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# Influence of combined thermomechanical treatment on impurity segregation in ferritic–martensitic and austenitic stainless steels

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## Abstract

In this study 13Cr2MoVNb ferritic–martensitic steel (FMS) and 16Cr15Ni3MoNb austenitic stainless steel (ASS) tensile specimens were subjected to standard heat treatments and divided into two groups. Specimens in group 1 (FMS only) were aged at 400°C in a stress free and in an elastically stressed state with a tensile load (100 MPa) then doped with hydrogen in an electrolytic cell. Specimens in group 2 were subjected to cold work (up to 10%) and exposed to short-time heating at 500° for 0.5 h. All specimens were fractured at room temperature in an Auger spectrometer and Auger analysis of the fracture surfaces was performed in situ after fracturing. A noticeable increase of N and P segregation levels and a widening of the depth distribution on the grain boundary facets were observed in the FMS after aging in the stressed state. Cold-worked FMS and ASS showed a ductile dimple mode of fracture, but relatively high levels of S, P and N were observed on the dimple surfaces. We consider the origin of such effects in terms of the stressed state and plastic-deformation-enhanced segregation. © 2000 Elsevier Science B.V. All rights reserved.

## 1. Introduction

The effect of impurities on the properties of structural materials is a long-standing issue, especially for fusion reactor materials exposed to extreme service conditions. It has been shown previously that grain boundary segregation processes in austenitic stainless steels, induced by irradiation with helium and hydrogen ions, reflected the main features found in the unirradiated state, but in many cases displayed greater intensity and a more unfavorable effect on mechanical properties [1,2]. It is reasonable to study atomic segregation in materials subjected to surrogate conditions, in order to predict the main features of such phenomena after irradiation. Recently, we have demonstrated the effect of an elastically stressed state at a medium temperature on the chemistry of grain boundaries in low-alloy CrMoV steel [3]. In the present study, we used Auger electron spectroscopy to examine the formation of impurity segregation in a ferritic–martensitic steel (FMS) and an austenitic stainless steel (ASS) exposed to aging in an elastically stressed state and after cold working and aging under a tensile loading.

## 2. Experimental procedure

The basic chemical compositions of the FMS and ASS used are given in Table 1. The geometry of the tensile specimens used is shown in Fig. 1. FMS and ASS tensile specimens were homogenized at 1050°C for 1 h. After that, FMS specimens were tempered at 720°C for 1 h. Afterwards one group of FMS specimens was aged at 400°C for 2 h in a stress-free state (AF-specimens) and one group was aged in an elastically stressed (100 MPa tensile stress) state (AS-specimens). Specimens were

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Table 1
Chemical composition of the materials (wt%)

| | Cr | Ni | Mo | Nb | C | P | S | B | V | Fe |
|---|---|---|---|---|---|---|---|---|---|---|
| ASS | 16 | 15 | 3 | 1.0 | 0.1 | 0.03 | 0.02 | | | Bal |
| FMS | 13 | – | 2.6 | – | 0.1 | 0.003 | 0.003 | 0.006 | 0.5 | Bal |

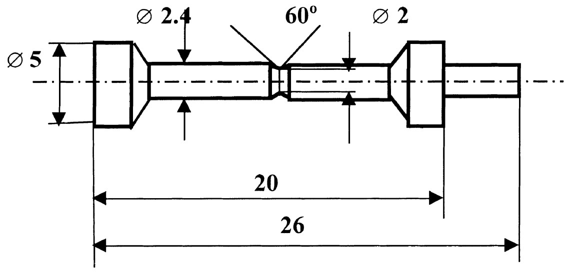

Fig. 1. Geometry of the specimen (all dimensions in mm).

charged with hydrogen in an electrolytic cell in order to produce favorable conditions for brittle grain boundary fracture. This process was performed in a $H_2SO_4$ solution with small addition of $Na_2S$ with a current density of 800 A/m$^2$ at 30°C for times up to 20 h. Another group of FMS and ASS specimens was subjected to cold work (up to 10%) under vacuum and then exposed to short-time heating at 500°C for 0.5 h in a tensile stressed state.

Specimens doped with hydrogen were fractured by low-speed tensile testing ($5 \times 10^{-5}\,s^{-1}$) at room temperature. Final fracturing and Auger analysis of the fracture surfaces were performed in situ under high-vacuum conditions ($2 \times 10^{-7}$ Pa) within the chamber of an Auger electron spectrometer [4]. The primary electron beam energy and the current intensity were 2.5 keV and 6 μA, respectively. In all cases, there was a large contribution of carbon from grain boundary carbides determined using the Auger carbon peak fine structure. Sputtering the grain boundary fracture surfaces by $Ar^+$ (800 eV) was used in order to determine impurity profiles near the grain boundary. Data presented in Fig. 3 were obtained as follows: sputtering was conducted in 5 min time intervals followed by Auger analysis with a probe size of about 100 μm on the sputtered surface. Every point in Fig. 3 is a statistical average from several 2–3 min scans. The Auger peak heights (relative to Fe 703 eV) were converted into atomic concentrations.

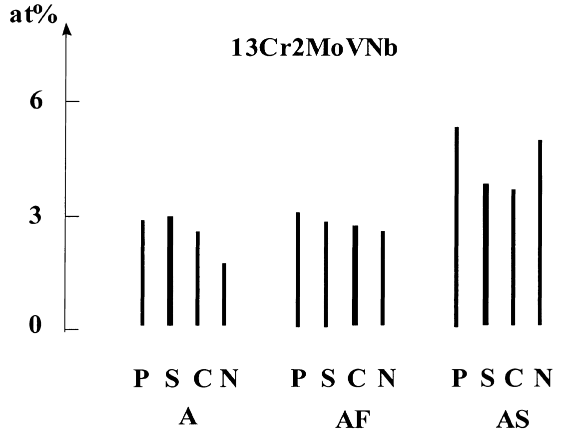

Fig. 2. Elemental composition (at.%) of the grain boundaries after different preliminary thermomechnical treatments of the 13Cr2MoVNb steel. A: 1050°C + 720°C (1 h); AF: aging at 400°C (2 h) in free state, AS: aging at 400°C (1 h) in stressed state (100 MPa). The average relative error for concentrations was 12%.

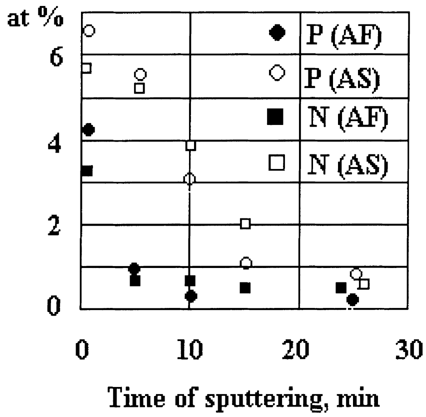

Fig. 3. Phosphorus and nitrogen levels on the grain boundary surface as a function of the $Ar^+$ ion-sputtering time ($E_{ion} = 800$ eV). Relative statistical error was 18%.

## 3. Results

Results of the Auger analyses are given in Figs. 2–4. Hydrogen-charged specimens failed intergranularly, while the cold-worked specimens failed in a ductile manner. A small amount of impurity segregation appeared on the grain boundaries in the FMS after 400°C aging. In all cases the oxygen level on the fracture surfaces was very small (less than 1 at.%). One can see from the data in Fig. 2 that the effect of the elastically stressed state at 400°C was to increase grain boundary segrega-

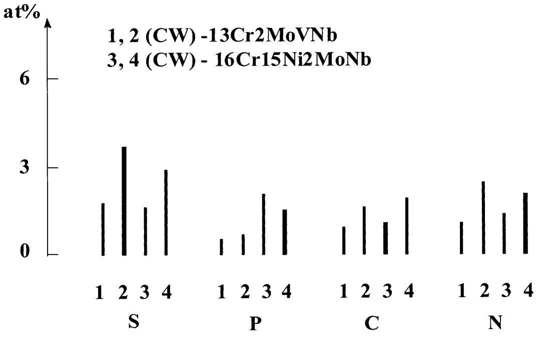

Fig. 4. Elemental composition (at.%) of the ductile fracture surfaces after different thermomechanical treatments. 1,2: 13Cr2MoVNb, 1: without CW, annealed at 500°C; 2: 10% CW, annealed at 500°C, 0.5 h; 3,4: Cr16Ni15MoNb, 3: without CW, annealed at 500°C, 0.5 h; 4: 10% CW, 0.5 h at 500°C. All specimens were fractured at room temperature. The average relative error for the impurity concentration values was 15%.

tion levels for phosphorus and nitrogen. Fig. 3 presents plots of measured levels P and N on the grain boundary surface as a function of the $Ar^+$ ion-sputtering time. In Fig. 4, results are given for FMS and ASS specimens subjected to cold work and aging. Despite the fact that all specimens fractured by a ductile mode, relatively high levels of S, P and N were observed on the fracture surfaces having a predominantly dimple structure.

## 4. Discussion

We consider the origin of effects due to chemical and elastic interactions of impurity atoms with grain boundaries in the stressed state. When a grain boundary in a polycrystal is elastically stressed in tension, this results in some change of grain boundary energy and of the effective capability of the grain boundary to absorb impurity atoms. In a previous paper [3], we have demonstrated the effect of a tensile stress on widening the depth profiles for grain boundary phosphorus segregation in low-alloy Cr–Mo–V steel. One can see from Fig. 3 that in the FMS used in the present study, similar widening of the depth profiles occurred for phosphorus and nitrogen.

For the cold worked material, plastic deformation produces a high density of dislocations and defects in the grain interior, and these defects have a high interaction energy with some of the impurity atoms. In the stressed lattice and at temperatures high enough for significant atomic diffusion, solutes can segregate to the dislocations and other kinds of defects instead of segregating on the grain boundaries, a so-called competition effect between these two main kinds of sinks. During final tensile loading and fracturing the internal defects and impurity sinks can serve as preferable sites of microvoid nucleation. After fracture impurity segregation can be observed on the ductile fracture surface within the dimple fracture areas.

## 5. Conclusion

Auger electron spectroscopy was conducted on the fracture surfaces of a 13Cr2MoVNb ferritic–martensitic steel and a Cr16Ni15MoNb austenitic stainless steel after different thermomechanical treatments, including aging in a stressed state and cold work and aging. A noticeable increase of grain boundary segregation levels as well as a widening of the depth profiles of P and N was found in ferritic–martensitic steel specimens subject to an elastic tensile stressed state (100 MPa) during aging at 400°C. For both 13Cr2MoVNb and 16Cr15Ni-MoNb steels annealed at 500°C after 10% cold work, significantly higher levels of S, P and N segregation were found on fracture surfaces in comparison with specimens without cold work.

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