

ORIGINATION OF TITANIUM NITRIDE IN A LOW-CARBON STEEL

Dobrovský L., Dobrovská J.

*Faculty of Metallurgy and Material Engineering, Technical University (VŠB-TU),
av. 17.listopadu 15, 708 33 Ostrava 8, Czech Republic*

TVORBA NITRIDU TITANU V NÍZKOUHLÍKOVÉ OCELI

Dobrovský L., Dobrovská J.

*Fakulta metalurgie a materiálového inženýrství, Vysoká škola báňská-Technická Univerzita Ostrava,
tř.17.listopadu 15, 708 33 Ostrava 8, Česká republika*

Abstrakt

V předložené práci jsou sledovány podmínky vzniku nitridu titanu a jeho vliv na vznik trhlin v nízkouhlíkových ocelích obsahujících titan. Různé typy oxidů titanu a nitrid titanu vznikají po dezoxidaci železa titanem v závislosti na stupni chemického přesycení taveniny, který je nutný pro tvorbu těchto vměstků. Pro homogenní nukleaci oxidu titaničitého byl určen stupeň chemického přesycení $\alpha_{\text{TiO}_2} = 10^2$, pro nitrid titanu $\alpha_{\text{TiN}} = 10^8$. Vysoký stupeň chemického přesycení pro homogenní nukleaci nitridu titanu se v tavenině železa nedosahuje, proto nitrid titanu nukleuje heterogenně na oxidech při stupni chemického přesycení přibližně 10^2 . Vznik trhlin je v práci vysvětlován na základě oxidace nitridu (příp. karbonitridu) titanu, která je spojena s transformací vměstků $\text{TiN} \rightarrow \text{TiO}$ a zvětšením jeho molového objemu přibližně o 10%, čímž vzniká pnutí v kovové matici.

Abstract

In this work an investigation into conditions of origination of the titanium nitride and its effect on initiation of cracks in low-carbon steels with titanium is presented. Various sorts of titanium oxides and titanium nitride are originating after deoxidation of iron by titanium in relation with the degree of chemical oversaturation of the melt, whereby the oversaturation is necessary for origination of such inclusions. For a homogeneous nucleation of titanium dioxide there has been determined the degree of chemical oversaturation of $\alpha_{\text{TiO}_2} = 10^2$, while for the titanium nitride of $\alpha_{\text{TiN}} = 10^8$. The high degree of chemical oversaturation for the homogeneous nucleation of titanium nitride is not attained in an iron melt and thus, the titanium nitride is nucleating in a heterogeneous way at the oxides with a degree of chemical oversaturation of approx. 10^2 .

The origination of cracks is dealt here with on the basis of oxidation of titanium nitride (and/or carbonitride) that is associated with a transformation of the inclusions of $\text{TiN} \rightarrow \text{TiO}$ and with enlargement its molar volume by approx. 10 % and thus, stress is originating in the metallic matrix.

Introduction

The stainless steels with titanium find a wide application in various industrial branches. Titanium plays in such steels the role of a stabilizer. It hinders the origination of intercrystalline corrosion due to a higher affinity for carbon than chromium and it forms more stable carbides. In addition titanium has a high affinity for oxygen and nitrogen and so oxides and nitrides are originating in liquid steel. In stainless steels with titanium the oxides and nitrides form the dominant non-metallic phase. Their concentration may reach to 90 % of all non-metallic inclusions. The inclusions affect considerably the steel quality and are frequently the reason for reduced mechanical properties.

The steels stabilized with titanium are known to be strongly liable to initiation of cracks after welding. The occurrence of cracks and fissures is investigated in the heat-affected zone that tightly adheres to the melting zone of the weld joint and its formation is associated with presence of titanium nitride.

Experimental

Investigation into conditions of origination of various sorts of inclusions has been carried out by the method of counter-current diffusion of the reagents going out from the principle of reaction diffusion [1 - 3]. This method allows to get in the sample all sorts of inclusions originating with various concentration of titanium. The content of titanium in samples has changed from tens weight-percents down to zero content, which is in conformity with the actual conditions encountering at dissolution of ferrotitanium in liquid steel.

The tests were run with material having the following composition: C-0.009 wt-%, S-0.002 wt-%, Si and Al less than 0.01 wt-% and after melting down in a Tamman furnace was blasted by nitrogen at a temperature of 1600°C. Samples of 4 mm in dia. and 25 to 30 mm long were taken-off from the liquid steel. The samples were put into corundum crucibles of 5 mm in dia. and melted down under argon atmosphere. At a temperature of 1600°C titanium was added to the bath surface. Then, isothermal dwell period of 2 to 20 minutes followed in order to induce origination of a concentration gradient of titanium down the height of sample. After such dwell period the sample was furnace cooled (100°C/minute). Thin sections were prepared at the samples. The inclusions were analyzed metallographically and by a microprobe that determined also the distribution in concentration of titanium down the height of the sample, see Fig.1. In view of the starting concentration of oxygen and nitrogen before the deoxidation the experiments carried out here can be split into two series (Table 1).

Fig.1 Macrostructure and concentration distribution of titanium in sample 2.series

Etched with Nital. Magn. 4x

Table 1 The initial concentration of oxygen and nitrogen in samples before the deoxidation

The metallographic examination of the individual samples showed various sorts of non-metallic inclusions of titanium. In the first series in which the initial nitrogen content was less than 0.006 wt-%, the oxidic inclusions were found only. No titanium nitride was found in this series of samples. Origination of titanium nitride was experimentally confirmed in samples of the second series in which the concentration of oxygen and nitrogen was approximately the same. Here, both the oxidic inclusions and the nitridic inclusions of titanium were determined.

In the upper part of samples the TiO and TiO₂ oxides occurred only, see Fig.2a. At a distance of about 3 mm the titanium nitride encountered, see Fig.2b.

Fig.2a The inclusions of TiO and TiO₂

Fig.2b The inclusions of titanium nitride

These inclusions were some 2 to 10 μm in sizes, with sharply bounded shape and with a characteristic envelope in dark field. Precipitation of such inclusions took place in a heterogeneous way on the existing oxidic phases having nucleated from the solution at first. In the down part of samples the oxides of mFe.nTiO_2 - type spherical in shape were found. The macrostructure of sample (Fig.1) has shown cracks (Fig.3a, 3b).

Analysis of results

On the basis of experimental examinations the thermodynamic and kinetic analysis of the condition of origination of titanium nitride has been carried out for the concentrations of titanium and nitrogen in question.

The thermodynamic calculation of the ΔG_{1873} reaction of origination of titanium nitride have been carried out with the ΔG^0_{1873} - values and with the interaction coefficients of the Refs. [4 to 10]. The obtained results of calculation are shown in Fig.4. From the results of the thermodynamic calculation is obvious that the titanium nitride may originate in the second series only.

The experimental examination showed the inclusions of titanium nitride to nucleate in a heterogeneous way at the titanium oxides. This knowledge was compared with the kinetic analysis of origination of titanium nitride.

The degree of chemical oversaturation for a homogeneous nucleation of TiN can be expressed as follows [11]

$$(1)$$

where

$\alpha = K_s/K$ - degree of chemical oversaturation,

K_s and K - the actual and/or equilibrium activity of titanium and nitrogen in the melt

V - the molar volume of titanium nitride

σ_{v-k} - the interphase tension at the interface of nitride-metal

k - the Boltzmann constant

H - the frequency factor.

As there are lacking in the literature data on the interphase tension at the interface of nitride-metal, this value was calculated. The calculated interface tension at the interface of titanium nitride-metal makes 4020 mJ.m^{-2} . The calculated degree of chemical oversaturation, as per Eq(1) for homogeneous nucleation of titanium nitride, attains 2.10^8 . Such a high chemical oversaturation cannot be achieved in liquid iron even with concentration of dissolved nitrogen of 0.04 wt-% [12].

It is known that for a heterogeneous nucleation a lower activation energy (lower degree of chemical oversaturation) is necessary than that for a homogenous nucleation. As the change in free enthalpy at origination of a nucleus varies proportionally with the interphase tension, in the case of nucleation of titanium nitride at an oxidic particle the ΔG_{het} is about four times smaller than the ΔG_{hom} [12].

Then, it can be written

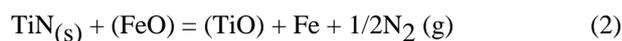
and thus, , and accordingly, the heterogeneous nucleation of titanium nitride takes place with substantially lower values of chemical oversaturation.

The calculated α_{het} is in conformity with the chemical oversaturation as calculated experimentally ($10^2 - 10^3$). The course of the heterogeneous nucleation of titanium nitride is confirmed in Figs.2b and 5, where the nitride has nucleated at the complex inclusions of iron oxide and titanium with a high content of FeO.

Fig.5 TiN precipitated in a heterogeneous way (light envelope) at a complex globular oxide of $m\text{TiO}_2 \cdot n\text{FeO}$

Figure 1 illustrates a zone (from 6 to 12 mm) in the sample in which the cracks are concentrated in longitudinal and in transversal direction. The metallographic examination showed the presence of both titanium and complex oxides with a high content of FeO in that part of sample. Above that zone the titanium nitride was found, however, no oxides with a higher content of FeO were found and even no cracks encountered in that part of sample. Thus, it is evidenced that the presence of titanium nitride and FeO is the condition for initiation of cracks in the steels stabilized by titanium.

Titanium nitride has a high affinity for oxygen and also for FeO. In Ref. [13] there was evidenced the possible oxidation of TiN by means of the iron oxides according to the following reaction



(J/mol)

(the originating titanium monoxide will be further oxidized to Ti_2O_3).

As the parameters of the cubic lattices of FeO, TiN and TiO are negligibly different, very low degree of chemical oversaturation is necessary for origination of a new TiO-phase. The transformation of the inclusions of TiN \rightarrow TiO is associated with enlargement of the molar volume by approx. 10 %, which produces origination of stress in the metallic matrix and initiation of cracks. A crack can be readily initiated at the interphase boundary of inclusion vs. metallic matrix, i.e. in the zone with concentration of tension (Fig.3a, b).

It is obvious from the above mentioned that initiation of cracks in steels with titanium is conditioned by the presence of titanium nitride (carbonnitride), of iron oxides and sufficient temperature for the reaction (2) (1075 K at least). All the three conditions of welding steel with titanium are fulfilled and thus, cracks may originate.

Conclusion

Various sorts of titanium oxides and titanium nitride are originating after deoxidation of iron by titanium in relation with the degree of chemical oversaturation of the melt, whereby the oversaturation is necessary for origination of such inclusions. For a homogeneous nucleation of titanium dioxide there has been determined the degree of chemical oversaturation of $\alpha_{\text{TiO}_2} = 10^2$, while for the titanium nitride of $\alpha_{\text{TiN}} = 10^8$. The high degree of chemical oversaturation for the homogeneous nucleation of titanium nitride is not attained in an iron melt and thus, the titanium nitride is nucleating in a heterogeneous way at the oxides with a degree of chemical oversaturation of approx. 10^2 .

The origination of cracks is dealt here with on the basis of oxidation of titanium nitride (and/or carbonnitride) that is associated with a transformation of the inclusions of TiN \rightarrow TiO and with enlargement its molar volume by approx. 10 % and thus, stress is originating in the metallic matrix.

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