UNIVERSITEIT VAN PRETORIA
UNIVERSITY OF PRETORIA
YUNIBESITHI YA PRETORIA

Effect of sulphur content on the recrystallisation behaviour of cold worked low carbon Aluminium-killed strip steels

Charles W. Siyasiya

UNIVERSITEIT VAN PRETORIA
UNIVERSITY OF PRETORIA
YUNIBESITHI YA PRETORIA

Effect of sulphur content on the recrystallisation behaviour of cold worked low carbon Aluminium-killed strip steels

By

Charles W. Siyasiya

Supervised by

Professor Waldo E. Stumpf

Submitted in partial fulfilment of the requirements for the degree

Philosophiae Doctor (Metallurgy)

in the

Department of Materials Science and Metallurgical Engineering

Faculty of Engineering, Built Environment and Information Technology

University of Pretoria

Republic South Africa

31st March 2007

Acknowledgement

Firstly, I would like to thank God for affording me the opportunity to study for this degree at the University of Pretoria.

I am greatly indebted to my supervisor Professor Waldo E. Stumpf for his invaluable guidance and input in this research project. I benefited a lot from his experience and insights during this research work.

I would like also to extend my gratitude for the valuable contribution from Professor Gerrit T. van Rooyen. His vast experience made life easier for me in setting up the experiments particularly for the thermoelectric power (TEP) technique.

I would like to express my sincere gratitude to my dear wife Daisy and children who have patiently allowed me to study at the expense of having good times together and countless other little things, all of which only love could endure.

I would like to thank Dr. Nic van der Berg for his contribution in the area of electron diffraction indexing and Mr C. van der Merve for helping with the transmission electron microscope. I would like also to thank Mr. Z. Tang for valuable help in the experimental work.

I would like to extend my gratitude to the IMMRI staff, in particular Mrs Alison Tuling and Mr Francois Verdoorn for the training and guidance during laboratory work in transmission electron microscope and Gleeble 1500™ simulator respectively.

I would like to thank Mrs Sarah Havenga, Elsie Snyman-Ferreira and Lilian Barlow for the administrative work.

I would like to acknowledge the cooperation, sponsorship, provision of materials and relevant data from Mittal Steel South Africa.

Finally I would like to thank the University of Pretoria, in particular the Materials Science and Metallurgical Engineering Department for the provision of facilities that made it possible for me to complete my studies successfully.

Summary

Charles W. Siyasiya

Supervisor: Professor Waldo. E. Stumpf

Department: Materials Science and Metallurgical Engineering

University: University of Pretoria

Degree: Philosophiae Doctor (Metallurgy)

The influence of the sulphur and nitrogen content on the static recrystallisation behaviour of cold worked low carbon Al-killed strip steels was investigated. This was in response to the observation made by some users of these steels that the recrystallisation process after cold work was "sluggish" in some steels and, therefore, this was affecting their productivity as the continuous annealing lines had to be run slower and the batch annealing cycles required a higher annealing temperature and thus more energy input.

Two groups of Al-killed low carbon strip steels, one with low (<10 ppm) and the other with medium to high (> 70 ppm) sulphur content were studied. It was found that sulphur had an indirect but significant effect on the recrystallisation behaviour after cold work of these steels. In the high sulphur content steels, the sulphur precipitated as manganese sulphide (MnS) and copper sulphide (CuS/Cu_2S) coarse particles. These sulphide particles, particularly MnS, were the favoured nucleation sites for aluminium nitride (AlN) and the heterogeneous nucleation encouraged the precipitation of AlN during coiling after hot rolling. The result was that the AlN in medium to high sulphur content steels was generally associated with coarse sulphides and, therefore, the mean particle size of the AlN/MnS particles in the as-coiled steel prior to cold working and annealing, was generally much coarser than in the steels with low sulphur content. In these low sulphur content steels, the AlN nucleated homogeneously in the matrix or heterogeneously on grain boundaries or dislocations during coiling. Consequently the mean particle size of AlN in these low sulphur content steels was significantly finer, often less than 30 nm in diameter and, therefore, these particles were more effective in retarding the recrystallisation process through Zener-pinning of dislocations and moving recrystallisation fronts.

The effect of lower sulphur content was exacerbated by lower coiling temperatures (~600 °C) i.e. the recrystallisation start time increased with a decrease in coiling temperature as the AlN particles remained small due to a low coarsening rate. On the contrary, no significant sensitivity to coiling temperature was observed in the time for the start of recrystallisation after cold work in medium to high sulphur steels within the coiling temperature range 600 to 650 °C. The conclusion was that sulphur, in the presence of manganese, does not hinder recrystallisation after cold work in Al-killed steels but promotes heterogeneous nucleation and growth of AlN on the coarser MnS. The effect is that the effective mean particle size of the AlN becomes much larger as it is not isolated homogeneously as in low sulphur steels but is tied to the sulphides. The sulphur (ppm) dependent empirical expressions for the recrystallisation start times $t_{5\%}$ at isothermal annealing temperature of 610 °C for steels coiled at temperatures of 600 and 650 °C were found to be:

$t_{5\%} = 33.78\exp(-0.0345S)$ for 600 °C and

$t_{5\%} = 0.99\exp(-0.008S)$ for 650 °C.

Recrystallisation arrest was observed during the annealing process after cold work of as-quenched specimens. The apparent activation energy of the process that led to the recrystallisation arrest, being 230 kJ mol^{-1}, is of the order of the activation energy for the diffusion of aluminium in ferrite, i.e. 196.5 kJ mol^{-1}. Since the precipitation process of AlN is controlled by the slower diffusion of aluminium, this was an indication of the nucleation/clustering of fine particles of AlN, which consequently halted the recrystallisation process through effective Zener drag. This Zener-pinning effect was used to estimate indirectly the precipitation start and finish times for the AlN during the isothermal annealing after cold work of these steels.

Summary

The solubility of AlN in austenite has mostly been studied by others using the Beeghly selective dissolution technique which has often been criticised for its limitations in its lack of sensitivity to the presence of very fine AlN particles, i.e. < 10 nm, and its failure to separate the AlN from other nitrides. In this study the thermoelectric power technique [TEP] was used to study the solubility of AlN in austenite in commercial low carbon Al-killed steels; one group with a medium to higher sulphur content and the other with a lower one. The equilibrium solubility equation thus obtained was determined as:

$$\text{Log}[\%\text{Al}][\%\text{N}] = 2.6 - \frac{9710}{T}$$

where the aluminium and the nitrogen contents are in weight percentages and T is the absolute solution temperature in Kelvin.

It was found that the AlN solubility equation derived here predicted slightly higher solubility temperatures for the AlN if compared to those derived from the Beeghly method. It was also confirmed that the equilibrium solubility of AlN was not sensitive to the sulphur content (unlike the precipitation behaviour), which is in agreement with the results from others obtained through the Beeghly technique.

Key words: Heterogeneous and homogeneous nucleation, Zener-pinning force, mean particle size, activation energy, driving force, static recrystallisation, Avrami exponent and constant.

Table of contents

Table of contents

Table of contents

Table of contents

Table of contents

Table of contents

Chapter 13

Discussion

List of figures

List of tables