

CHAPTER 1 - BACKGROUND

1. INTRODUCTION

Martensitic stainless steels were developed to satisfy a need in industry for corrosion resistant alloys that respond to hardening through heat treatment. These steels are alloyed with at least 10.5% chromium and up to 0.6% carbon, and are designed to be fully austenitic at elevated temperatures. The austenite can be hardened by quenching or cooling to room temperature from the austenitising temperature¹, which enables transformation to martensite^{1,2}. Due to their high alloying element content, martensitic stainless steels demonstrate excellent hardenability and are normally considered to be air hardening.

To develop optimal mechanical and corrosion properties in martensitic stainless steels, complete transformation to martensite on cooling is essential. The alloy therefore has to be fully austenitic at elevated temperatures, with a martensite transformation range above room temperature to allow the transformation to martensite to go to completion on cooling. Chromium imparts corrosion resistance to stainless steels, but is a strong ferrite-forming element, favouring ferrite at the expense of austenite at higher temperatures. The requirement for a fully austenitic structure at high temperature therefore limits the maximum chromium content of martensitic stainless steels to that defined by the stable austenite region on the binary Fe-Cr phase diagram (the γ -phase field in Figure 1.1³). Carbon is added to martensitic stainless steels to increase hardness and wear resistance, but also acts as a powerful austenite-former (it promotes austenite at the expense of ferrite). Carbon therefore expands the γ -phase field to higher chromium contents, allowing the addition of higher levels of chromium for improved corrosion resistance without compromising the stability of austenite at higher temperatures. The austenite phase field extends to about 18% chromium with the addition of 0.6% carbon. By definition martensitic stainless steels therefore lie within the chromium range of 11.5 to 18%, with the lower limit being governed by corrosion resistance and the upper limit by the requirement for the alloy to convert fully to austenite on heating.

In addition to chromium and carbon, martensitic stainless steels may also contain additions of molybdenum and vanadium. These alloying elements increase the

hardenability, temper resistance and high temperature hardness of the steel⁴. Like chromium, molybdenum and vanadium are strong carbide-formers⁵. The austenitising temperature employed during heat treatment determines the partitioning of carbon and alloying elements between the austenite and carbide phases, with an increase in temperature leading to increased carbide dissolution and higher dissolved alloying element contents. When in solid solution at temperatures above the carbide dissolution temperature, these carbide-forming elements affect the transformation to martensite by depressing the martensite transformation range and reducing the martensite start (M_s) and martensite finish (M_f) temperatures. If the M_f temperature is depressed to below room temperature or even to below 0°C , retained austenite may be present in the as-quenched microstructure as a result of the martensite transformation not going to completion². Retained austenite reduces the as-quenched hardness and may transform to brittle martensite during subsequent tempering operations.

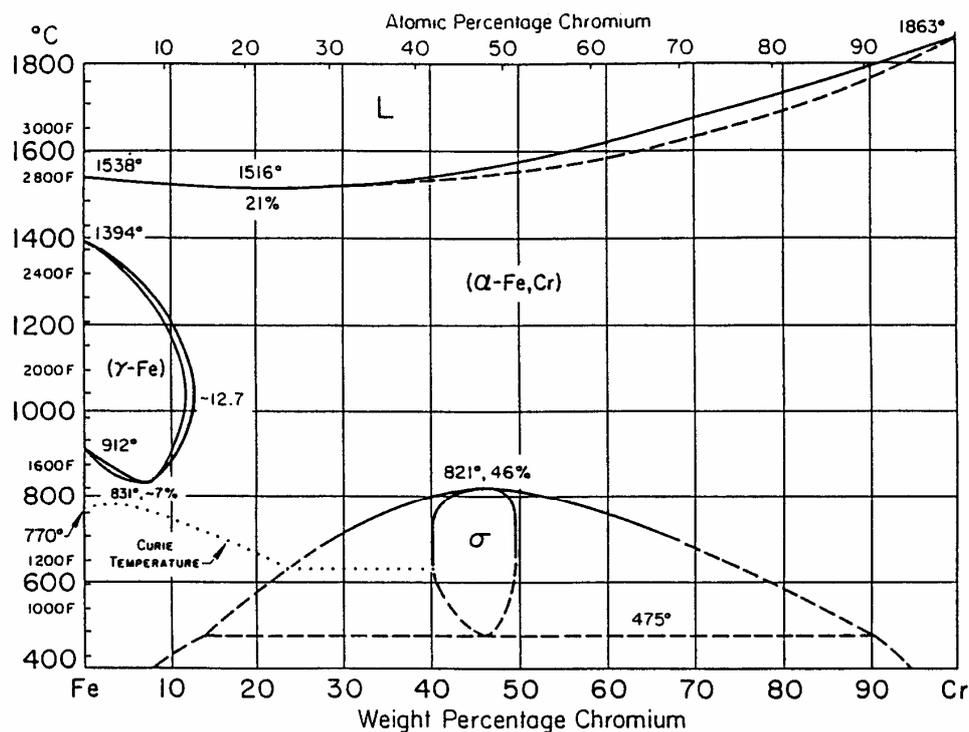


Figure 1.1: The binary Fe-Cr phase diagram.

The composition of martensitic stainless steels and their response to heat treatment therefore determine the resulting mechanical and corrosion properties. An overview of the relevant available literature on the metallurgy and heat treatment of these steels is given below.

2. LITERATURE OVERVIEW

In 1822, Michael Faraday initiated an investigation with the aim of producing an alloy steel for the manufacture of cutting tools and non-corrodable metals for reflectors. At this time only so-called plain-carbon steels were available – steels which do not perform satisfactorily in applications requiring high strength and corrosion resistance. One hundred years later, in 1922, Brearley discovered the stainless (“corrosion resistant”) properties of high-chromium steels. These high-chromium corrosion resistant alloy steels are now referred to as “stainless steels”⁴.

2.1 Martensitic stainless steels – an overview:

Martensitic stainless steels contain between 11.5% and 18% chromium, and are deliberately alloyed with up to 0.6% carbon. The development of this group of stainless steels was prompted by the need for corrosion resistant stainless steels that are hardenable by heat treatment. The resulting martensitic stainless steels are austenitic at elevated temperatures and harden through transformation to martensite during quenching or cooling to room temperature⁵. This results in an excellent combination of moderate to good corrosion resistance, high hardness and strength, good resistance to thermal and mechanical fatigue and excellent wear resistance.

The martensitic stainless steels are magnetic, can be cold-worked and hot-worked (especially at lower carbon contents), can be machined satisfactorily, display high toughness and possess good corrosion resistance to weather and some chemicals. They attain their best corrosion resistance in the hardened condition, but are generally not as corrosion resistant as the austenitic or ferritic stainless steels. Among corrosion-resistant applications, martensitic stainless steels are used in coal handling and in mining equipment, where advantage is taken of their high abrasion resistance and moderate corrosion resistance^{1,5}. The martensitic grades are usually hardened by heating above the transformation range to temperatures in the region of 1000°C, followed by cooling in air or oil. Time at temperature must be minimised to prevent decarburisation or excessive grain growth. In order to obtain mechanical properties suitable for engineering applications, the steels are tempered after quenching. The resulting mechanical properties depend strongly on the tempering temperature.

For a martensitic stainless steel to possess adequate hardness, wear resistance and corrosion resistance, no δ -ferrite should be present at the austenitising temperature (950°C to 1010°C), the martensite transformation range should be above room temperature (to reduce the risk of forming retained austenite) and the steel should exhibit maximum temper resistance. As the martensitic transformation is the dominant strengthening mechanism in these steels, the heat treatment of the alloy must be designed to ensure that no, or at best, minimal retained austenite is present after cooling⁶. This is complicated by the chemistry of the steel, and in particular the presence of additional alloying elements, which often depress the martensite finish temperature to below 0°C.

For applications involving wear or which require retention of sharp cutting surfaces in finished products, steels containing 11 to 14% chromium and between 0.3 and 0.4% carbon are preferred³. The medium to high carbon contents of these steels ensure the high as-quenched hardness values required in these applications. AISI 420 is a low-chromium, medium-carbon member of the martensitic family of stainless steels. In the hardened and tempered condition, AISI 420 has high strength and excellent wear resistance, which makes it the ideal choice for applications such as cutlery, hand tools, dental and surgical instruments, valve trim and parts, shafts, and plastic moulding. The typical chemical composition range specified for medium-carbon AISI 420 is shown in Table 1.1⁷. The steel is alloyed primarily with chromium and carbon. A brief discussion of these and other alloying elements routinely added to AISI 420 martensitic stainless steel is given below.

Table 1.1: Typical chemical composition of AISI 420 martensitic stainless steel (weight percentage, balance Fe)⁷.

C	Cr	Mn	Si	Mo	Ni	P	S
0.5 max.	12.0 to 14.0	1.0 max.	1.0 max.	1.0 max.	1.0 max.	0.04 max.	0.03 max.

2.2 The influence of alloying elements on the microstructure of martensitic stainless steels:

2.2.1 Chromium:

Chromium is the principal alloying element in stainless steels, added in amounts greater than approximately 10.5% to improve corrosion resistance and promote

passivation. Chromium is a strong ferrite-forming element and tends to restrict the austenite phase field and suppress the ferrite to austenite transformation during heating⁵. In binary Fe-Cr alloys, the austenite phase field extends to a maximum chromium content of approximately 12.7% (as shown in Figure 1.1). Beyond this chromium content, austenite is not thermodynamically stable.

This limits the amount of chromium that can be added to austenitic and martensitic stainless steels (these alloys have to transform completely to austenite at higher temperatures). In alloys requiring higher chromium contents for improved corrosion resistance, the austenite phase field can be expanded to higher chromium levels by adding strong austenite-forming elements, such as carbon, nitrogen or nickel. In the presence of sufficient carbon, steels containing in excess of 12% chromium can be fully austenitic above a certain temperature (this temperature being dependant on the carbon:chromium ratio)⁸. As shown in Table 1.1, AISI 420 contains 12 to 14% chromium. Chromium is also instrumental in increasing the hardness and wear resistance of the steel. It increases the hardenability and temper resistance of the steel³ and facilitates the formation of secondary chromium-rich alloy carbides, such as M_7C_3 or $M_{23}C_6$ ⁴.

2.2.2 Carbon:

Carbon is the single most important alloying element in steels and plays an important role in martensitic stainless steels. It is a strong austenite-forming element, promoting the formation of an austenitic structure at elevated temperatures at the expense of ferrite. An increase in carbon content up to approximately 1% enlarges the austenite phase field and allows steels with up to 16% chromium to be fully martensitic after appropriate hardening treatment¹. The carbon content of martensite also determines the hardness of the martensite, with the hardness increasing with an increase in carbon concentration (provided retained austenite does not form in significant amounts). Higher carbon steels are therefore preferred for applications requiring high hardness and wear resistance. The hardness of high-carbon martensitic steels can be increased further through precipitation of carbides on slow cooling from the austenite region³. However, the formation of massive chromium-rich $M_{23}C_6$ carbides lowers the corrosion resistance of the steel, a phenomenon known as sensitisation. These chromium-rich carbide particles introduce a second phase into

the metal which promotes galvanic corrosion⁹, and cause chromium depletion adjacent to the grain boundaries. Medium-carbon AISI 420 stainless steel contains up to 0.5% carbon for optimal hardness and wear resistance.

2.2.3 Molybdenum:

Although the standard AISI 420 stainless steel grades do not contain molybdenum as a deliberate alloying addition, this alloying element imparts certain beneficial properties to martensitic stainless steels that may justify its addition to AISI 420. Alloying with molybdenum results in a general improvement in corrosion resistance, machinability and mechanical properties. Molybdenum increases the hardness and temper resistance of the steel at higher temperatures⁴ and promotes secondary hardening during tempering.

Molybdenum in solid solution is a strong ferrite-forming element which enlarges the austenite phase field and retards the transformation of ferrite to austenite on heating. The addition of molybdenum to martensitic stainless steels therefore needs to be balanced with the addition of a suitable austenite-forming element to ensure a fully austenitic structure at elevated temperatures where molybdenum is more likely to be in solid solution. Molybdenum forms carbides readily and reacts with carbon to form various alloy carbides, such as Mo_2C , $\text{Fe}_4\text{Mo}_2\text{C}$ and $\text{Fe}_{21}\text{Mo}_2\text{C}_6$ ⁴. Molybdenum may also form part of the complex M_{23}C_6 carbide that precipitates on slow cooling from the austenite phase field.

2.2.4 Vanadium:

Vanadium has an important grain refining function in martensitic stainless steels, with as little as 0.1% effectively restricting grain growth during normal hardening heat treatments. Vanadium is a strong carbide-former and is normally present in the microstructure as finely dispersed carbides or carbonitrides which inhibit excessive grain growth⁴. On dissolving in the steel at higher temperatures, vanadium acts as an effective ferrite-forming element.

Since the stability of alloy carbides and their dissolution at higher temperatures have an important influence on the as-quenched microstructure and properties of martensitic stainless steels, the effect of alloying elements on the stability of carbides in these stainless steels is briefly considered below.

2.3 The effect of alloying elements on the formation and stability of carbides:

Alloying elements added to stainless steel either dissolve in the ferrite or austenite matrix, or react with carbon to form alloy carbides. Elements known to dissolve preferentially include aluminium, copper, silicon, phosphorous, nickel and zirconium. Those elements with a strong tendency to form carbides include, amongst others, chromium, tungsten, molybdenum, vanadium and titanium¹⁰. The partitioning of these carbide-forming elements between the matrix and carbide particles plays an important role in determining the microstructure and properties of martensitic stainless steels.

Higher chromium contents result in improved corrosion resistance, while higher carbon contents increase the strength, hardness and wear resistance of the steel. The presence of higher carbon contents in martensitic stainless steels is, however, associated with several disadvantages, including lower toughness, degradation of weldability and a reduction in corrosion resistance due to the formation of chromium-rich carbides. Higher carbon contents tend to increase the volume fraction of carbides present after cooling, often necessitating the use of high austenitising temperatures which result in grain growth and reduced impact properties².

Various authors have published reports detailing investigations into the nature of the different carbides that form in martensitic stainless steels^{6,11}. It has been shown that steels with more than 0.2% carbon and between 12 and 13% chromium (including AISI 420) typically contain M_3C , M_7C_3 and $M_{23}C_6$ carbides. The precipitation of these carbides is time dependent, and appears to occur in a typical precipitation sequence that involves initial precipitation of M_3C , followed by M_7C_3 and then $M_{23}C_6$ ¹¹. The addition of approximately 1% molybdenum to 12% chromium steels retards the coarsening of the carbide particles.

The stability of these carbides and their gradual dissolution at higher temperatures control the partitioning of carbon and alloying elements between the austenite matrix and the carbide precipitates. Dissolution of carbides during heat treatment reduces the M_s and M_f temperatures of the steel, and may result in the presence of significant amounts of retained austenite after cooling. The heat treatment of these grades of martensitic stainless steel therefore has a major influence on the microstructure and properties of the alloys, and is described in more detail below.

2.4 Heat treatment of martensitic stainless steels:

Heat treatment of steel causes internal physical changes which produce a wide range of microstructures in the alloy. These transformations affect the mechanical properties of the steel, and the heat treatment procedure can usually be manipulated to obtain a wide range of strength, toughness and hardness values¹².

The typical heat treatment sequence for martensitic stainless steels includes annealing to soften the steel in preparation for subsequent cold work or machining, austenitising to form an austenitic structure and fully or partially dissolve carbides, cooling or quenching to transform the austenite to martensite, followed by tempering of the martensitic structure to improve toughness and ductility. The final microstructure of AISI 420 is very dependent on the prior heat treatment that the steel received, and typically consists of martensite, undissolved and/or reprecipitated carbides and retained austenite. The volume fraction and size of the carbide particles present in the steel and the amount of retained austenite play a major role in determining the hardness, strength, toughness, corrosion resistance and wear resistance of the steel¹³. The typical heat treatments used in the processing of martensitic stainless steels are discussed below.

2.4.1 Annealing:

Martensitic stainless steel is often supplied in the fully annealed condition, allowing the material to be easily formed and machined by the fabricator or user. Once the component is in its final and near-final form, the fabricator or user performs the required hardening heat treatments to develop the desired strength, hardness and wear properties.

Annealing is defined as the process whereby a material is heated to and held at a suitable temperature and then cooled at a well-defined rate to reduce hardness, improve machinability, facilitate cold work, produce a specific microstructure, or obtain desired mechanical, physical or other properties¹⁴. Annealing of AISI 420 martensitic stainless steel softens the steel by producing a fully ferritic matrix with the majority of the carbon precipitated as coarse, globular carbide particles. Since the precipitation of chromium carbide is diffusion-controlled, the annealing conditions of AISI 420 have to be optimised to ensure sufficient softening within a reasonable

annealing time. Calliari *et al*¹⁵ reported that the best compromise between annealing temperature and holding time is obtained by annealing at a temperature of 750 °C for 2 hours, which yields hardness values in the region of 284 HV (hardness on the Vickers scale). Actual plant data supplied by Columbus Stainless for the annealing of AISI 420 indicate that a spheroidise annealing treatment at 860 °C, followed by further annealing at a reduced temperature of 775 °C, yields hardness values of 195 HV to 210 HV. Annealing at higher temperatures has been shown to reduce the hardness even further, but excessive annealing temperatures increase the risk of adverse grain growth.

Type AISI 420 stainless steel is often supplied in the spheroidise annealed condition to facilitate cold work and machining. De Andrés *et al*¹⁶ observed randomly dispersed globular carbides ($M_{23}C_6$) within a ferrite matrix in AISI 420 stainless steel after extended times at the annealing temperature (as illustrated in Figure 1.2). A scanning electron micrograph of AISI 420 after annealing at 750 °C for 2 hours (consisting of ferrite and chromium-rich $M_{23}C_6$ carbides) is shown in Figure 1.3.

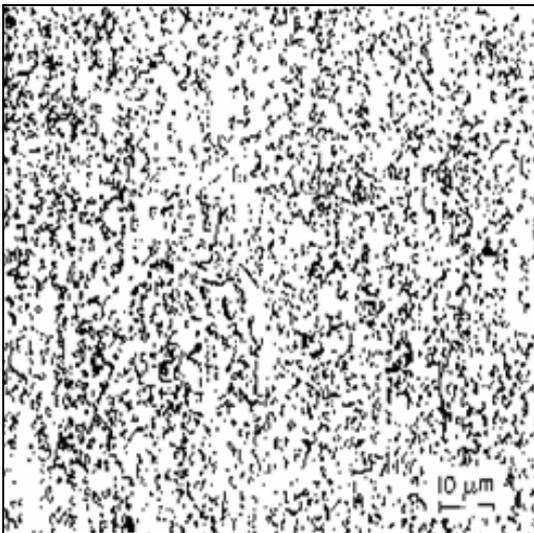


Figure 1.2: Optical micrograph of AISI 420 in the spheroidise annealed form. The microstructure consists of carbides in a ferrite matrix. Etchant: Vilella's reagent¹⁶.

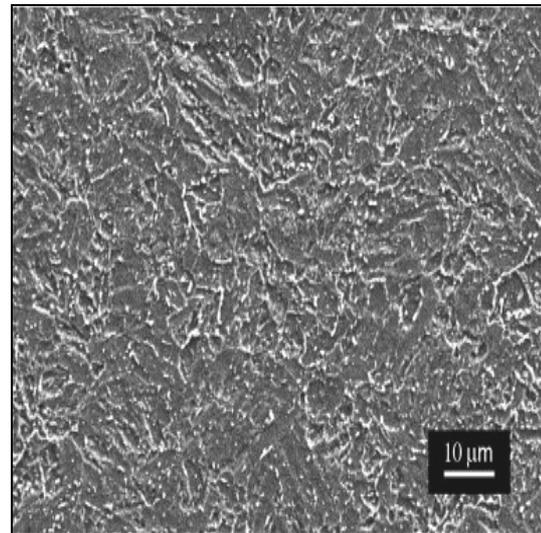


Figure 1.3: Scanning electron micrograph of AISI 420 annealed at 750 °C for 2 hours. The microstructure consists of carbides in a ferrite matrix. Etchant: Vilella's reagent¹⁵.

2.4.2 Austenitising:

The hardening heat treatment specified for martensitic stainless steels typically consists of heating to a temperature high enough to ensure an austenitic structure

with carbon in solid solution, followed by rapid cooling (air cooling or oil quenching) to form martensite. Air cooling of a fully austenitic structure usually produces full hardening in AISI 420, but oil quenching is used for larger sections to ensure complete transformation to martensite.

The austenitising treatment is of critical importance in the hardening of martensitic stainless steels. During austenitising, the final alloying element partitioning occurs between the austenite matrix (that transforms to martensite on cooling) and the retained carbides. An excessively high austenitising temperature will cause alloy carbides to coarsen or dissolve, resulting in undesirable grain growth. Alloying elements in solid solution in the austenite matrix also affect the hardenability, M_s and M_f temperatures, retained austenite content and secondary hardening potential of the steel. The volume fraction and size of undissolved carbides not only influence the wear resistance, but also affect the austenite grain size.

The effect of austenitising temperature on the microstructure and properties of martensitic stainless steels has been the subject of several investigations. Calliari *et al*¹⁵ reported that the maximum as-quenched hardness in AISI 420 martensitic stainless steel is found after austenitising at a temperature of 1050°C, as complete carbide dissolution is assumed to have occurred at this temperature. Tavares *et al*¹⁷ proposed austenitising temperatures in the range of 980°C to 1100°C for an AISI 420 martensitic steel (containing 0.4 wt% C, 13.5 wt% Cr and 0.008 wt% S). This range is considered to be too wide to guarantee consistent as-quenched hardness values, particularly in view of the strict requirements stated for the steels examined in the current investigation. Latrobe¹⁸ reported in their data sheet for LSS 420 HC stainless steel that the steel is fully austenitic after heating above 860°C, with a hardness peak of 660 HV and minimal retained austenite after air cooling from 1025°C. (The chemical compositions of the steels examined by De Andrés *et al*⁶, Calliari *et al*¹⁵, Tavares *et al*¹⁷ and Latrobe¹⁸ are shown in Table 1.2).

De Andrés *et al*⁶ investigated the effect of carbide-forming elements on the response to thermal treatment of two medium-carbon AISI 420 martensitic stainless steels. The steel designated X45Cr13 in this investigation conforms in composition to that specified for medium-carbon AISI 420, whereas the grade referred to as X45CrMoV14 contain deliberate additions of molybdenum and vanadium (refer to

Table 1.2 for the chemical compositions of these steels). Dilatometer tests were performed on small samples (12 mm in length and 2 mm in diameter) during heat treatment carried out by heating the specimens at a constant rate of 0.5°C per second to austenitising temperatures in the range of 1000°C to 1250°C, soaking for 60 seconds, followed by cooling at a constant rate of 2°C per second.

Table 1.2: The chemical compositions (wt %) of X45Cr13 martensitic stainless steel⁶, AISI 420¹⁷, LSS 420 HC¹⁸ and a Ni-Mo martensitic steel¹⁵, balance Fe (nr = not reported).

Grade	C	Si	Mn	P	S	Cr	Ni	Mo	V
X45CrMoV14 ⁶	0.460	0.46	0.44	0.018	0.003	14.3	0.16	0.51	0.13
X45Cr13 ⁶	0.450	0.32	0.44	0.030	0.016	13.0	0.38	nr	nr
AISI 420 ¹⁷	0.400	nr	nr	nr	0.008	13.5	nr	nr	nr
LSS 420 HC ¹⁸	0.460	0.40	0.40	nr	nr	13.0	nr	nr	0.30
Ni-Mo martensitic steel ¹⁵	0.195	nr	0.21	nr	nr	12.9	1.07	1.71	nr

The steels examined by De Andrés *et al*⁶ were observed to form $M_{23}C_6$ precipitates at the prior austenite grain boundaries on heating to temperatures of 550°C or higher. The authors contended that, as AISI 420 is an air-hardening steel, the as-quenched microstructure will always consist of martensite and complex carbides. It should be noted, however, that the austenitising temperature plays a major role in determining the as-quenched microstructure of the steel and the risk of retained austenite increases with an increase in austenitising temperature.

In a different study, De Andrés *et al*¹⁶ examined the effect of heating rate on the microstructure of AISI 420. The authors reported that dissolution of the $M_{23}C_6$ carbides in the austenite phase starts during heating of the steel to the austenitising temperature. They noted that the temperature at which all the carbides are dissolved (designated the A_{cc} temperature) is a function of the heating rate, as illustrated in Figure 1.4. It is evident that the temperature required for total dissolution of the carbides increases dramatically with an increase in heating rate, with the carbides dissolving completely at 1110°C for a heating rate of 0.5°C per second.

In an earlier phase of the investigation, De Andrés *et al*¹⁶ examined the effect of austenitising temperature on the as-quenched microstructure and properties of AISI 420 stainless steel at a constant heating rate of 0.5°C per second. This heating rate was selected as it is representative of heating rates commonly used in continuous

heat treatment plants in industry. The samples were held at various austenitising temperatures for 60 seconds, followed by oil quenching.

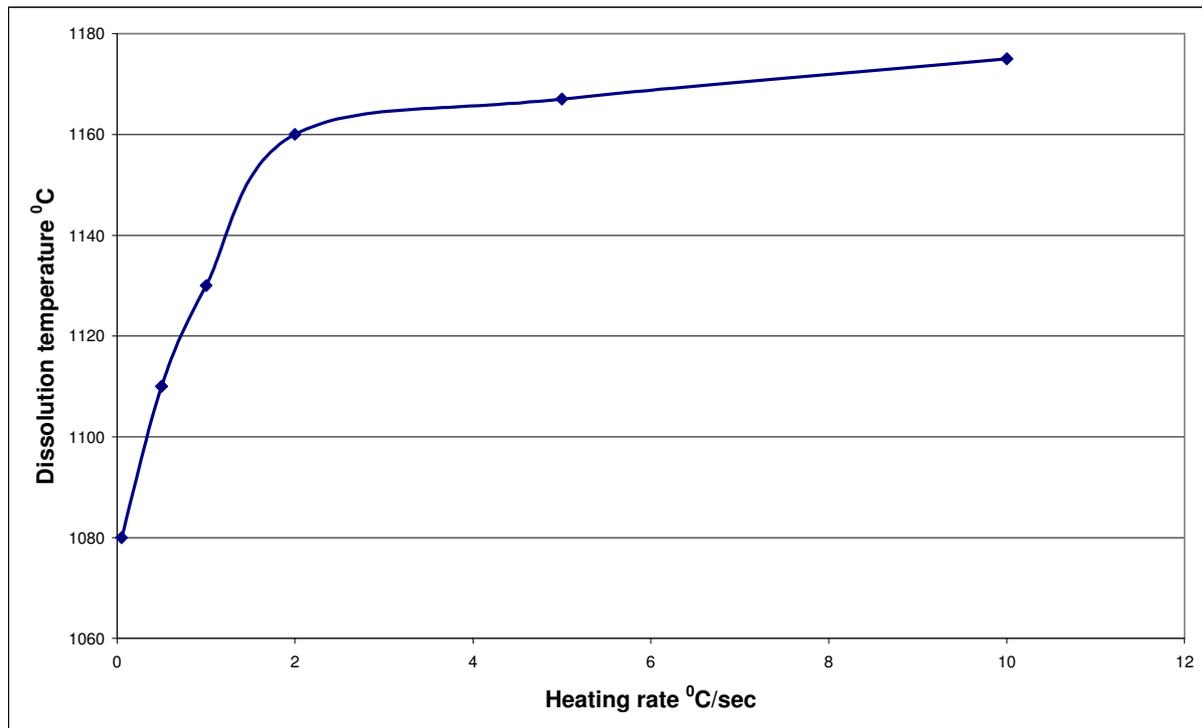


Figure 1.4: The influence of the heating rate on the A_{cc} temperature¹⁶.

The area percentage of carbides within the microstructure was measured by means of image analysis techniques and was shown to decrease with an increase in austenitising temperature (as illustrated in Figure 1.5). As more carbides dissolve at higher austenitising temperatures, it is expected that the risk of retained austenite in the as-quenched microstructure will increase. The gradual dissolution of $M_{23}C_6$ results in enrichment of carbide-forming elements and carbon in the austenite matrix, which may depress the martensite transformation range to below 0°C.

De Andrés *et al*¹⁶ reported that AISI 420 exhibits as-quenched peak hardness values of approximately 710 HV after austenitising at 1120°C for the grade containing no molybdenum, and 1130°C for the molybdenum-containing grade (as shown in Figure 1.6). The carbide volume fraction is less than 1% in both alloys after austenitising at these temperatures. As the austenitising temperature is raised further, the presence of retained austenite – which is considerably softer than martensite – reduces the as-quenched hardness values to 560 HV and 660 HV, respectively. Complete dissolution of the carbide precipitates requires a higher austenitising temperature in the presence of molybdenum.

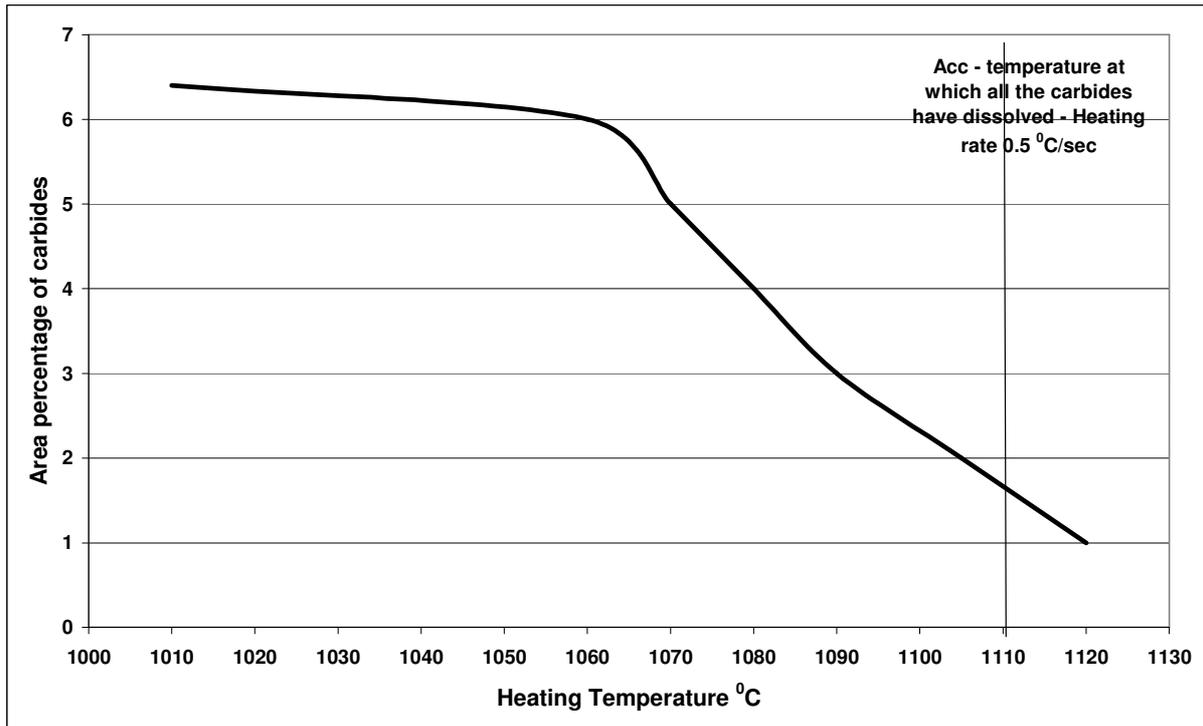


Figure 1.5: The area percentage of carbides after quenching as a function of austenitising temperature¹⁶.

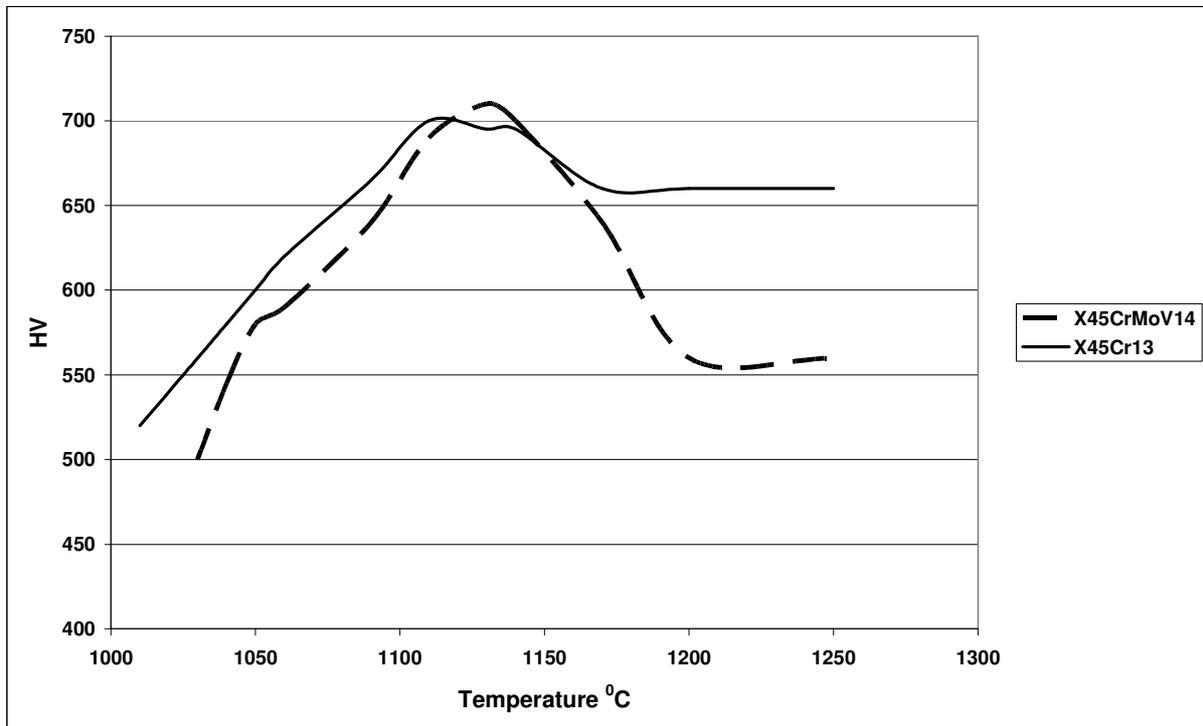


Figure 1.6: Vickers hardness after austenitising for 60 seconds at various temperatures¹⁶.

Candelaria *et al*¹⁹ reported complete dissolution of $M_{23}C_6$ carbides after oil quenching from austenitising temperatures between 900°C and 1100°C. The as-quenched

hardness increases with higher austenitising temperatures up to 1050°C. This is attributed to the gradual dissolution of $M_{23}C_6$ which increases the level of carbon supersaturation in the austenite phase, resulting in higher as-quenched martensite hardness values. At austenitising temperatures higher than approximately 1100°C, the hardness decreases as the high concentration of carbide-forming elements and carbon in solid solution in the austenite due to carbide dissolution reduces the martensite transformation range below 0°C. The martensite transformation does not go to completion and the as-quenched microstructure contains increasing amounts of retained austenite.

The influence of soaking time on the as-quenched microstructure and properties is less apparent. The Latrobe Steel¹⁸ data sheet for AISI 420 martensitic stainless steel states that a slow reduction in hardness is observed on increasing the soaking time at the austenitising temperature. This conclusion is apparently contradicted by the results shown in Figure 1.7, which indicate that longer austenitising times of 30 and 60 minutes, as used by Latrobe¹⁸ and Candelaria¹⁹, result in very similar peak hardness values as the results obtained by De Andrés *et al*¹⁶ for a soaking time of 60 seconds. The peak hardness values were, however, achieved at much higher austenitising temperatures in the investigation by De Andrés *et al*. The kinetics of carbide dissolution is governed by both time and temperature, and despite the small sample sizes used by De Andrés *et al*, the short 60 second austenitising time was probably insufficient to develop peak as-quenched hardness values at the same austenitising temperatures as those reported for the other two investigations.

Once the steels had been austenitised, quenching or cooling to below the martensite transformation range results in the formation of martensite⁶. The M_s temperature of AISI 420 martensitic stainless steel is reported to be in the range of 300°C to 70°C, whereas the M_f temperature is estimated to be approximately 150°C to 200°C lower than the M_s temperature. Almost all alloying elements in solid solution reduce the M_s and M_f temperatures, with carbon having the greatest effect. If the M_f temperature is depressed to below room temperature or even 0°C, the more highly alloyed martensitic steels may contain retained austenite after quenching due to the sub-zero temperatures required to transform all the austenite to martensite.

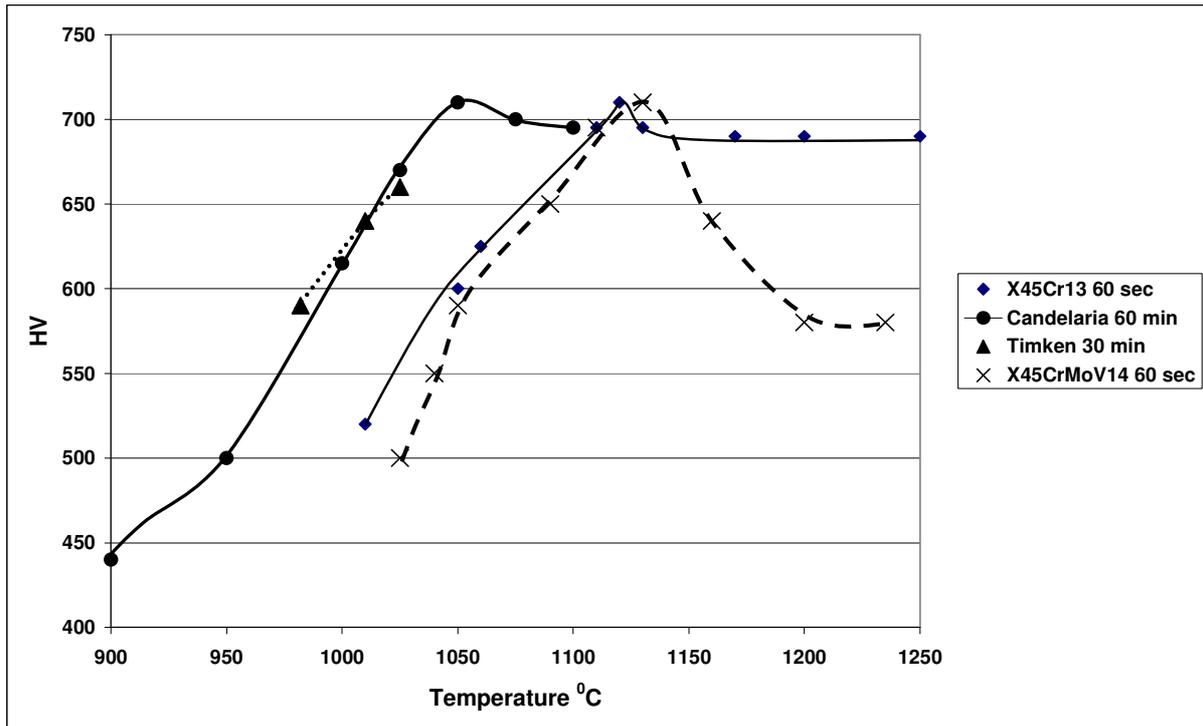


Figure 1.7: The effect of austenitising temperature on as-quenched hardness (from De Andrés¹⁶, Candelaria¹⁹ and Latrobe (labelled Timken)¹⁸).

De Andres *et al*⁶ reported no measurable retained austenite in either grade of martensitic stainless steel after austenitising at temperatures up to 1150°C. Austenitising at temperatures above 1150°C resulted in as-quenched microstructures containing lath martensite and retained austenite. Excessive grain growth was observed at austenitising temperatures above 1120°C, with a corresponding decrease in carbide volume fraction to approximately 1%. The temperatures required for complete carbide dissolution were reported to be 1130°C for X45Cr13 (no deliberate molybdenum addition) and 1170°C for X45CrMoV14 (alloyed with molybdenum).

Figures 1.8 to 1.11 show the as-quenched microstructures of X45CrMoV14 after austenitising at various temperatures for 60 seconds. An increase in retained austenite content is evident with an increase in austenitising temperature, and at austenitising temperatures of 1200°C or higher the microstructures contained no visible carbide particles. The conclusion was drawn that all carbides had dissolved at the higher heat treatment temperatures, reducing the martensite transformation range and favouring retained austenite. The lower carbide volume fraction also allowed uncontrolled grain growth during the austenitising treatment.

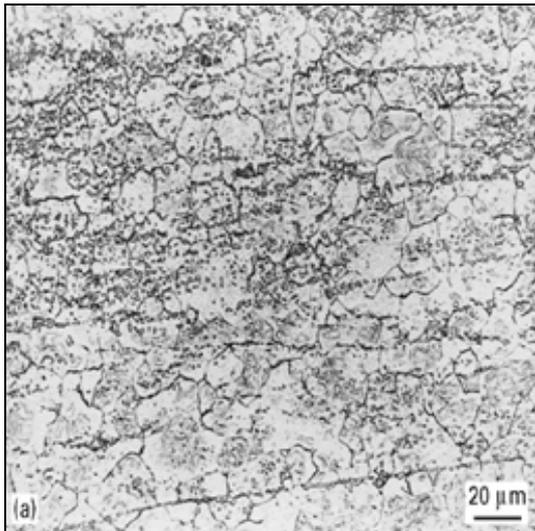


Figure 1.8: Optical photomicrograph of X45CrMoV14 in the as-quenched condition (austenitised at 1100 °C). The structure consists predominantly of carbides in a fine martensitic matrix. The hardness is 670 HV⁶.

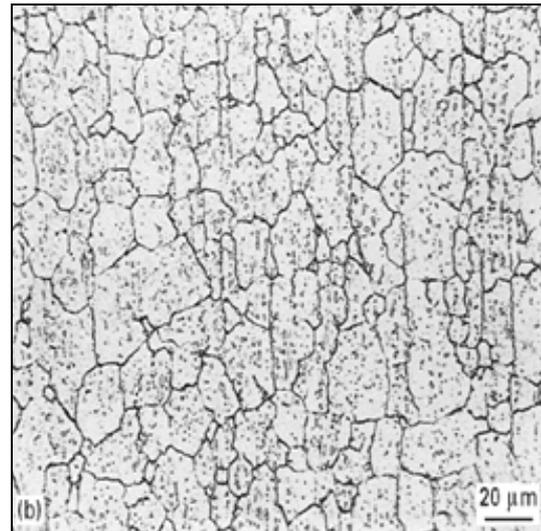


Figure 1.9: Optical photomicrograph of X45CrMoV14 in the as-quenched condition (austenitised at 1150 °C). The structure consists predominantly of carbides in a fine martensitic matrix. The hardness is 630 HV⁶.

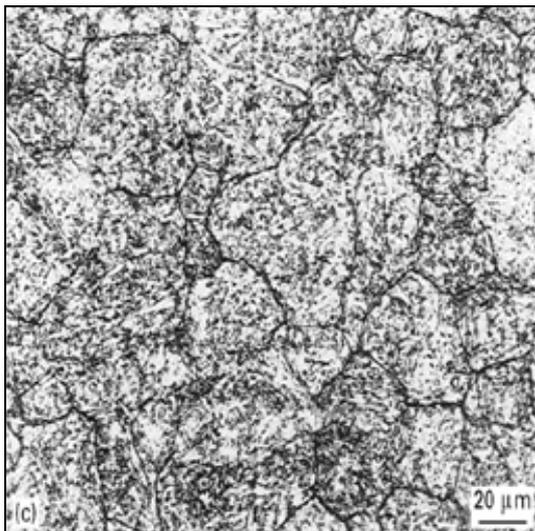


Figure 1.10: Optical photomicrograph of X45CrMoV14 in the as-quenched condition (austenitised at 1200 °C). The structure consists predominantly of retained austenite and some undissolved carbides in a fine martensitic matrix. The hardness is 580 HV⁶.

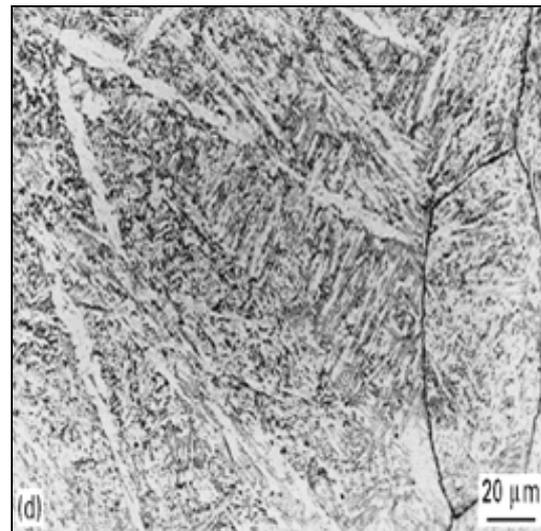


Figure 1.11: Optical photomicrograph of X45CrMoV14 in the as-quenched condition (austenitised at 1250 °C). The structure consists predominantly of retained austenite in a martensitic matrix. The hardness is 580 HV⁶.

Figure 1.12 demonstrates the effect of austenitising temperature on the carbide volume fraction in these steels, as determined by De Andrés *et al*⁶. It is evident that the volume fraction of carbide particles decreases from almost 7% at an austenitising

temperature of 1060 °C, to less than 2% at 1130 °C and 1120 °C for X45CrMoV14 and X45Cr13, respectively. This confirms that the carbide particles gradually dissolve with increasing austenitising temperatures.

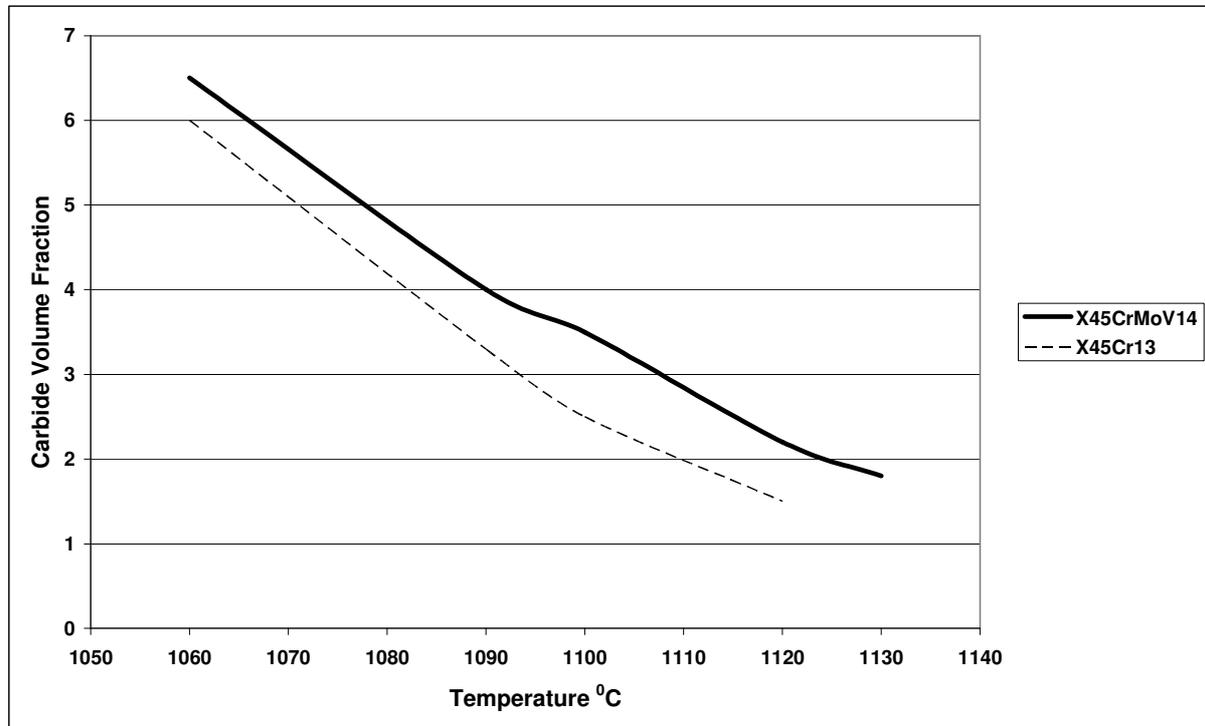


Figure 1.12: Effect of austenitising temperature on the carbide volume fraction in martensitic stainless steels⁶.

Figure 1.12 also illustrates that the volume fraction of carbides in the molybdenum-containing steel (X45CrMoV14) is consistently higher than that of the steel with no molybdenum addition. Molybdenum is reported to combine with carbon to form Mo_2C or to form part of the chromium-rich M_{23}C_6 carbide that is commonly observed in martensitic stainless steels. The presence of molybdenum is expected to retard the coarsening and dissolution of M_{23}C_6 . Higher austenitising temperatures are therefore required for complete dissolution of carbides in the presence of molybdenum.

Figure 1.13 shows the volume fraction of retained austenite as a function of the austenitising temperature for X45CrMoV14, the molybdenum-alloyed grade studied by De Andrés *et al*⁶. As the austenitising temperature increases and the carbides go into solution, the M_s transformation temperature is depressed with a corresponding increase in the volume fraction retained austenite in the as-quenched steel. Figure 1.13 indicates that retained austenite is observed after quenching from austenitising temperatures in excess of approximately 1100 °C in this alloy. This temperature

corresponds well with the temperature range in which increasing dissolution of carbides was observed in this alloy. In the molybdenum-containing alloy the percentage retained austenite stabilises at approximately 34% at temperatures above 1200 °C.

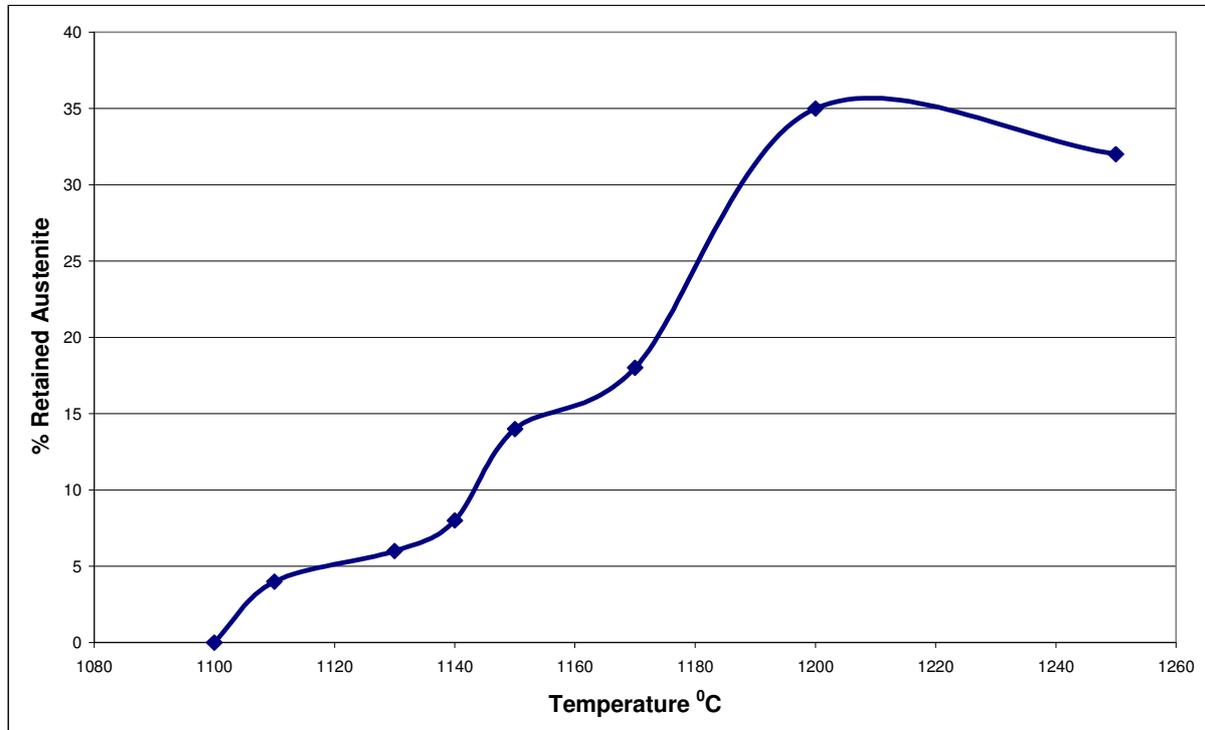


Figure 1.13: Retained austenite volume fraction as a function of the austenitising temperature⁶.

2.4.3 Quenching:

After austenitising the steel is cooled or quenched to form martensite. Most martensitic stainless steels are air-hardening, but larger sections are routinely oil quenched to ensure full transformation to martensite. Slow cooling rates promote precipitation or incomplete hardening, whereas excessive cooling rates may cause distortion or quench cracking. An unwelcome complication of AISI 420 is, as described earlier, the tendency to retain austenite after quenching. As shown in Figure 1.13, this steel may contain up to 35% retained austenite after quenching. The presence of significant amounts of retained austenite reduces the as-quenched hardness of the alloy, and may promote embrittlement if fresh, untempered martensite forms during tempering. Multiple tempering steps can be used to temper the fresh martensite, or cryogenic (sub-zero) tempering²⁰ can be used to reduce the retained austenite content prior to tempering.

2.4.4 Tempering:

In its “as-quenched” martensitic condition, the steel is hard and brittle and may contain pockets of retained austenite. Quenching is therefore followed by tempering to reduce brittleness, increase ductility and toughness and reduce residual stresses. During tempering the steel is kept at a temperature below the austenite transformation range, and cooled at a prescribed rate²¹. Tempering allows controlled precipitation of fine carbide particles, transformation of retained austenite, and recovery and recrystallisation of the highly distorted martensite matrix. Due to its high temper resistance, AISI 420 martensitic stainless steel is usually tempered at temperatures higher than approximately 550°C. Secondary hardening due to the precipitation of alloy carbides may increase the hardness during the tempering of martensitic stainless steels.

If the steel contains a significant volume fraction of retained austenite after quenching, carbide precipitation during tempering may reduce the alloying element content of the austenite, thereby increasing the M_s temperature and promoting transformation of retained austenite to martensite on cooling after tempering. This martensite is untempered and may reduce the toughness of the tempered structure. The formation of fresh martensite during tempering can be prevented using a cryogenic treatment after quenching to transform any retained austenite to martensite prior to tempering, or by using multiple tempering steps.

2.4.5 Cryogenic or sub-zero treatment:

AISI 420 martensitic stainless steel is likely to retain as much as 35% by volume retained austenite in the as-quenched structure. The ASM Handbook²² reports that the cold treating of steel is widely accepted as a treatment to promote the transformation of austenite to martensite after quenching. To complete the transformation of retained austenite to martensite, the steel needs to be cooled to a temperature below the M_f temperature. In cryogenic treatment²¹, the temperature of the steel is reduced from room temperature to temperatures well below 0°C. Refrigeration or cooling in dry ice or liquid nitrogen is commonly used, and slow cooling rates in the region of 2°C per minute are recommended to prevent thermal shock. The material must be kept at this temperature for a period of 24 to 36 hours. At sub-zero temperatures, austenite converts to martensite very slowly, but more

complete transformation to martensite may be obtained provided the cryogenic treatment temperature is below the M_f temperature of the steel.

2.4.6 Multiple tempering steps:

Multiple tempering steps can be used to temper martensite that forms as a result of the transformation of retained austenite during tempering. Carbide precipitation during tempering reduces the alloying element content of the austenite, thereby increasing the M_s temperature and promoting transformation of retained austenite to martensite on cooling after tempering. This martensite will be untempered and may reduce the toughness of the tempered structure. A second (or even third) tempering step is required to temper this fresh martensite. Tempering, or multiple tempering, of martensitic stainless steels appears to be more effective when preceded by a sub-zero quench²³.

3. HEAT TREATMENT OPTIMISATION

The preceding discussion emphasised the importance of heat treatment in developing the desired mechanical properties in martensitic stainless steels. Since these steels are often supplied in the annealed condition to facilitate machining or cold work, the consumer or fabricator is required to perform the final hardening heat treatments to ensure high hardness and wear resistance in the final component. Well-defined heat treatment guidelines are therefore required to assist the consumer or fabricator in performing appropriate hardening heat treatments in order to develop optimal properties. Although such guidelines are available in literature, the published heat treatment parameters are often inconsistent and the recommended temperature ranges too wide to ensure consistent properties.

During the course of this investigation, the heat treatment of two alloys conforming in composition to the range specified for medium-carbon type AISI 420 martensitic stainless steel was optimised with the aim of obtaining fully martensitic microstructures with minimal retained austenite and hardness values between 610 and 740 HV. More details on the primary objectives of this investigation are given in Chapter 2.

CHAPTER 2 – OBJECTIVES OF THE INVESTIGATION

1. BACKGROUND

AISI 420 is a low-chromium martensitic stainless steel that is often recommended for use in applications requiring a combination of corrosion resistance, high hardness and good wear resistance. Two heats of medium-carbon AISI 420 material were supplied by Columbus Stainless, a primary steel mill in South Africa, for the purpose of this investigation. These steels, with internal heat numbers of 349628 and 350052, are referred to as HEAT 1 and HEAT 2 in the remainder of this report. The chemistry of the two heats (to be considered in more detail in Chapter 3) are similar except that HEAT 1 contains 14.33% chromium and 0.62% molybdenum, whereas HEAT 2 contains 13.48% chromium and 0.025% molybdenum.

A percentage of the AISI 420 stainless steel produced by Columbus Stainless is earmarked for the production of razor blades. For optimal wear resistance and good edge retention in this application, the steel is required to have a fully martensitic structure with minimal retained austenite, a final hardness of between 610 and 740 HV after hardening, and evenly dispersed spherical carbides.

The plant heat treatment of this grade of stainless steel consists of a standard spheroidise annealing treatment to facilitate the formation of globular carbides in a ferrite matrix and to obtain maximum softness in preparation for further cold working or machining operations. The steel is supplied to the consumer in the annealed condition and the consumer or fabricator is required to perform the hardening heat treatments to ensure high hardness and wear resistance in the final component. Well-defined heat treatment guidelines are therefore required to assist the consumer or fabricator in performing the hardening treatments in such a way that optimal properties are achieved.

2. OBJECTIVES OF THE INVESTIGATION

This investigation aimed at identifying the heat treatment parameters (including the austenitising temperature, austenitising time, temper temperature and temper time) required to produce a martensitic structure, with minimal retained austenite and evenly dispersed spherical carbides, and hardness of between 610 HV and 740 HV

(hardness on the Vickers scale) in two medium-carbon AISI 420 martensitic stainless steels.

To examine the influence of these critical heat treatment parameters, two heats of AISI 420 martensitic stainless steel were subjected to various heat treatments. Different austenitising and temper treatments were used to form a detailed picture of the effect of heat treatment parameters on the properties and microstructure of the steels. Vickers hardness measurements were performed on all the samples to determine the hardness of the steel in each heat treatment condition. Optical and scanning electron microscopy was used to characterise the as-quenched and tempered microstructures. The average austenite grain size was determined by means of the mean lineal intercept method and the average carbide diameter was measured using image analysis techniques. The average number of carbides in a given area was determined, and the carbides were identified using X-ray diffraction techniques.

Once the effect of the heat treatment parameters on the microstructure and properties of the two heats had been established, thermodynamic predictions (using the CALPHAD™ model) of the solubility of the carbide particles in the matrix at various austenitising temperatures were used to explain the results obtained.

The experimental procedure used during the course of this investigation is described in Chapter 3.

CHAPTER 3 – OVERVIEW OF THE EXPERIMENTAL PROCEDURE

This chapter provides an overview of the experimental procedure followed during the course of this investigation. This procedure aimed at identifying the heat treatment parameters required to fully austenitise the steel, dissolve the majority of the carbides and convert the austenite to martensite on cooling. For optimal performance, the resulting microstructures are required to be martensitic, with minimal retained austenite and evenly dispersed spherical carbides, and a hardness of between 610 HV and 740 HV (hardness on the Vickers scale). More detailed information on the experimental procedure is supplied in Chapter 4.

1. STAINLESS STEEL ALLOYS STUDIED IN THIS INVESTIGATION

1.1 Chemical compositions:

Grade AISI 420 martensitic stainless steel is commercially available in a low-carbon version (with a specified carbon content of less than 0.15%), and a medium-carbon version (with a maximum carbon content of 0.5%). Two medium-carbon heats of AISI 420 martensitic stainless steel (containing approximately 0.47% carbon) were supplied by Columbus Stainless for the purpose of this investigation. As shown in Table 3.1, the steels contain 13.48% and 14.33% chromium, respectively, with small additions of copper, nickel and vanadium. The major difference between the two heats is the deliberate addition of molybdenum to HEAT 1. Molybdenum is expected to increase the hardenability, raise the temper resistance and improve the high temperature strength of the alloy.

Table 3.1: Chemical compositions of the AISI 420 heats examined during the course of this investigation (weight %, balance Fe).

Heat	C	Mn	Si	Cu	Mo	Cr	Ni	N	V
1	0.472	0.62	0.41	0.10	0.623	14.33	0.22	0.0165	0.13
2	0.471	0.62	0.33	0.08	0.025	13.48	0.17	0.0120	0.10

1.2 Plant heat treatment:

The two steels were received in the spheroidise annealed condition, involving heat treatment at 860 °C for 20 hours, followed by slow cooling to 770 °C to facilitate the

formation of globular carbides in a ferrite matrix and to obtain maximum softness for forming. The steels were supplied in the form of 5 mm thick plate material.

2. HEAT TREATMENTS USED IN THIS INVESTIGATION

Samples with dimensions of 5 mm x 10 mm x 5 mm were sectioned from the as-supplied plate material. The samples were austenitised in a muffle furnace at various temperatures between 1000 °C and 1200 °C. An average heating rate of approximately 0.2 °C per second and a holding time of 15 minutes were used. The austenitising heat treatment was followed by oil quenching in all cases.

Tempering heat treatments were performed at various temperatures for samples austenitised at 1075 °C, 1150 °C and 1175 °C. The effect of double tempering on the retained austenite content and hardness was investigated for samples austenitised at 1150 °C and 1175 °C.

Samples austenitised at 1100 °C, 1130 °C, 1150 °C and 1175 °C were sub-zero treated in liquid nitrogen at -196 °C. After sub-zero treatment in liquid nitrogen, the samples were tempered for one hour at 550 °C, 650 °C or 700 °C.

3. METALLOGRAPHIC INVESTIGATION

Each heat treated sample was sectioned and mounted in black phenolic resin. The mounted samples were ground, diamond polished to a mirror finish and etched using Vilella's reagent (consisting of 1 g picric acid, 10 ml hydrochloric acid and 100 ml ethanol) to reveal the general microstructure. The etched samples were examined microscopically using optical and scanning electron microscopes, and photomicrographs were taken of each sample. Following the general microscopic examination, the austenite grain size, average carbide diameter and the carbide density of the samples were determined, as described below.

3.1 Austenite grain size:

The mean lineal intercept method was used to estimate the ASTM grain size (G) of the metallographic samples. Five uniformly distributed test lines were drawn across a printed micrograph, and the number of times a given line intersected the grain boundaries was recorded. Equation (3.1) was used to calculate the mean lineal intercept length, L_L .

$$L_L = \frac{L_T}{PM} \quad \dots(3.1)$$

where: L_L is the mean lineal intercept length,
 L_T is the total length of the test lines,
 P is the total number of grain boundary intersections, and
 M is the magnification.

The ASTM grain size, G , was then determined using equation (3.2).

$$G = -3.2877 - 6.6439 \log L_L \quad \dots(3.2)$$

(This method is based on an article presented by George Vander Voort on the occasion of the 75th anniversary of Committee E-4 on Metallography, and originally appeared in *ASTM Standardization News*, May 1991, as "Committee E-4 and Grain Size Measurements").

3.2 The average carbide diameter and carbide density:

The average diameter of the carbide particles observed in each heat treated sample was measured using image analysis techniques. To determine the carbide density, scanning electron micrographs were divided into squares with a total area of 2300 μm^2 . The number of carbides in each square was determined, and the carbide density was reported as the number of carbides per mm^2 .

4. HARDNESS MEASUREMENTS

Calibrated Vickers hardness measurements with an applied load of 10 kg were performed on all the heat treated samples. The results were reported as the average of five tests per sample.

5. X-RAY DIFFRACTION

In order to quantify the volume fraction of retained austenite present in various heat treated samples, X-ray diffraction (XRD) analyses were performed. XRD was also used to identify the carbide particles observed in the samples. Since the carbide particles were too small to be identified using SEM-EDS analysis, and too large for TEM (transmission electron microscope) analysis, the carbides were extracted by dissolving the martensitic matrix in hydrochloric acid. The sediment was filtered

through glass-fibre micropaper, washed in distilled water and rinsed with acetone. The carbide residue was collected and subjected to XRD analysis.

6. THERMODYNAMIC PREDICTIONS

Computational simulations were performed using CALPHAD™ software, and phase diagrams of the two heats of AISI 420 martensitic stainless steel were compiled at four austenitising temperatures (1075°C, 1100°C, 1130°C and 1175°C) to determine the phase stability and the equilibrium dissolution temperatures of the carbides.

Chapter 4 provides more detail on the experimental procedure and presents the results of this investigation.