite, which seems to nucleate most readily at grain boundaries develops in sufficient quantity to form an envelope around each grain. These structures account for the low ductility and reduced strength of austenitic manganese steel after reheating.

The carbides along or near the grain boundaries of the specimens contain a high level of Fe, Mn and Cr, indicating the presence of M_3C type carbides. M represents (Fe, Mn, Cr), Fe is a carbide forming element and Mn dissolves in Fe_3C . It is known that austenitic microstructure contains carbides of $(Fe\ Mn)_3C$ in the standard Hadfield steels [14,15]. If there is an alloying element which can form carbide and dissolve in cementite, then alloying element takes the place of Fe in cementite. Other alloying elements, which can not dissolve in cementite, form their own carbide.

4.4.2 Variations in microstructure and mechanical properties

Almost all samples include rounded MnS inclusions. It has been reported that the sulfur content seldom influences the properties of manganese steels. Because of its scavenging effect, Mn eliminates sulfur by fixing it in the form of innocuous, rounded, sulfide inclusions. In cast steels, these inclusions are harmless [1], however, it is aimed to keep sulfur as low as possible and to make sulfur float out in the slag in order to minimize the number of inclusions.

Hadfield steel parts are sometimes designed primarily for tension service, as in chains, but in most cases, tensile stresses are only one of the hazards of a part selected to resist wear. Toughness is the most desired quality parameter, which places a premium on ductility and strength together. Grain size, grain boundary thickness, and carbide precipitates affect toughness. Since the area under stress-strain curve is a measure of toughness, by multiplying true fracture strength with percent elongation ‘the merit number’ is obtained as an approximation of toughness (Table 4.5).

Among the 12-14Mn specimens austenitized at 1050°C for 35, 70 and 140 minutes, the highest toughness (merit number) was obtained for 70 minute solutionizing. 1050°C/35min specimen has the lowest toughness due to the presence of carbides along the grain boundaries. When 950°C/70min, 1050°C/70min, 1150°C/70min specimens of 12-14Mn steel are compared, it is seen that although the hardness values are almost the same, by 70 minute solutionizing at 1050°C, the

maximum merit number and the acceptable values for yield strength, true fracture strength and percent elongation were achieved. At higher solutionizing temperatures, relatively high ductility values are obtained, however, the increase in the true fracture strength is slight. Ductility of 1050°C/70min specimen is almost 2 times higher than that of 950°C/70min specimen. It points out the critical role of solutionizing temperature for carbide dissolution. In SEM investigation of the 950°C/70min specimen, both rod-like and spherical M_3C type carbides having the similar composition were observed. The undissolved carbides are the main reason of low ductility and low toughness.

At 1050°C, among the 12-14Mn specimens austenitized for the periods of 35, 70 and 140 minutes, the 1050°C/35min specimen has the highest yield strength. Yield strength of 1050°C/70min and 1050°C/140min specimens are almost the same, but there is a big difference between the elongation values. Although the yield strength of 1050°C/70min specimen is less than that of other two specimens, its ductility is almost two times higher than that of 1050°C/35min, and 25% higher than that of 1050°C/140min. Therefore, it has higher toughness. On the other hand, 1050°C/140min specimen contains less carbide along grain boundaries indicating that more carbide was dissolved in the matrix. This is especially important and critical for heavy castings.

For the given heat treatment consisting of solutionizing at 1050°C for 70 minutes, and then quenching, higher yield strength and ductility was obtained in 12-14Mn specimen in comparison to 16-18Mn due partly to the better carbide dispersion and partly to the less stable austenite. 16-18Mn specimen has coarser grains, and M_3C -type carbides exist along the grain boundaries. The results are in agreement with literature reporting that if Mn% is increased beyond 14% ductility decreases [5,7]. Moreover, the hardness of 16-18Mn specimen is higher than that of 12-14Mn, and whenever higher hardness is needed it seems the most appropriate way of increasing hardness by Mn addition.

When 12-14Mn, 12-14Mn 1.5Cr, 16-18Mn, and 16-18Mn 2Cr specimens are compared, the effect of Cr can be seen. The mechanical test results show that Cr has a positive effect on yield strength and hardness, but its effect on ductility is limited. For example, in the case of 16-18Mn steel, 2% Cr addition resulted in about 25% (i.e., 100 Mpa) increase in the yield strength, but, the variation in the elongation is about 0.5%. These results are in agreement with the literature [1,7]. However, it has also been reported that if more than 2% Cr is added, elongation and strength values would drop drastically [5,7]. Indeed, the addition of Cr tends to accentuate the formation of carbide networks around grain boundaries, and therefore, reduce the ductility of Hadfield steels. For that reason, higher solutionizing temperatures (about 1050°C) are usually applied prior to water quench because Cr has a stabilizing effect on iron carbide.

M₃C carbides exist in 16-18Mn 2Cr specimen similar to 16-18Mn specimen. However, the form of the carbides is both rod and spherical type. Since the EDS analysis showed that the compositions of the carbides are almost the same, shape difference can be mentioned by crystallographic precipitation difference or by position difference. Since there is only one crystallographic possibility for precipitation, the positional difference seems to be the main reason. These carbides are normally of coarse fish-like shape, and if it is at right angle to the examination plane their appearance is spherical, and if it is zero angle (horizontal) to the examination plane then it is seen as rod like.

The effect of Mo addition was investigated for 16-18Mn steel. In the 16-18Mn 2Mo specimen, there are globular type of carbides containing about 36% Mo. These carbides are believed to form from the melt in interdendritic sites, and they minimize the development of grain boundary Fe₃C type carbides. It has been previously reported that the globular type of carbide formed in the as cast 2% Mo steels should permit the use of higher C contents, possibly up to as high as 1.7% in commercial castings. These carbides are believed to be types of M₆C carbides [7]. Mo addition up to 2% increases yield strength like Cr addition, but it does not lower the ductility and tensile strength as Cr addition does. In this study, by addition of Mo,

yield strength increased from 455 MPa to 555 MPa (22%), and there was also 10% increase in hardness. Ductility was also improved by Mo addition. The tendency to premature failure by cracking is less than that to the plain manganese steels. Mo addition improved toughness (highest merit number among the steel types studied) since its presence results in an increase in both fracture strength and ductility. Grain boundaries of 16-18Mn 2Mo specimen are so narrow that it is difficult to recognize. Since the thickness of the boundaries is related to toughness [5], heat treatment is said to be successful if boundaries scarcely detectable. Therefore, Mo addition with modifications in thermal treatment seems to be more advantageous compared to Cr addition in austenitic manganese steels.

4.4.3 Variations in ultrasound velocity

The effect of austenitic structures on the behaviour of ultrasound depends largely on grain size. Coarse grain cast structures have marked effects, leading to increased scatter and attenuation, variations in sound velocity, and often to beam distortion. The effects are primarily due to the anisotropic nature of the austenitic columnar grains [14]. When travelling through the coarse grained anisotropic material the wavefronts are not generally at right angles to the beam axes. In general, the propagation velocity depends on the angle between the wavefront and the major axes of the grains. Moreover, the width of the ultrasound beam will vary depending on the angle of the incident beam to the long axes of grains. Experimentally it has been that longitudinal wave beams are most divergent when directed at 0° (and 90°). Because of variations in beam shape, amplitude methods are less reliable for austenitic structures. A major practical problem is the occurrence of severe attenuation and of back scattered ultrasound (grain noise) which varies with the direction of the ultrasonic beam. Attenuation is very much related to scattering. The scattering increases with grain size, frequency, and elastic anisotropy, and also depends on materials properties, density, and sound velocity.

After modifying the microstructure of as-cast Hadfield steels by heat treatment at about 1050°C, it is expected to minimize these adverse effects on ultrasonic measurements. The amplitude of the ultrasonic backscattered signal increases with the testing frequency, and the grain-noise amplitude also increases. Therefore, the application of low frequency probe like 1 MHz with short pulses is advantageous.

As seen in Fig. 4.21 and Fig.4.22, the propagation velocity of ultrasonic longitudinal waves in the austenitic manganese steel studied is between 5540 m/s and 5870 m/s. The ultrasonic velocity data about austenitic steels in literature is very limited, such that only 5660 m/s and 5740 m/s values have been found for ASTM A302 and A347 austenitic stainless steels, respectively.

Ultrasonic velocity results show that whatever affects the transmittance of the sound oscillations across grain boundaries also affects the ultrasound velocity. For 12-14Mn steels, in the case of longer solutionizing time at 1050°C, ultrasonic velocity increased. This result is more obvious when 1050°C/70min and 1050°C/140min specimens are compared. On the other hand, for 70-minute solutionizing time, higher solutionizing temperature (1150°C) resulted in higher ultrasonic velocity. The reasons seem to be the grain coarsening and better carbide dissolution.

Variations in the chemical composition of austenitic manganese steels gave different results. As Mn content is increased, for the same heat treatment conditions, the ultrasonic velocity decreased. However, increased amount of either Cr or Mo caused an increase in the ultrasonic velocity.

The correlations with mechanical properties showed a direct relationship between ultrasonic velocity and yield strength. However, the relationship with other mechanical properties is not so strong. Indeed, the elastic modulus is the dominant property affecting the ultrasonic velocity, however, for other steel types several researchers have reported some correlations between ultrasonic velocity and

mechanical properties. Particularly for this study, it can be said that ultrasonic velocity measurements are sensitive to the microstructural variations due to both heat treatment and alloying additions in the Hadfield steels, especially grain coarsening and carbide precipitation along grain boundaries.

CHAPTER V

CONCLUSION

In this study, the effect of solutionizing temperature and soaking time, and also the effect of Mn, Cr and Mo addition on microstructure, mechanical properties, and ultrasonic velocity of Hadfield steels were investigated. The conclusions can be stated as follows.

In the case of 12-14Mn steel, for a given solutionizing time of 70 minutes, 1050°C is the most suitable solutionizing temperature compared to 950°C, and 1150°C, since optimum microstructure and mechanical properties are achieved. Solutionizing at 950°C is not sufficient for carbide dissolution, and 1150°C results in coarsening of grains. For a given solutionizing temperature of 1050°C, 70 minute gives the best toughness value. Similar to the effect of solutionizing temperature, 35 minute solutionizing is too short for carbide dissolution, and 140 minutes results in grain coarsening. The carbides are mainly $(\text{Fe-Mn})_3\text{C}$ type, and exist either as continuous or discontinuous network along grain boundaries and/or as round precipitates near the grain boundaries.

For the given heat treatment (solutionizing at 1050°C for 70 minutes, then quenching), different results were obtained when the chemical composition has been changed. Higher Mn content results in a considerable improvement of strength, however, the increase in hardness seems remarkable. Cr or Mo addition yields improvements in tensile properties and hardness. Mo emerges as the one able to increase the yield with no impairment of ductility. 16-18Mn 2Cr and 16-18Mn 2Mo specimens have carbides as M_3C (12%Cr, spherical and rod type) and M_6C (36%Mo, globular) respectively. Since these alloying elements are added to obtain better mechanical properties and wear resistance without injuring toughness, proper

dispersion of carbides is vital. To avoid the formation of embrittling carbides, the form in which carbides occur must be controlled either by addition of other alloying elements and/or special heat treatments. So, the desired objective of producing fine carbide dispersions does not appear to be feasible with the conventional solution treatment used in this study. Which heat treatments are required to produce an optimum dispersion of carbides is unclear since there are many conflicting data and opinions. So, it may be recommended to further research on the microstructures and mechanical properties of Cr and Mo alloyed Hadfield steels resulting from various heat treatments to choose the optimum one.

Whatever affects the transmittance of the sound oscillations across grain boundaries also affects the ultrasound velocity. Ultrasonic velocity measurements are sensitive to the microstructural variations due to heat treatment and alloy additions in the Hadfield steels. Grain coarsening and carbide precipitation along grain boundaries due to various solutionizing procedures directly affect the ultrasonic velocity. Addition of Cr or Mo results in a definite increase in the ultrasonic velocity, in contrast to the increase in Mn content. The correlations with mechanical properties showed a direct relationship between ultrasonic velocity and yield strength. However, the relationship with other mechanical properties is not so clear. Although ultrasonic investigation is rather difficult in austenitic structures, this method seems promising for quality control of austenitic manganese steels, and further research is necessary.

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