

Department of Materials Science and Metallurgical Engineering

STRENGTHENING OF A COLD WORKED 17% CHROMIUM FERRITIC STAINLESS STEEL BY HEAT TREATMENT

by Michelle Sephton

A thesis submitted in partial fulfillment of the requirements for the

Masters in Engineering

degree in the Faculty of Engineering, University of Pretoria,

Pretoria

Supervisor: Professor P.C. Pistorius

February 1997

© University of Pretoria



Acknowledgements

I would like to thank Professor P.C. Pistorius for his invaluable help and contributions, Mintek for their financial support, Dr. M.B. Cortie for new ideas and directions, my mother and father for their support and encouragement, and my Father without whom I would not have been able to do anything.



Abstract

Slat-band chains are used as conveyors by the food industry, breweries and bottling plants. The operating conditions require abrasion resistance and strength which are at the limit of the capabilities of the current material of choice, cold worked type 430. In an unconventional way of strengthening this material, Mintek developed a process in which the cold worked material is aged between 450°C and 500°C. The present work aims to elucidate the strengthening mechanism, using type 430 stainless steel containing 16.42% Cr and 0.036% C, in the cold-rolled condition (38% reduction in area), with and without prior solution heat treatment.

The Cr-rich precipitate α " may form in the 450°C to 500°C range (due to the miscibility gap in the Fe-Cr system), resulting in the increased hardness and lowered ductility. Mössbauer studies confirmed that the α ", at this composition and temperature, forms through the process of nucleation and growth. Hardening due to α " precipitation was only observed after aging for 64 hours or more, however. After increasing the dissolved interstitial content by solution heat treatments (in the vicinity of 900°C), increases in Vickers hardness of 30-50 kg/mm² could be obtained after only 8 minutes at 475°C. This hardness increase corresponds to an increase in tensile strength of more than 100 MPa. The increased hardness does not appear to be caused by strain aging, and presumably results from fine carbide or nitride precipitation. Solution treatment at 930°C also introduced some martensite (α ') into the microstructure, which raised the hardness of the unaged cold worked material.

Overaging of the carbide and nitride precipitates was observed at 475°C, but not at 450°C, probably due to the lower diffusion rates at the lower temperature. No overaging of the α " precipitates occurred, for aging times up to 2072 hours.

Samples aged for selected periods of time at 475°C had low impact strengths – even well before the formation of α " – and revealed predominantly cleavage fracture with some ductile fracture areas, mostly at grain boundaries. Both impact strength and lateral expansion



calculation of critical crack lengths from the impact data, however, revealed that a maximum flaw length of 0.8 mm, for specimens solution treated at 880°C, could be tolerated before catastrophic failure. Since it is not expected that flaws of that size would exist in the asmanufactured links, fatigue will probably determine the lifetime of the chains, although the lower K_{Ic} values indicate that less crack propagation will be tolerated before brittle fracture.

During the aging treatment, the strength may be lowered by recrystallisation of the coldworked material. Transmission electron microscopy (TEM) revealed the start of recovery, but no recrystallisation. Some large precipitates (around $1\mu m$ in diameter) were present. These were identified, through their diffraction patterns, as $M_{23}C_6$; these carbides were present in both aged and unaged material and hence represent precipitates which had not dissolved during the initial solution treatments. The α " precipitates – and the presumed newly formed nitride and carbide precipitates – were too fine for detection by TEM.

Potentiodynamic testing of the treated material in a 0.5M H₂SO₄ solution indicated that, although the probable hardening mechanisms imply localised Cr depletion of the matrix, the general corrosion resistance and passivation behaviour were not affected.

It is concluded that the strength of the chain may be increased markedly by short-term heat treatments at 475° C, with lowered toughness, but with no decrease in corrosion resistance. Martensite, work hardening, and precipitation of carbides and nitrides all contribute to the final strength, with α " formation only becoming significant after longer aging times.



Keywords

slat-band chain

Type 430 ferritic stainless steel

475°C embrittlement

carbide and nitride precipitation

cold work

martensite

strengthening through heat treatment

corrosion resistance

alpha (double) prime



Opsomming

Vervoerbandkettings word veral in die voedselbedryf, brouerye en bottelarye gebruik. Die gebruikstoestande vereis slytasieweerstand, sterkte en korrosiebestandheid. Tipe 430 ferritiese roesvrye staal word tans tot by sy sterktelimiet gebruik. 'n Onkonvensionele versterkingsproses is deur Mintek ontwikkel waarin die bestaande materiaal tussen 450°C en 500°C verouder word. Die doel van hierdie studie is om die moontlike versterkingsmeganismes wat betrokke is, te identifiseer deur van 'n 430 roesvrye staal, met 16.42% Cr en 0.036% C, gebruik te maak. Die materiaal is in die koudverwerkte toestand (38% reduksie in area) getoets, met en sonder voorafgaande oploshittebehandelings.

Die Cr-ryke presipitaat (α") vorm in die 450°C tot 500°C gebied (a.g.v. 'n onmengbaarheidsarea in die Fe-Cr fasediagram) en veroorsaak 'n toename in hardheid en afname in taaiheid. Dit is deur middel van Mössbauer-studies bevestig dat die α", by hierdie samestelling en temperatuur, vorm deur 'n proses van kernvorming en groei van partikels. Verharding deur die α"-presipitate is egter eers waargeneem na veroudering vir meer as 64 uur by 475°C. Nadat die opgeloste interstisiële inhoud verhoog is deur addisionele oploshittebehandelings (in die omgewing van 900°C), is gevind dat 'n toename in Vickershardheid van 30-50 kg/mm² verkry kan word binne 'n verouderingstyd van 8 minute. Dié toename stem ooreen met 'n verhoging in treksterkte van meer as 100 MPa. Dit blyk dat die verhoging nie die gevolg van rekveroudering is nie, maar wel waarskynlik toegeskryf kan word aan die presipitasie van fyn karbiede en nitriede. Oplosbehandeling by 930°C het ook die vorming van martensiet tot gevolg, wat die hardheid van die onverouderde materiaal verhoog.

Oorveroudering van die karbied- en nitriedpresipitate is by 475° C waargeneem, maar nie by 450° C nie, moontlik as gevolg van die laer diffusietempo's by die laer temperatuur. Geen oorveroudering van die α "-presipitate is waargeneem nie, selfs vir verouderingstye van tot 2072 uur.



Veroudering by 475°C het lae slagsterktes tot gevolg, selfs voor die vorming van α ". Breukvlakke het hoofsaaklik uit splytingsvlakke bestaan, met smeebare breukareas meestal op korrelgrense. Beide die slagsterkte en die laterale uitsetting het getoon dat verbrossing gepaardgaan met die verhoging in hardheid wat verkry word deur veroudering. Die berekening van kritieke kraaklengtes uit die impakdata het egter getoon dat, vir oplosbehandelings by 880°C, die maksimum defekgrootte - voor katastrofiese faling - 0.8 mm is. Dit word nie verwag dat defekte van hierdie grootte in die soos-vervaardigde skakels teenwoordig sal wees nie, en daarom sal die leeftyd van die kettings waarskynlik deur vermoeidheid bepaal word. Die laer K_{Ic} waardes toon egter dat minder kraakvoortplanting plaas sal kan vind voor bros faling.

Tydens veroudering kan die sterkte van die materiaal moontlik weens herkristallisasie verlaag. Deur transmissie-elektronmikroskopie (TEM) is dit wel waargeneem dat herstel, maar geen herkristallisasie nie, plaasvind. Presipitate (van ongeveer 1 μ m in diameter) is deur middel van hul diffraksiepatrone as $M_{23}C_6$ geëien, en aangesien die presipitate teenwoordig was in beide die verouderde en onverouderde materiaal, is dit waarskynlik dat die presipitate nie opgelos het tydens die oorspronklike oplosbehandelings nie. Die α " en nuutgevormde karbied- en nitriedpresipitate was te fyn om deur middel van TEM waargeneem te word.

Potensiodinamiese toetse in 'n 0.5M H₂SO₄ oplossing het getoon dat, alhoewel die waarskynlike versterkingsmeganismes gelokaliseerde chroomverarming tot gevolg het, die algemene korrosieweerstand en passiveringsgedrag nie deur die hittebehandelings beïnvloed word nie.

Dit kan gevolglik afgelei word dat die sterkte van die materiaal noemenswaardig verhoog kan word deur koue verwerking, en hittebehandeling by 475° C. Dit gaan gepaard met 'n afname in taaiheid, maar algemene korrosiebestandheid word nie beïnvloed nie. Martensiet, werksverharding en die presipitasie van fyn karbiede en nitriede dra by tot die finale sterkte, terwyl α " eers 'n invloed na langer verouderingsperiodes het.



Sleutelwoorde

vervoerbandkettings

Tipe 430 ferritiese roesvrye staal

475°C verbrossing

karbied- en nitriedpresipitasie

koue verwerking

martensiet

versterking deur hittebehandeling

korrosie weerstand

alfa (dubbel) aksent



Table of Contents

| List of tables | V | |
|---|---------------------------------------|----|
| List o | of figures | V |
| Chap | ter 1 Introduction | 1 |
| | | |
| Chap | Chapter 2 Literature Survey | |
| 2.1 | Material | 4 |
| 2.1.1 | Ferritic stainless steels | 4 |
| 2.1.2 | Type 430 ferritic stainless steel | 11 |
| 2.2 | Strengthening mechanisms | 11 |
| 2.2.1 | Cold work | 11 |
| 2.2.2 | Solution treatment and aging | 13 |
| 2.2.3 | Fine particles | 16 |
| 2.2.4 | 475°C embrittlement | 17 |
| 2.3 | Microstructure | 30 |
| 2.3.1 | Grain size | 30 |
| 2.3.2 | Martensitic-ferritic stainless steels | 30 |
| | | |
| Chapter 3 Material and Experimental Procedure | | 31 |
| 3.1 | Material | 31 |
| 3.1.1 | Slat band chain | 31 |
| 3.1.2 | Sheet material | 31 |



| 3.3 Handling of material and sample selection Chapter 4 The Effects of Cold work, Recovery and Strain aging on the Hardness of Aged Cold-worked 430 4.1 Effect of cold work on the hardness and aging behaviour of as-received material (8mm thick) 4.1.1 Hardness and microstructure 4.1.2 Aging behaviour 38 4.2 Recovery 41 4.2.1 Background 41 4.2.2 Aging at 475°C 41 |
|---|
| the Hardness of Aged Cold-worked 430 4.1 Effect of cold work on the hardness and aging behaviour of as-received material (8mm thick) 4.1.1 Hardness and microstructure 4.1.2 Aging behaviour 36 4.2 Recovery 41 4.2.1 Background |
| the Hardness of Aged Cold-worked 430 4.1 Effect of cold work on the hardness and aging behaviour of as-received material (8mm thick) 4.1.1 Hardness and microstructure 4.1.2 Aging behaviour 36 4.2 Recovery 41 4.2.1 Background |
| the Hardness of Aged Cold-worked 430 4.1 Effect of cold work on the hardness and aging behaviour of as-received material (8mm thick) 4.1.1 Hardness and microstructure 4.1.2 Aging behaviour 36 4.2 Recovery 41 4.2.1 Background |
| 4.1 Effect of cold work on the hardness and aging behaviour of as-received material (8mm thick) 4.1.1 Hardness and microstructure 36 4.1.2 Aging behaviour 38 4.2 Recovery 41 4.2.1 Background 41 |
| material (8mm thick) 36 4.1.1 Hardness and microstructure 36 4.1.2 Aging behaviour 38 4.2 Recovery 41 4.2.1 Background 41 |
| material (8mm thick) 36 4.1.1 Hardness and microstructure 36 4.1.2 Aging behaviour 38 4.2 Recovery 41 4.2.1 Background 41 |
| 4.1.1 Hardness and microstructure364.1.2 Aging behaviour384.2 Recovery414.2.1 Background41 |
| 4.1.2 Aging behaviour 4.2 Recovery 4.2.1 Background 41 |
| 4.2 Recovery 41 4.2.1 Background 41 |
| 4.2.1 Background 41 |
| 4.2.1 Background 41 |
| |
| 4.2.2 Aging at 475°C 41 |
| |
| |
| 4.3 Strain aging 42 |
| 4.3.1 Background 42 |
| 4.3.2 Aging at 100°C 43 |
| |
| 4.4 Conclusions 44 |
| T.T Conclusions |
| |
| |
| Chapter 5 The Effect of Aging on the Hardness of Chain Links and |
| Cold-worked 430 (No Prior Solution Treatments) 46 |
| |
| 5.1 Aging behaviour 46 |
| 5.2 Conclusions 50 |



| Chap | pter 6 The Effect of Solution treatments on Aging Behaviour | |
|-------|---|----|
| 6.1 | Determination of Ac ₁ temperature | 51 |
| 6.1.1 | Solution treatments | 51 |
| 6.1.2 | Influence of cooling rate after solution treatments | 53 |
| 6.2 | Choice of acceptible solution temperatures | 54 |
| 6.2.1 | Solution treatment below the Ac ₁ temperature | 54 |
| 6.2.2 | Solution treatment above the Ac ₁ temperature | 54 |
| 6.3 | Effect of solution treatments on aging behaviour | 57 |
| 6.3.1 | Solution treatnment at 880°C and 930°C, and aging at 475°C | 57 |
| 6.3.2 | Solution treatnment at 880°C and 930°C, and aging at 450°C | 61 |
| 6.4 | Strengthening mechanisms | 62 |
| 6.4.1 | Carbide and nitride precipitation | 62 |
| 6.4.2 | α" precipitation | 64 |
| 6.5 | Conclusions | 69 |
| Chap | Chapter 7 The Effect of Solution Treatments, Cold Rolling and | |
| | Aging on Mechanical Properties | 71 |
| 7.1 | Impact strength | 71 |
| 7.2 | Fracture surfaces | 76 |
| 7.3 | Tensile tests | 79 |



| Chap | Chapter 8 Corrosion resistance | | 97 |
|------|--------------------------------|--|-----|
| 8.1 | No s | olution treatment, solution treatment at 880°C and 930°C | 97 |
| 8.2 | Solu | tion treatment at 990°C | 99 |
| 8.3 | Cold | work | 100 |
| 8.4 | Solut | tion treatment without cold working | 100 |
| 8.5 | Conc | lusions | 101 |
| Chap | Chapter 9 Summary | | 102 |
| | | References | 104 |
| | | Appendices | 112 |



List of Tables

| 2.1 | Composition of Type 430 | 11 |
|-----|---|----|
| 3.1 | Composition of the slat band chain | 31 |
| 3.2 | Composition of sheet material | 32 |
| 3.3 | Aging treatments and testing procedures on the 8mm hot rolled sheet | 33 |
| | List of Figures | |
| 1.1 | Slat band chain used as conveyor belt | 1 |
| 2.1 | Iron-chromium phase diagram | 5 |
| 2.2 | Pseudo-binary phase diagram at 16.4% Cr | 7 |
| 2.3 | True stress-true strain curve | 12 |
| 2.4 | The influence of temperature on precipitation | |
| | 14 | |
| 2.5 | Schematic diagram of lattice structure consisting of two elements | 15 |
| 2.6 | Effect of aging time on mechanical properties | 16 |
| 2.7 | Schematic time-temperature dependence diagram for the formation | |
| | of sigma phase and 475°C embrittlement | 19 |
| 2.8 | Thermodynamic assessment of the Fe-Cr system | 21 |
| 2.9 | Schematic evaluation of concentration profiles to illustrate the difference | |
| | between the spinodal mechanism and nucleation and growth | 23 |
| 3.1 | Flowsheet of experimental procedure | 32 |
| 3.2 | Dimensions of tensile and impact samples | 34 |
| 4.1 | Microstructure of (a) as-received sheet material - 8mm thick, and | |
| | (b) sheet material after cold rolling - 38% reduction in area (5mm thick) | 37 |
| 4.2 | TEM micrographs (bright field) of as-received material (a) before cold work | |
| | and (b) after cold work (38% reduction in area) | 38 |



| 4.3 | Comparison of aging behaviour (at 475°C) of sheet material | |
|-----|---|----|
| | solution treated at 920°C for 15 minutes, before and after cold rolling | |
| | (38% reduction in area) | 39 |
| 4.4 | Polarisation diagram of sheet material solution treated at 920°C, | |
| | water quenched and aged at 475°C for 64 hours (0.5M H ₂ SO ₄ test solution) | |
| | 40 | |
| 4.5 | TEM micrograph (bright field) of the matrix after cold working with | |
| | (a) no aging and (b) aging at 475°C for 260 hours | 41 |
| 4.6 | Hardness of chain links aged at 100°C | 43 |
| 4.7 | Hardness of sheet material solution treated at 930°C (45 minutes), | |
| | water quenched, cold rolled (38% reduction in area) and aged at 100°C | 44 |
| | | |
| 5.1 | Hardness of chain links aged at 475°C and of sheet material aged at 475°C | |
| | (after cold rolling - 38% reduction in area) | 47 |
| 5.2 | Hardness of chain links aged at 450°C and 475°C | 48 |
| 5.3 | Hardness of cold rolled sheet material, after aging at 400°C, 475°C and 500°C | 49 |
| 5.4 | Expected equilibrium volume fractions of α " in an alloy | |
| | containing 16.4% Cr at different temperatures | 50 |
| | | |
| 6.1 | Hardness of samples solution treated at different temperatures, | |
| | a plot of the percentage martensite is superimposed | 52 |
| 6.2 | Configuration of test specimen and thermocouple to determine cooling rates | |
| | 53 | |
| 6.3 | Microstructures after solution treatment (15 min) at (a) 930°C and (b) 990°C | 55 |
| 6.4 | Hardness after aging at 475°C. Samples solution treated at 930°C and 990°C | |
| | respectively before cold rolling. For comparison the curve of the material not | |
| | solution treated is included | 56 |
| 6.5 | Hardness of samples solution treated at 880°C and 930°C, cold rolled | |
| | and aged at 475°C | 57 |
| 6.6 | Microstructure after solution treatment at 880°C and cold rolling | |
| | (38% reduction), (a) before aging and (b) after aging at 475°C for 2072 hours | 59 |
| 6.7 | Microstructure after solution treatment at 930°C and cold rolling | |
| | (38% reduction). (a) before aging and (b) after aging at 475°C for 2072 hours | 60 |



| 6.8 | Hardness after solution treatment at 880°C and 930°C, | |
|------|--|----|
| | cold rolling and aging at 450°C | 61 |
| 6.9 | TEM micrograph of precipitate and selected diffraction pattern | |
| | (sample solution treated at 930°C and aged for 260 hours at 475°C) | |
| | 63 | |
| 6.10 | The effect of the principal hyperfine interactions | 65 |
| 6.11 | Distribution of hyperfine field with aging time at 475°C | 66 |
| 6.12 | Mössbauer spectrum of 930°C solution treated sample, cold worked | |
| | and aged at 475°C for 2072 hours | 67 |
| 6.13 | Field distribution of 880°C solution treated specimens | 68 |
| 6.14 | Field distribution of 930°C solution treated specimens | 68 |
| 7.1 | Impact strength of specimens aged at 475°C after solution treatment | |
| | (at 880°C and 930°C respectively), and cold rolling | 72 |
| 7.2 | Lateral expansion of impact specimens, aged at 475°C | |
| | after solution treatment at 880°C and 930°C and cold rolling | 73 |
| 7.3 | Calculated critical crack lengths (in mm) of specimens | |
| | solution treated at 880°C and 930°C, cold rolled and aged at 475°C | 75 |
| 7.4 | SEM photos of fracture surfaces (a) transgranular cleavage fracture | |
| | (930°C solution treatment, aged at 475°C for 277 hours | |
| | (b) ductile fracture at grain boundaries (880°C solution treatment, | |
| | aged at 475°C for 8 minutes) | 77 |
| 7.5 | SEM photos of fracture surfaces (a) microvoid coalescence | |
| | (solution treatment at 880°C and aged for 8 minutes at 475°C) | |
| | (b) transition between shear and cleavage fracture zones of | |
| | an unaged specimen, solution treated at 880°C and cold rolled, | |
| | having an impact strength of approximately 150 J/cm ² | 78 |
| 7.6 | Results of the calculation of true stress/true plastic strain curves | |
| | from engineering stress and strain values by subtracting the elastic | |
| | component of the strain | 80 |
| 7.7 | Typical true stress/true plastic strain curves of undeformed samples | 81 |
| 7.8 | Typical engineering stress/strain curves of cold rolled and aged samples | 82 |
| 79 | True stress/true plastic strain of cold rolled and aged samples | 83 |



| 7.10 | Uniform plastic strain (true strain at the onset of necking | 84 |
|-------|---|----|
| 7.11 | The effect of plastic strain on the work hardening rate (θ) of samples | |
| | solution treated at 880°C, cold rolled and aged at 475°C | 86 |
| 7.12 | The effect of plastic strain on the work hardening rate (θ) of samples | |
| | solution treated at 930°C, cold rolled and aged at 475°C | 86 |
| 7.13 | Strain-to-failure in the width and thickness directions of specimens | |
| | solution treated at 880°C | 88 |
| 7.14 | Strain-to-failure in the width and thickness directions of specimens | |
| | solution treated at 930°C | 88 |
| 7.15 | R-values of the true strains | 89 |
| 7.16 | Difference between the true strain in the neck at fracture and the true strain | |
| | at necking (in the thickness direction) | 91 |
| 7.17a | Outlines of the necks after fracture of the deformed and undeformed | |
| | specimens (solution treated at 880°C) | 92 |
| 7.17b | Outlines of the necks after fracture of the deformed and undeformed | |
| | specimens (solution treated at 930°C) | 93 |
| 7.18 | Hardness curves of samples solution treated at 880°C and 930°C, | |
| | cold rolled and aged at 475°C | 94 |
| 7.19 | Tensile strength and 0.2% yield stress of samples solution treated | |
| | at 880°C and 930°C, cold rolled and aged at 475°C | 95 |
| 7.20 | A plot of the average strength and toughness values, for both | |
| | the 880°C and 930°C solution treatments | 95 |
| | | |
| 8.1 | Polarisation diagrams of (a) solution treatment at 880°C, no aging; | |
| | (b) solution treatment at 880°C, aging at 475°C for 2072 hours; | |
| | (c) solution treatment at 930°C, no aging; and | |
| | (d)solution treatment at 930°C, aging at 475°C for 2072 hours | 98 |
| 8.2 | Pitting corrosion tests of specimens with and without aging | |
| | (260 hours at 475°C) after cold rolling | 98 |



8.3 Second anodic current peak in sample aged at 475°C for 16 hours

(solution treated at 990°C)

99

8.4 Potentiostatic tests at 0V in 0.5M H₂SO₄ of samples (a) aged at 475°C

for 16 hours and (b) before aging (solution treatment at 990°C)

100