DEGRADATION OF PROTECTIVE EFFECT OF SURFACE LAYER ON Ni_3Al-Cr IN HYDROGEN ENVIRONMENT

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ABSTRACT

Protective effect of surface layer on Cr-doped (4 and 8 at. % Cr) Ni_3Al intermetallic was studied by high-temperature hydrogen permeation tests that were carried out at temperatures in the interval 775 - 1223 K. Hydrogen with about 1 vol. ppm O_2 and 2 vol. ppm of H_2O was used for the gas-permeation tests. It was observed that the addition of Cr degrades the – otherwise very good –high-temperature protective ability of oxide-containing surface layer of Ni_3Al-Cr at strongly reducing hydrogen environment.

KEYWORDS

Ni_3Al, surface protective layer, hydrogen, oxidation resistance

INTRODUCTION

The alloying with Cr is frequently used both in steel industry and in the production of high-tech materials as a relatively reliable means that ensures corrosion resistance of the material. This is also the case of materials based on Ni_3Al, where the chromium addition suppresses the so-called dynamic embrittlement at elevated temperatures, caused by oxygen [1]. The beneficial effect is believed to be associated with rapid formation of chromium oxide films that reduce the penetration of oxygen along grain boundaries. [2]. However, Cr promotes also the growth of a dense protective oxide layer covering the whole surface and influences both the chemical composition of surface oxides and their structure.

The formation of chromium and nickel oxide would require a higher oxygen partial pressure [3]. If the material is exposed to reducing atmosphere, the formation of protective layer (which is otherwise controlled by oxidation rate only) may be changed considerably, since in such a case the competition of oxidation and reduction should be considered. This situation may be often encountered, because the materials based on Ni_3Al with Cr additions are applied as high-temperature structural materials operating up to 1400 K in air-containing environments or in special combustion gasses [3].

In the previous paper [4], it was shown that hydrogen permeation rate is sensitive to oxidation state of the CMSX-4 superalloy surface. It was observed that the measurement of hydrogen permeation flux J in dependence on the sample thickness d might supply information on relative importance of the surface and volume hydrogen permeability. Dense and compact surface oxides suppress the hydrogen invasion into the material, which implies very weak dependence of J on d. On the other hand, cracked, buckled or discontinuous protective layers, makes no protection against hydrogen permeation, and hence, the hydrogen permeation is controlled primarily by the volume permeation. This implies the dependence of the flux *J* on *d*.

The aim of the present work is to study the quality of surface protective layer covering the Ni_3Al intermetallic alloyed with 4 and 8 at. % Cr. To separate the effect of Cr addition, the measurements were done also with non-alloyed Ni_3Al. Various experimental temperatures enabled to gain more detailed information on protective characteristic of the surface layer under oxidation/reduction, which simulates the real operating conditions in technical practice.

EXPERIMENTAL

Experimental alloys were prepared by induction melting from pure elements Ni (3N7), Al (5N) and Cr (3N8). Chemical composition of alloys was checked by SEM Philips/EDAX. It was designed in a way that assured that both the alloys were in γ' lobe in the temperature region where the experiments were carried out. A small amount of boron (~ 0.1 at.%) was added in order to suppress the brittleness of experimental samples.

The ingots were cylindrical with diameter of about 15 mm. They were homogenization annealed at 1533 K/1 h in vacuum. After that, the samples were machined into a cylindrical form with diameter of 13 mm, spark-cut to thickness of 0.8 mm, and metallographically ground down to the final thickness of tens to hundreds of μm (the last grade of paper was 2400). The working diameter of the foil-like samples was 10 mm.

The structure of heat-treated alloys was examined by optical metallography and SEM/EDAX. The samples had radial structure with wedge-like grains, width of which was about 10^2 μm at radius ca 5 mm. All of them were homogeneous (γ') at room temperature.

The experimental method used in the present work was described in detail elsewhere [5]. It is based on the measurement of the total flow rate *J* through the sample of thickness *d*. According to Richardson's equation, the hydrogen flux *J* through a unit surface area is inversely proportional to *d* by pressure P_1 at the up-stream side and P_2 at the down-stream side of the foil

$$J = D\,S\,\frac{\sqrt{P_1}-\sqrt{P_2}}{d} = \Phi\,\frac{\sqrt{P}}{d}\,. \tag{1}$$

A proportionality constant, *Φ,* is called permeability and it can be expressed as a product of diffusion coefficient *D* and solubility constant *S* relating solubility limit *c* and pressure *P* in Sievert's law $c = S\,(P)^{1/n}$ (for *n*-atom gas molecule). If the pressure P_2 at the down-stream side can be omitted, the nominator in Richardson's equation can be simplified as indicated in Eq.1.

The *J* was measured absolutely, using the velocity *v* of moving Hg index in a capillary (inner diameter 1.6 mm). The pressure difference between the two sides of the sample was always 1.01×10^5 Pa (i.e., normal pressure of hydrogen at the upstream side, and vacuum of about 5×10^{-4} Pa at the downstream side). The measurements with each sample were performed for varied thickness *d* to estimate whether the hydrogen permeability is controlled either by surface reaction or rather by transport through the bulk. Each sample was mounted into the apparatus (for details see [5]), and tempered at the chosen permeation temperature with hydrogen at the up-stream side and vacuum at down-stream side. Measurement of the permeation flux *J* was performed after the stationary permeation conditions had been achieved.

The purity of the hydrogen used for the experiment in vol. ppm was following: $O_2 \leq 1$, $N_2 \leq 3$, $H_2O \leq 2$ and $C_nH_m \leq 0.2$. This means that the partial pressure of oxygen at the upstream side was in the order of 10^{-1} Pa.

RESULTS

The primary results obtained were the time dependences of location *x* of Hg index in the capillary that varied with volume *V* of hydrogen passed through the sample. Knowing the diameter of the capillary and the velocity *v* of the mercury index in the capillary, the time dependence of *V* could be calculated. Examples of measured *x(t)* are shown in Fig.1.

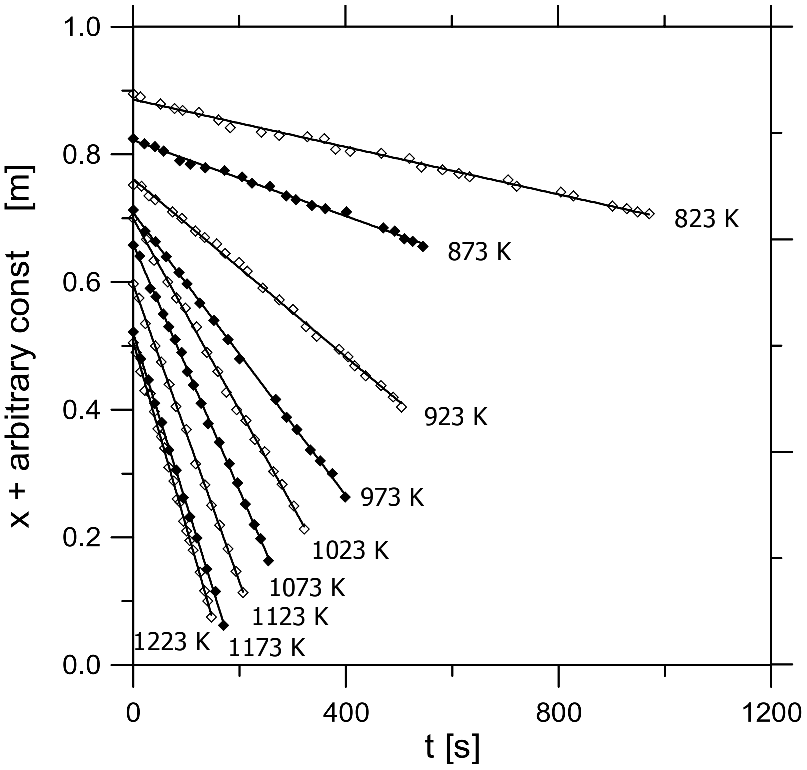

Fig.1 Index locations *x* – measured for Ni_3Al-8Cr; *d* = 48 μm.

The values of *v* were only taken in account, which were registered after the stationary flow had been achieved (after a certain initial time period t_o). The stationary conditions were indicated by linearity of *x(t)* – see Fig.1 (arbitrary constant enables a convenient vertical shift only of the experimental points). The permeation flux *J* of hydrogen passing trough the unit area of sample was calculated from the constant slope of *x(t)* using known surface area of samples (their working diameter was about 10 mm).

Hydrogen permeation in unalloyed Ni_3Al was investigated which enabled the assessment of the effect of Cr addition. Temperature dependence of J measured for different thickness d is plotted in Fig.2.

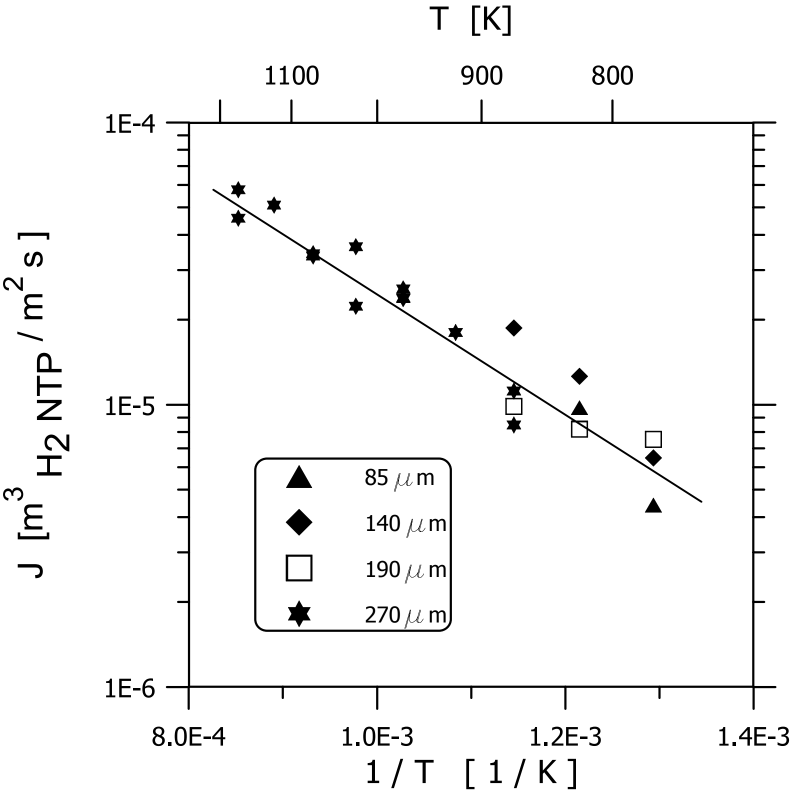

Fig.2 Permeation flux J in Ni_3Al

The Ni_3Al samples charged by hydrogen were prone to brittle fraction and, therefore, especially thin samples could not be measured at higher temperatures. Typical mode of failure of tested pure Ni_3Al alloy was a macroscopic intergranular crack nucleated under the copper gasket. The failure of a sample was detected by repeated measurement: significantly enhanced *J's* obtained in the second run were taken as a sign of failure.

Results, obtained with alloys modified by Cr, are shown in Figs.3,4. It was observed that addition of Cr remarkably suppressed the brittleness of materials under study and therefore, the thinner samples could be measured quite easily. It is obvious from Figs.3,4 that - contrary to non-alloyed Ni_3Al - the measured values of J depend on the sample thickness d.

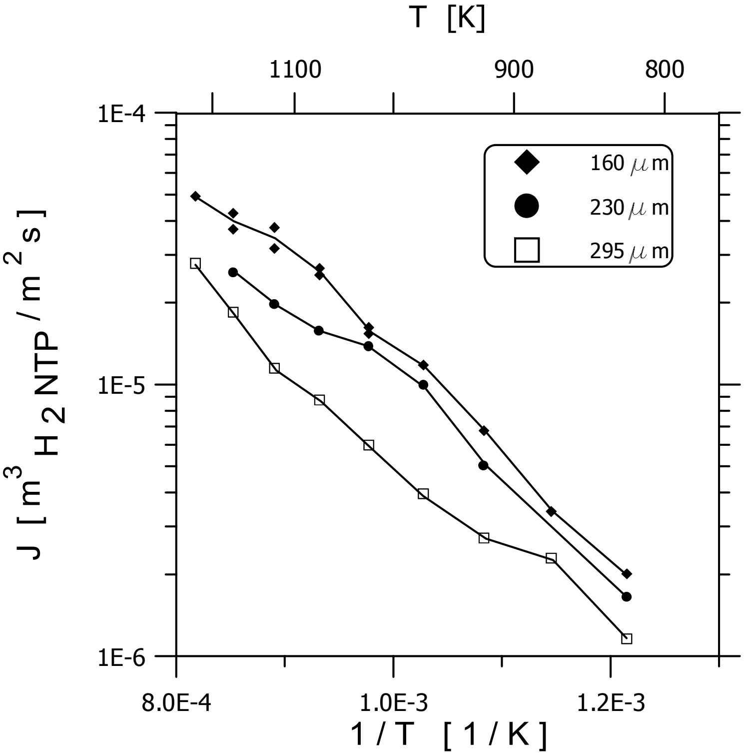

Fig.3 Permeation flux *J* in Ni_3Al-4Cr.

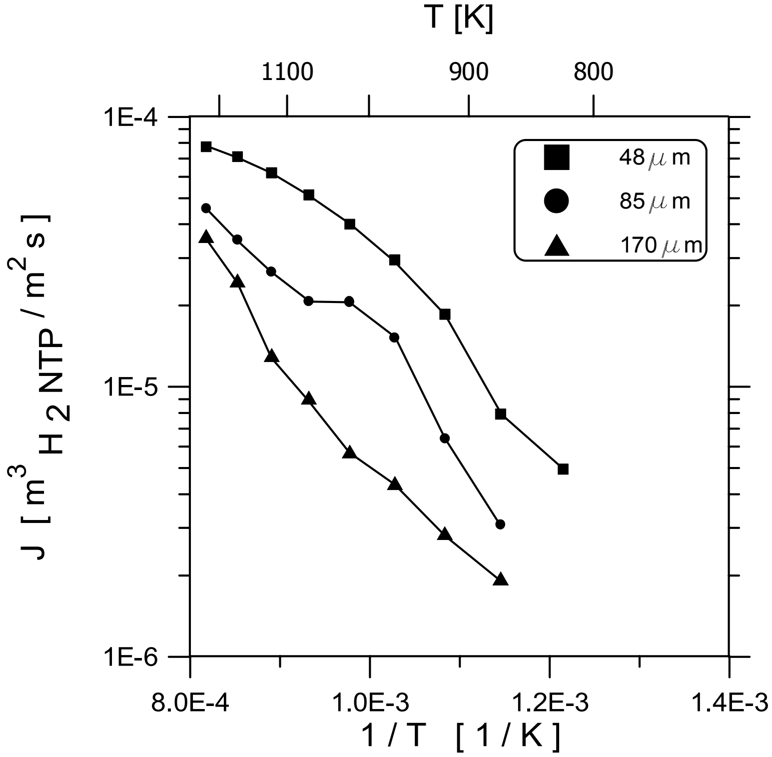

Fig.4 Permeation flux *J* in Ni_3Al-8Cr.

DISCUSSION

The permeation of hydrogen through the matter is described by Eq.(1) that expresses the proportionality between J and d^{-1}. It can be seen, however, that this relation does not hold for the permeation in non-alloyed Ni_3Al membranes (Fig.2). This can be explained by known mechanism of surface oxidation in oxidation environments [6]: So called *native oxide* (alumina) always present at the Ni_3Al surface is changed at higher temperatures in a layered structure composed of outer NiO scale, mixed Ni/γ' (Ni_3Al)/ γ-Al_2O_3 layer and inner Ni_3Al substrate [6,7]. It can be expected that in strongly reducing environment applied in the present paper, the NiO growth is dramatically suppressed due to its lower decomposition energy (compared to that of alumina) [8,9] and that the surface is covered by more or less compact alumina scale (see schematically in Fig.5a). This implies for the observed mode of hydrogen permeation that the rate controlling process is the slow hydrogen permeation through the scaled surface rather then the diffusion of the hydrogen through the bulk of the membrane.

The hydrogen permeation through membranes of Ni_3Al alloyed by Cr, on the other hand, shows a significant dependence on the membrane thickness d – see in Figs.3,4. This is most likely caused by the modification of Al oxide nucleation and its growth by chromium. It is known that Cr oxides nucleate easily and that they act as nucleation centers for alumina [10]. Hence, it can be expected that the structure of the surface scales losses its compactness and that channels are formed for easy hydrogen invasion as it is illustrated in Fig.5b.

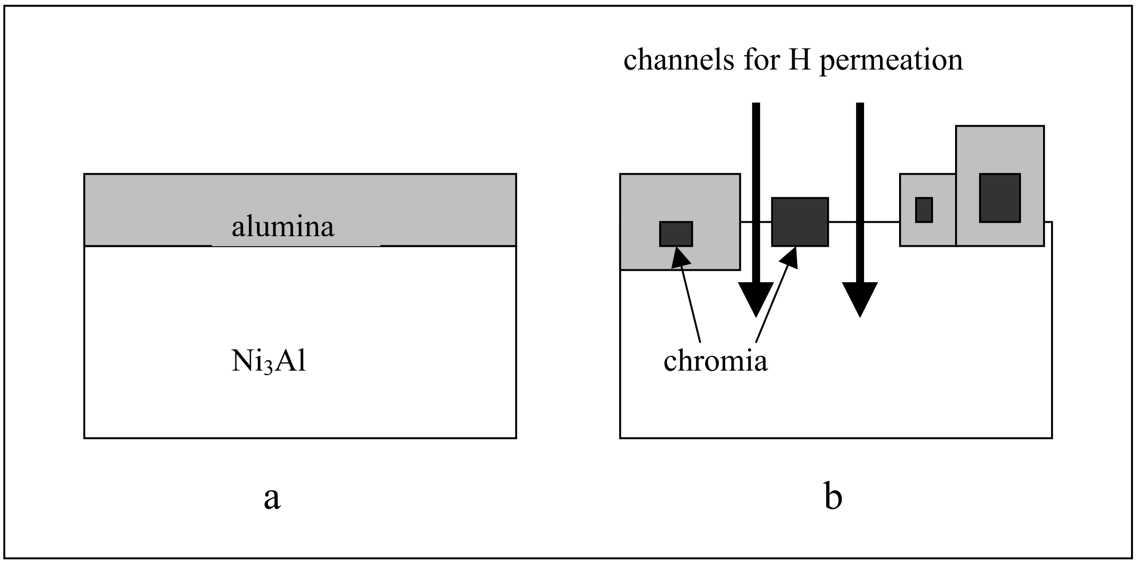

Fig.5 Structure of outer scales on Ni_3Al (a) and on Ni_3Al-Cr

It is also interesting to note that in this case, J's show certain decreasing dependence on increasing Cr concentration: Comparing values of J measured for similar values d in alloy with 4 and in alloy with 8 at. % Cr (J for d = 160 µm in Fig.3 and J for d = 170 µm in Fig.4), it can be concluded that increasing content of Cr decreases the hydrogen permeation flux J. This may be due to trapping hydrogen by Cr atoms [11]. This idea can be also supported by a more expressive dependence of J on d observed in alloy with 8 at. % Cr compared to that in alloy with 4 at. % Cr.

CONCLUSION

Permeation of hydrogen was used to an assessment of the protective function of surface layer covering Ni_3Al and in Ni_3Al-Cr in oxidation/reduction environment at high temperatures. It was observed that chromium that is frequently introduced before all to improve the oxidation resistance of the materials, might – surprisingly – cause an undesired degradation of protective surface layer on Ni_3Al-based materials in reduction environments.

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