Materials Science & Engineering A 684 (2017) 435–441

Contents lists available at ScienceDirect

Materials Science & Engineering A

journal homepage: www.elsevier.com/locate/msea

Experimental and computational study of nitride precipitation in a CrMnN austenitic stainless steel

Niklas Pettersson[a,*], Karin Frisk[a], Rainer Fluch[b]

[a] Swerea KIMAB AB, P.O. Box 7047, 164 07 Kista, Sweden
[b] Böhler Edelstahl Gmbh, Mariazeller Strasse 25, 8605 Kapfenberg, Austria

ARTICLE INFO

Keywords:
Precipitation
Aging
Nitrides
Electron microscopy
Simulations
Mechanical properties

ABSTRACT

The austenitic CrMnN stainless steels are high-strength, tough, and non-magnetic, and are used in oil field applications. The steels have high alloying contents, and precipitation of Cr-nitrides and/or intermetallic phases can occur when cooling through the temperature region 950–700 °C. The nitride precipitates appear in the grain boundaries but can be difficult to observe in the microstructure due to their small size. However, there is an effect of precipitation on corrosion and impact strength and a modelling approach to predict precipitation is valuable for alloy and process development. In the present work precipitation simulations were applied to a CrMnN steel composition, and coupled to experimental investigations after heat treatments at 700 and 800 °C. The early stages, with short heat-treatment times, were studied. The simulations were performed using TC-PRISMA, a software for calculation of multiphase precipitation kinetics, using multicomponent nucleation and growth models. Dedicated thermodynamic and kinetic databases were used for the simulations. The main precipitate was identified by experiments and simulations to be the Cr_2N nitride, and the precipitation during isothermal heat treatments was investigated. Isothermal precipitation diagrams are simulated, and the influence of precipitation kinetics on toughness is discussed.

1. Introduction

Computational thermodynamics and kinetics are valuable tools for alloy development, and can be applied for prediction of the effects of composition and process variations on the microstructure development. In the present work computational techniques are applied to study precipitation in the CrMnN austenitic stainless steels. Typical applications for these steels is in oil field applications, where a material is required with high strength and toughness, good resistance to stress and pitting corrosion, and that is non-magnetic to not cause any disturbance on the corresponding monitoring equipment [1]. The CrMnN grades generally contain high levels of Cr and N, and the levels can be further increased in grades to be used under aggressive conditions.

The alloying, however, makes the CrMnN steels prone to precipitation of nitrides and/or intermetallic phases during cooling through the temperature range of 950–700 °C. The main precipitates for CrMnN steels are Cr-nitrides (Cr_2N) [2–7]. Sigma phase (σ) is sometimes present together with the nitrides [2–4], and sometimes also Chi phase (χ) [4,7]. The Cr_2N precipitates appear as discrete particles at the grain boundaries after short aging times, but after longer aging times cellular precipitation has been observed [4]. The precipitation can be detrimental to the properties and affect both the mechanical properties [4,5] and the corrosion resistance [8].

Studies where computational tools have been applied to simulate the precipitation of nitrides in austenitic stainless steels are limited. In a work by Dai et al. [9] a semi-empirical estimate of the incubation time (assuming steady state nucleation) was used to predict the Cr_2N precipitation kinetics at different temperatures for a CrMnN steel. The model did, however, not include any descriptions for the thermodynamics and kinetics, and the influence of alloying elements was simply included through fitting of a parameter expression by regression analysis. Reddy et al. [10] analysed experimental data from the literature using a neural network model and presented results showing the influence of different alloying elements on the Cr_2N precipitation. They stressed the importance of the incubation time for the precipitation, however, did not discuss the critical amount of nitride precipitation that defines the incubation time. Simmons [11] investigated the mechanical properties of isothermally aged high-nitrogen stainless steel and related the properties to the Cr_2N precipitation. The precipitation was observed in grain boundaries and severely reduced the tensile ductility and impact toughness. The drop in impact

* Corresponding author.
E-mail address: niklas.pettersson@swerea.se (N. Pettersson).

http://dx.doi.org/10.1016/j.msea.2016.12.071
Received 12 September 2016; Received in revised form 14 December 2016; Accepted 16 December 2016
Available online 21 December 2016
0921-5093/

toughness was related to the grain boundary coverage, where 40% grain boundary coverage was reported to be the critical limit after which the toughness was degraded. They also compared solution annealed and cold-rolled material, and found that the precipitation kinetics were significantly encanced in cold-rolled material.

These previous works illustrate the complexity of the effect of time, temperature and composition on the precipitation, and a comprehensive method to analyse these effects is of interest. The recent development of computational tools now makes it possible to simulate nucleation and growth in multicomponent and multi-phase systems where both thermodynamics and kinetics are included through the use of CALPHAD databases [12]. The selection of the thermodynamic and kinetic data is critical for the results of precipitation simulations. The thermodynamic database determines the driving force for precipitation which is a critical factor in the modelling of nucleation. The kinetic database determines the mobilities of the elements, which are crucial for the growth and coarsening rates of the precipitates.

The focus of this work has been to study precipitation in a CrMnN steel at 700 and 800 °C using computational techniques and electron microscopy. The emphasis has been on shorter heat treatment times to maintain the practical relevance to process variations, e.g. the influence of indirect cooling after heat treatments during which the temperature could enter a critical range for a shorter period of time. The main purpose was to investigate early stages of precipitations and to increase the understanding of the critical amount of nitrides that affect the properties. The purpose was also to investigate if the simulations can describe this early stage of precipitation. Since experimental characterisation of small precipitates is challenging, a simulation tool would be very useful in this range. The impact toughness has been evaluated to establish when precipitation first starts to affect the mechanical properties, and the influence of precipitation kinetics on the toughness degredation is discussed.

2. Experimental and simulation techniques

2.1. Materials and heat treatments

The material was supplied by Böhler Edelstahl GmbH & Co, and the steel composition is listed in Table 1. For the isothermal heat treatments it is important that the heating and cooling will not affect the precipitation in the samples. The heat treatments were performed in a Gleeble on impact testing samples by conductive heating on a small area to ensure rapid heating and cooling. Before the isothermal heat treatments in the Gleeble the as-received material was solution annealed at 1025 °C for 40 min, followed by quenching in water to room temperature. The solution annealed samples were then heat treated isothermally 0.5, 1, 2, 3, 4, 5, 6, 7, 8, 9, 10 and 30 min in the Gleeble by conductive heating at 800 °C. At 700 °C samples were heat treated 2, 4, 6, 8, 10, 12, 14, 16 and 18 min. The shorter times up to 10 min were of main interest, however, the 30 min 800 °C heat treatment was added with the purpose of providing information for nitride quantification.

2.2. Impact testing

Impact toughness testing was performed at ambient temperature on standard 10 mm×10 mm×55 mm Charpy specimens. The V-notch was introduced in the area where the Gleeble heat treatment had been applied. Two tests were performed for each heat treatment condition.

Table 1
Composition of the CrMnN steel in wt% (with Fe as balance).

C	Si	Mn	Cr	Mo	Ni	N
0.03	0.13	21.3	18.6	0.55	1.65	0.59

2.3. Electron microscopy

Preparation of metallographic cross-sections for electron microscopy was done by grinding on SiC-paper followed by polishing to 0.25 μm diamond finish. Final preparation was done by a short polishing (10 min) in acidic aluminum oxide solution followed by final polishing in a neutral colloidal silica solution at low load using a vibratory polisher for minimum 5 h.

The metallographic cross-sections were examined by scanning electron microscopy (SEM) in backscattered electron (BE) mode using a JEOL 7000F field emission gun (FEG) microscope. The microscope was equipped with a silicon drift detector (X-Max from Oxford Instruments) for energy dispersive X-ray spectroscopy (EDS). Phase identification was done by electron backscattered diffraction (EBSD) using NordlysNano EBSD detector and the AZtec software (post-processing was done with the CHANNEL5 software).Automated particle analysis was performed on samples heat treated 10 and 30 min at 800 °C using the INCA Feature software in order to estimate the area fraction and average size of precipitates for correlation with the precipitation simulations. Precipitates were identified using a BE contrast threshold, and objects were classified as nitrides if nitrogen was identified in the EDS spectrum since the level in the matrix was too low for detection. The size of the nitrides was given by a conversion of the detected particle area into an equivalent circle diameter (ECD). A total of 200 image fields acquired at random positioning was used for each sample.

One selected sample was further analysed with transmission electron microscopy (TEM) to check if any precipitates are missed in SEM due to their size. Thin foils were produced by electrolytic polishing at 12 V in Tenupol-5 using a solution of 15% perchloric acid in methanol held at −18 °C. Analysis was performed using a JEOL 200 kV 2100F FEG TEM equipped with windowless EDS detector (X-Max^N TLE from Oxford Instruments).

2.4. Thermodynamic calculations and precipitation simulations

The precipitation simulations were performed using TC-PRISMA [12], which is based on the Langer-Schwartz theory [13], and uses Kampmann-Wagner numerical method [14] for nucleation, growth, and coarsening of dispersed precipitate phases in multicomponent systems. The parameters that are needed for the simulations are the driving forces (thermodynamic description) and the phases that are expected to precipitate, the mobilities (defining the diffusion), the surface energies of the precipitated phases, the molar volumes of the phases, and the nucleation sites.The thermodynamic and kinetics were included by the use of databases. For the thermodynamics an internal database based on the thermodynamic descriptions by Frisk [15] and Qiu [16] was used. This database was also used to calculated the molar volumes of the phases using the Thermo-Calc software [17]. For the kinetics the standard steel mobility database MOBFE2 [18] was used. The diffusivities of the respective species are then given by $D = RTM$ where the mobility M (from the database) is a function of activation energy and temperature. When precipitation occurs in the grain boundaries were the activation energies for diffusion are lower compared to those for volume diffusion in the bulk, the grain boundary diffusion rates could then be several orders of magnitude larger than the diffusion rates in the bulk. The effective diffusion rates could then be higher than those given by the mobility database that only describes bulk diffusion. In such cases a mobility scaling in TC-PRISMA can be introduced by defining the mobility enhancement prefactor k, and the diffusivities will then be given by $D = RTkM$. This parameter was fitted as will be explained later.Nucleation was considered in the grain boundaries and the number of nucleation sites was defined by the grain size. A value of 50 μm (diameter) was used according to an estimation of the grain size (by circle intercept method) in the solution annealed condition.The interfacial energies are not known and were