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Journal of Nuclear Materials 252 (1998) 168–170

journal of nuclear materials

Letter to the Editors

Some features of grain boundary segregations in sensitized austenitic stainless steel

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Received 14 July 1997; accepted 24 October 1997

Abstract

The paper presents results of Auger spectroscopy on fracture surfaces of the austenitic stainless steel 16Cr15Ni3Mo1Nb subjected to thermal sensitization in the temperature range 550–700°C followed by doping with deuterium to produce grain boundary brittle fracture by in situ tensile testing. Non-uniformity of Cr distribution and segregation of P, Ni, N and S in the grain boundary regions, depletion of Cr and noticeable replacing of C by high-level P and S have been shown. © 1998 Elsevier Science B.V.

1. Introduction

The austenitic stainless steels are well known as materials of very great importance for nuclear energy plants and thermonuclear reactors. But they can lose partially the significant technological property, resistance to intergranular corrosion (IGC), and at the same time they become more sensitive to hydrogen embrittlement. This dual effect takes place upon the temperature treatment or slow cooling of stainless steels in the temperature region 600–750°C. The main explanation includes a process which is based on the Cr depletion of the grain boundary regions and in adjacent grain volumes of intensive grain boundary Cr carbide formation. Recent papers [1–3] have shown that some impurity grain boundary segregations forming in this temperature interval may correlate with such a detrimental effect. It must be noticed that the role of impurities other than carbon is not well enough investigated. For instance, in Ref. [2] the essential role of S segregation was demonstrated producing a susceptibility of the 18Cr10Ni1Ti stainless steel to IGC and to hydrogen embrittlement after the treatment at 700°C. However, it was shown in Ref. [3] that the main impurity in 16Cr15Ni3Mo1Nb stainless steel segregated at the same temperature was phosphorus and grain boundary hydrogen brittleness was achieved. The goal of this paper is to study in more detail at least the main features of the grain boundary segregation in the process of forming a sensitized state in 16Cr15Ni3Mo1Nb steel.

2. Experimental

The commercial austenitic stainless steel 16Cr15Ni3Mo1Nb was the model material in the experiment. The chemical composition of the steel was as follows: Cr 16, Ni 15, Mo 3, Nb 1, Si 0.3, S 0.02, P 0.03 (wt%). The specimens were solution annealed at 1050°C (0.5 h) in a protective argon atmosphere, followed by water quenching. They were then subjected to a heat treatment at 550°C, 650°C (100 h) and at 700°C (10 and 100 h). Afterwards they were electrolytically doped with deuterium (in D_2O) by a current density of approximately 6×10^3 A/m^2 in order to cause brittle intergranular fracture. The samples with a shape as in the paper published recently [4] were fractured by slow tension tests in situ in a self-made special Auger spectrometer provided with fracture devices [5].

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PII S0022-3115(97)00335-8

3. Discussion

The Auger data obtained are given in Fig. 1. One can see that the levels of some impurity segregations and the contribution of carbon for carbide formation increased with the treatment temperature. A higher level of brittle GB fracture was obtained after deuterium doping of the samples treated at 700°C for 100 h. The concentration values of the samples fractured after long-time treatment were averaged across the spot about 50 μm in size to minimize a random error. It must be noticed that the large-scale results show only small changes of the grain boundary Cr level in the sensitized state. The local measurements were carried out on the specimens annealed at 700°C for 10 h. The values of the local Auger analysis in different regions of the fracture surface are presented in Fig. 2(a). In the case where the GB carbides occupied only a part of the GB facets it was possible to investigate the regions between the particles. A non-uniform distribution of Cr and the impurities on the GB surface was evidently shown. One can see a very high level of P, S and Ni in the regions, with noticeable depletion of Cr. The depth distribution of the GB impurities is shown in Fig. 2(b) (ion-sputtering by Ar^+, $E = 600$ eV). The measurement showed a Cr depletion not only in grain boundary facets but also in adjacent layers of the matrix. A noticeable increase of the carbon level with sputtering time suggests that carbon atoms were replaced as a result of interaction by impurity segregation from the grain boundary into the depth. The grain boundary particle surface was characterized by a high level of carbon and Cr in carbide form. It has been shown that nitrogen segregated on the grain boundaries, nevertheless it is difficult to corellate its behavior with the effect of the sensitizing process. These results were averaged on the spot with about 8 μm diameter.

The results presented show a diversity of sensitization processes in austenitic stainless steels. This includes the chemically active chromium depletion of grain boundaries as well as the detrimental effect of carbide–grain boundary interfaces. They are combined by strong impurity segregations which can change essentially the physical properties in a microscale and tend at least to hydrogen produced cracking. We take into account the results obtained in [2] for the 18Cr10Ni1Ti steel where a large level of S was measured on the GB surface and a high degree of intergranular corrosion (IGC) was achieved. It should be pro-

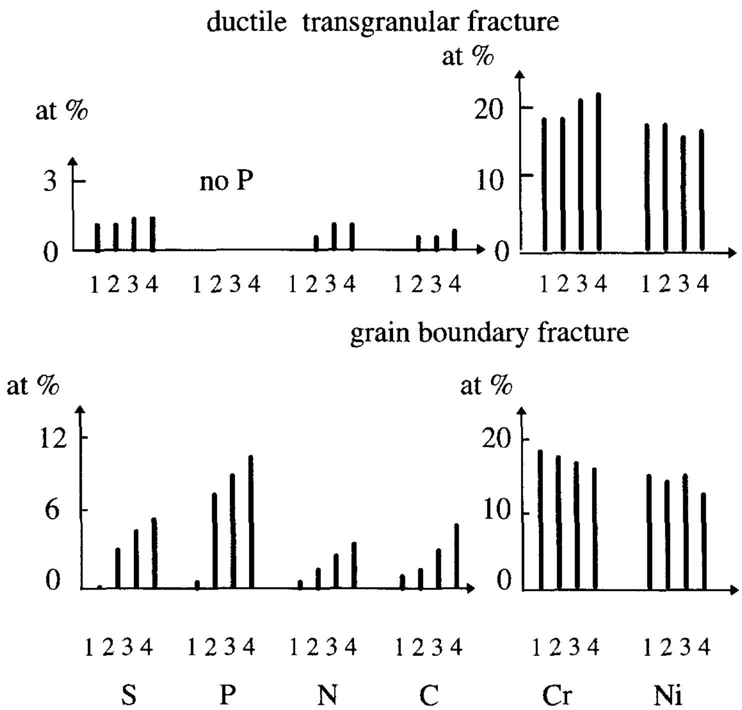

Fig. 1. Elemental composition of the fracture surfaces (in situ tensile testing) of 16Cr15Ni3Mo1Nb stainless steel after thermal treatment (ductile fracture with transgranular surface) and doped additionally by deuterium to produce brittle grain boundary fracture. 1: 1050°C (0.5 h), H_2O quenched; 2: annealing at 550°C; 3: at 650°C; 4: at 700°C (for 100 h).

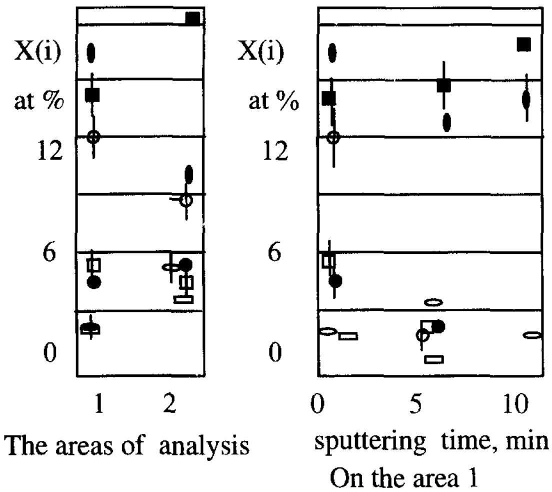

Fig. 2. (a) Non-uniform alloying and impurities distribution on the grain boundary facet after thermal treatment at 700°C, 10 h. 1: The area of analysis is situated between the grain boundary particles. 2: The area of analysis includes grain boundary particle. (b) Depth distribution of the GB segregation and the alloying elements for area 1. The segments show the scatter interval of the results. Ni (filled oval), Cr (filled square), S (open square), P (open circle), N (filled circle), C (open oval), B (open rectangle).

posed that when strong competition between P and S in GB segregation takes place it proves better resistance to IGC, but it does not decrease the influence of GB segregation on the formation of hydrogen embrittlement.

4. Conclusion

During the sensitization process of austenitic stainless steel a strong non-uniformity of chromium content has formed on the grain boundary facets and in the adjacent layers, and the rapid segregation of phosphorus, nitrogen, sulphur and nickel has been detected on the areas depleted of chromium.

The replacement of carbon and chromium from grain boundary areas with high level of phosphorus and sulphur segregation has been shown.

The level of the dual sensitization to intergranular corrosion and to hydrogen grain boundary embrittlement correlates with grain boundary carbides formation and with grain boundary segregation of phosphorus and/or sulphur.

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