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Development of nitride strengthened nickel-chromium alloys for high temperature applications

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To my parents,
who provided the genetical
basis of this work

Preface

This Ph.D thesis was carried out at the Institute of Metallurgy of the ETH Zurich under the supervision of Professor M. O. Speidel, to whom I would like to express my gratitude for giving me this opportunity and for according me a good deal of freedom and trust in this research.
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Finally, the support from my family and friends is not to be underestimated: a big thank to everybody.

Abstract

Nitrogen as an alloying element has been successfully used to develop a number of commercial steels in which it stabilizes the austenitic phase and allows the precipitation of nitrides. It is well established that interstitial nitrogen in steels causes a remarkably high strengthening and the mechanism is quite well understood. On the other side, a lot less is known on the properties of nickel-base alloys containing nitrogen.

This thesis describes the development of a new nickel-chromium alloy concept based on nitride stabilized grain boundary strengthening and solid solution hardening. The grain boundary stabilizing effect of nitrides and the properties of nickel-chromium alloys were combined in order to develop a new high temperature material.

By means of lab experiments combined with thermodynamical calculations and careful literature studies a suitable alloy composition was designed. In particular, this was selected in order to allow the manufacturing by ingot metallurgy, which had to be carried out under high nitrogen partial pressure in order to achieve sufficient nitriding.

Firstly, the properties of nitrided nickel-chromium alloys have been investigated in detail focusing on the influence of alloying elements on solid state and melt nitrogen solubilities, nitrogen solid solution strengthening at room and high temperature and the precipitation behavior. Technically and scientifically interesting achieved results include a remarkable nitrogen solid solution hardening at both room and high temperatures and the increased nitrogen solubility by chromium and tungsten addition.

Secondly, high nitrogen pressure melt nitriding was carried out to produce nitride strengthened polycristalline nickel-25chromium-10tungsten alloys in the lab and their precipitation behavior, high temperature workability and thermal stability were investigated.

Finally, this alloy concept was transferred to large scale production and two loads with different compositions were produced by the industrial partner; their thermal stability and mechanical properties at room and high temperature were investigated, with particular emphasis on creep properties. The tensile strength of these new alloys resulted higher than that of comparable carbide strengthened nickel-chromium commercial alloys. The creep resistance was found to be strongly dependent on heat treatment affecting the precipitation state on grain boundaries. Interesting results were achieved at 800°C while at 1000°C the thermal stability of precipitates was not sufficient to hinder grain boundary sliding although higher strengths is expected with higher nitrogen contents.

Zusammenfassung

Durch Zulegieren von Stickstoff wurden zahlreiche kommerziell erfolgreiche Stähle entwickelt. Der Stickstoff als Legierungselement stabilisiert die Austenitphase und erlaubt die Nitridausscheidung. Interstitiell gelöst erhöht er durch eine ausserordentliche Mischkristallhärtung die Festigkeit erheblich und die dafür verantwortlichen Mechanismen werden ziemlich gut verstanden. Andererseits wurden die Eigenschaften von stickstoffhaltigen Nickelbasislegierungen viel weniger untersucht.
Diese Dissertation beschreibt die Entwicklung eines neuartigen Nickel-Chrom-Legierungskonzeptes, welches auf nitridsstabilisierte Korngrenzen- und Mischkristallhärtung beruht. Der Korngrenzenstabilisierungseffekt der Nitride wurde mit den Eigenschaften der Nickel-Chrom-Legierungen kombiniert um einen neuartigen Hochtemperaturwerkstoff zu erzielen.
Eine geeignete Legierungszusammensetzung wurde mittels experimenteller Untersuchungen, parallellaufender thermodynamischer Berechnungen sowie durch eingehende Literaturrecherchen bestimmt. Dabei wurde besonders darauf geachtet eine schmelzmetallurgische Herstellung zu ermöglichen; dazu war ein Hochdruckverfahren notwendig um einen genügend hohen Stickstoffgehalt zu erreichen.
Zunächst wurden die Eigenschaften aufgestickter Nickel-Chrom-Legierungen im Hinblick auf den Einfluß der Legierungselemente auf die Stickstofflöslichkeit in der festen und flüssigen Phase, auf den Mischkristallhärtungseffekt des Stickstoffs und auf das Ausscheidungsverhalten untersucht. Technisch und wissenschaftlich bedeutend sind dabei der ausserodentliche Mischkristallhärtungseffekt durch Stickstoff bei Raum- sowie hohen Temperaturen und die Erhöhung der Stichstofflöslichkeit durch Zugabe von Chrom und Wolfram.
Danach wurden nitridverstärkte, polykristalline Ni-25Cr-10W-Legierungen durch Aufsticken bei einem hohen Stickstoffpartialdruck hergestellt und das Ausscheidungsverhalten, die Warmumformbarkeit und die thermische Stabilität untersucht.
Schließlich wurde dieses Legierungskonzept für die Herstellung zweier industriell umgeschmolzener Grosschargen bei einem Industriepartner eingesetzt; dazu wurden zwei unterschiedliche Zusammensetzungen ausgewählt. Die thermische Stabilität sowie die mechanischen Eigenschaften bei Raum- und hoher Temperatur wurden mit besonderer Aufmerksamkeit auf das Kriechverhalten charakterisiert. Diese Legierungen weisen eine höhere Zugfestigkeit als vergleichbare kommerzielle karbidverstärkte Legierungen auf. Das Kriechverhalten ist stark vom Ausscheidungszustand an den Korngrenzen abhängig, welcher durch Wärmebehandlung gesteuert werden kann. Vielversprechende Ergebnisse wurden bei 800°C erreicht. Bei 1000°C reichte die thermische Stabilität der Nitride nicht mehr aus um das Korngrenzengleiten zu verhindern. Es wird jedoch bei dieser Temperatur eine höhere Kriechfestigkeit durch eine deutliche Erhöhung des Stickstoffgehaltes erwartet.

Riassunto

L'azoto come elemento di lega è ben conosciuto nell'ambito delle leghe ferrose, grazie al quale è stata sviluppata tutta una serie di acciai, nei quali questo elemento ha l'effetto di stabilizzare l'austenite e produrre precipitazione di nitruri. In questi acciai l'azoto in soluzione solida provoca un forte rafforzamento per soluzione solida e i meccanismi che lo determinano sono piuttosto ben conosciuti, mentre invece poco o nulla si conosce delle proprietà di leghe azotate a base di nichel e cromo.
Questo lavoro di tesi descrive lo sviluppo di un nuovo concetto di lega a base di nichel e cromo fondato sul rafforzamento per affinamento di grano stabilizzato da particelle di nitruri e sul rafforzamento per soluzione solida. Si tratta di associare l'elevata stabilità termodinamica dei nitruri, se confrontati ai carburi, e le proprietà delle leghe a base di nickel e cromo ottenendo così un nuovo materiale adatto per impieghi a temperature elevate.
Tramite esperimenti di laboratorio, simulazioni termodinamiche ed un attento studio della letteratura è stata elaborata una composizione chimica di lega tale da permetterne la produzione per fusione, con la particolarità di dover essere eseguita sotto alta pressione per ottenere un alto contenuto di azoto.
In primo luogo sono state studiate in dettaglio le proprietà della lega nitrurata a base di nichel e cromo, analizzando in particolare l'effetto degli elementi di lega sulla solubilità dell'azoto in fase liquida e solida, il rafforzamento dovuto all'azoto in soluzione nonchè il comportamento di precipitazione. In questo ambito i risultati tecnicamente e scientificamente più interessanti includono l'effetto particolarmente marcato di rafforzamento per soluzione solida, provocato dall'azoto a temperatura ambiente come a temperature elevate, e l'aumento della solubilità dell'azoto provocato dall'aggiunta di cromo o tungsteno.
Successivamente leghe policristalline a base nichel-25cromo-10tungsteno rafforzate da nitruri sono state prodotte per nitrurazione ad alta pressione in fase liquida. Queste leghe sono state in seguito caratterizzate per quanto riguarda i fenomeni di precipitazione, la malleabilità ad alta temperatura e la stabilità termica.
Finalmente il concetto di lega è stato trasferito su larga scala e due colate con due diverse composizioni chimiche sono state prodotte da un partner industriale; la stabilità termica e le proprietà meccaniche sono state studiate, prestando particolare attenzione al comportamento in condizioni di scorrimento viscoso *(creep)*. La resistenza alla deformazione di queste leghe è superiore a quella di leghe commerciali comparabili, rafforzate da carburi. La resistenza al creep è risultata fortemente connessa allo stato di precipitazione ai bordi di grano, influenzato a sua volta dai trattamenti termici. Risultati interessanti sono stati ottenuti a 800°C mentre a 1000°C la stabilità termica dei precipitati non è risultata sufficiente per contrastare lo scorrimento dei bordi di grano; una migliore resistenza rimane comunque auspicabile aumentando considerevolmente il contenuto d'azoto.

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