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STEEL CLAD PLATES HYDROGEN DEGRADATION EVALUATION USING ULTRASONIC DEFECTOSCOPY METHOD

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S u m m a r y

This paper presents results of hydrogen degradation tests of steel clad plates by the ultrasonic defectoscopy. The subject of the tests were samples of low-alloy steel 12CrMo4-5 coated with austenitic steel X2CrNi19-11 using explosive cladding method. The samples were subjected to a thermocycling process within the temperature range from 25 to 450°C in the gaseous hydrogen atmosphere. Detailed microstructural and microanalytical tests of the areas indicated by the ultrasonic defectosopy were carried out to verify the results of the ultrasonic tests. The structural observations were carried out by light microscopy, scanning electron microscopy (SEM). X-ray microanalysis of chemical composition (EDS) was also performed. The results show that with properly selected measurement settings, the ultrasonic defectoscopy allows to detect early stages of hydrogen degradation in clad plates.

Keywords: hydrogen degradation, ultrasonic tests, clad sheet metal

Ocena degradacji wodorowej platerowanych blach stalowych metodą defektoskopii ultradźwiękowej

S t r e s z c z e n i e

W pracy przedstawiono wyniki badań degradacji wodorowej blach platerowanych metodami defektoskopii ultradźwiękowej. Przedmiotem badań jest blacha ze stali niskostopowej 13CrMo4-5 platerowana metodą wybuchową austenityczną stalą X2CrNi19-11. Wykonano cykliczną obróbkę cieplną w zakresie temperatury od 25 do 450°C w atmosferze wodoru. Weryfikację wyników badań ultradźwiękowych dokonano przez obserwację mikrostruktury stali w obszarach wytypowanych za pomocą badań ultradźwiękowych. Stosowano metody mikroskopii świetlnej, elektronowej mikroskopii skaningowej oraz mikroanalizę rentgenowską (EDS). Stwierdzono, że dobór parametrów pomiarowych metodą defektoskopii ultradźwiękowej umożliwia wykrywanie wczesnych etapów degradacji wodorowej mikrostruktury stali blach platerowanych.

Słowa kluczowe: degradacja wodorowa, badania ultradźwiękowe, blachy platerowane

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1. Introduction

Clad steels consist of a thin layer (ca. 3÷4 mm) of corrosion-resistant steel permanently joined with a base material (15÷25 mm) of non-alloy or low-alloy steel. They are widely used in petrochemical, automotive, and shipbuilding industries. Considering the savings related to the use of the lower content of alloy steel, they belong to the economic corrosion-resistant structural materials.

The clad steel corrosion resistance is ensured by separation of the aggressive, corrosive environment, by means of a cladding layer. The cladding protects the load bearing layer from corrosive environments. However, when in contact with gaseous hydrogen, or in a corrosive environment containing a source of hydrogen, the clad plates may suffer from material degradation caused by hydrogen intake. In the case of low-alloy steels with an austenitic steel cladding, the hydrogen degradation manifests with sub-cladding cracking, in a form of delaminations that decrease adhesion of the cladding to the base material [1]. The complex mechanism of that process is subject of extensive research driven by practical significance. In this context, the aim of this work was elaboration of detection method of sub-cladding defects, which are the result of hydrogen degradation.

2. Methodology of tests

2.1. Tested material

The tested samples were 160 x 25 x 10 mm plates, made of 13CrMo4-5 steel with X2CrNi 19-11 austenitic steel cladding. The cladding thickness was ca. 3 mm. The composition of both materials is given in Table 1. Samples of the supplied materials were subjected to ultrasonic defectoscopy tests to determine areas for microscopic observations.

Table 1. Chemical composition of the substrate and clad steel

Materials		**Chemical composition**									
		C	**Si**	**Mn**	**S**	**P**	**Cr**	**Ni**	**Mo**	**N**	**Cu**
Substrate	**13CrMo4-5**	0.1	0.35	0.6	0.01	0.02	1	–	0.40	0.018	0,30
Cladding	**X2CrNi 19-11**	0.03	0.70	1.0	0.02	0.03	19.5	11.0	–	0.10	–

The samples were ultrasonically tested before and after a thermocycling process involving 30 and 100 thermocycles. A single cycle included the following operations:

• heating to 450°C for 30 minutes in a gaseous hydrogen atmosphere, at the hydrogen pressure of 0.15-0.30 MPa,

• fast cooling to room temperature.

During the process, the heat was carried away from the ends of the sample clamped in the grips.

The thermocycling process used here was meant to simulate conditions of sudden stop and start of industrial installations.

2.2. Ultrasonic examinations

The ultrasonic tests were carried out using the Panametrics Epoch 4 defectoscope. The tests employed the echo contact method, using a straight-beam head [2], according to ASTM A 578 [3]. The standard suggests measurement frequency within the range of 2-5 MHz. Instead, a higher measurement frequency head of 20 MHz was used in order to increase the sensitivity of the test and to pinpoint small discontinuities [2]. The entire surface of the samples was scanned for discontinuities that may occur at the clad-substrate interface.

2.3. Microscopy examinations

Defects revealed by ultrasonic tests were examined by metallographic microscope and a scanning electron microscope (SEM) equipped with unit for chemical composition analysis (EDS). The tests were carried out on sample cross-sections, prepared using standard metallographic procedure.

3. Results

3.1. Ultrasonic examinations

The tests were performed using a head with a 3 mm transducer. The small dimensions and high measuring frequency (20 MHz) allow to detect very small material discontinuities and subtle changes in the material structure.

Some areas were identified in the samples where increased amplitude of the signal received from the clad-substrate interface was detected (Fig. 1). The amplitude rises along with the number of thermocycles. This indicates a progressive material degradation in the interface zone. Such degradation is related to both the difference of hydrogen diffusion and solubility in the joined materials and to hydrogen trapping [4, 5]. The hydrogen induced micro-cracks may eventually lead to delamination of the cladding.

It should be noted that the material, despite the occurring discontinuities, meets the requirements of the ASTM A 578 standard, because none of the peaks obtained from the clad-substrate interface exceeds 50% of the value of the peak from the sample bottom.

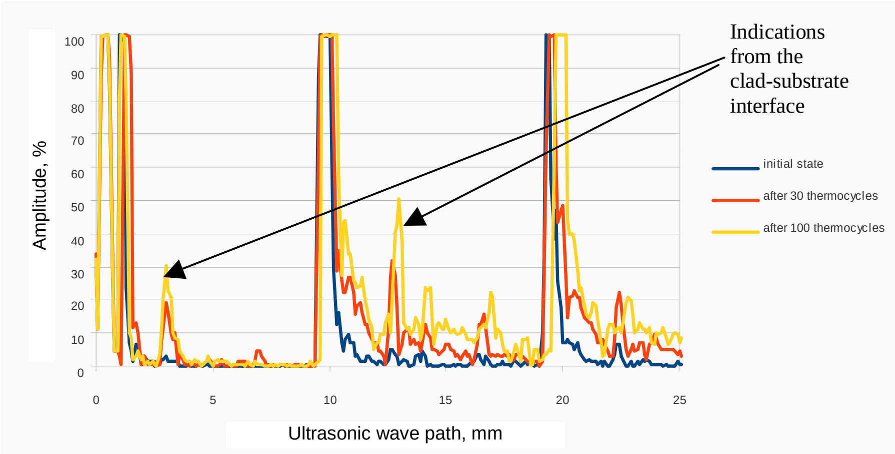

Fig. 1. Ultrasonic wave spectrum before and after thermocycling

3.2. Microscopy examinations

Microscopy examination was carried out in the areas showing increased amplitude of ultrasonic signal. The microscopic observations revealed a developed (wavy) character of the joint (Fig. 2a, 3a), and presence of transition zones as heavier etched areas (Fig. 2b, 3b). These structures are typical for joints made by an explosive method. The near interface zone was found to show porosity and non-metallic inclusions. Also linear discontinuities were revealed by the scanning electron microscopy (Fig. 4).

a) b)

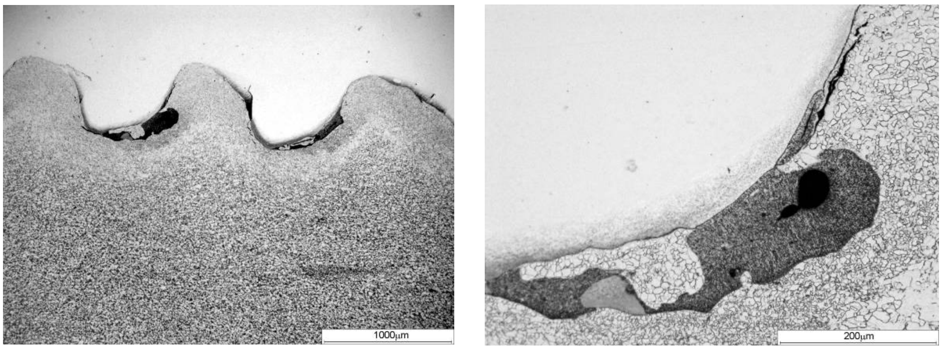

Fig. 2. Microstructure of clad-substrate interface after 30 thermocycles: a) magn. 100x, b) magn. 500x

The SEM examination revealed that the discontinuities observed in the base-cladding joint are of a micro-crack type (Fig. 4a, b). Non-metallic inclusions were found close to those micro-cracks. Their chemical composition, determined using the EDS method, revealed that they are rich in silicon (Fig. 5), which indicates the presence of sand particles at the joint zone. These sand particles are most likely trapped between the metal sheets during the explosive joining process. The results obtained here show that such type inclusions may be the cause of micro-crack initiation by hydrogen.

a) b)

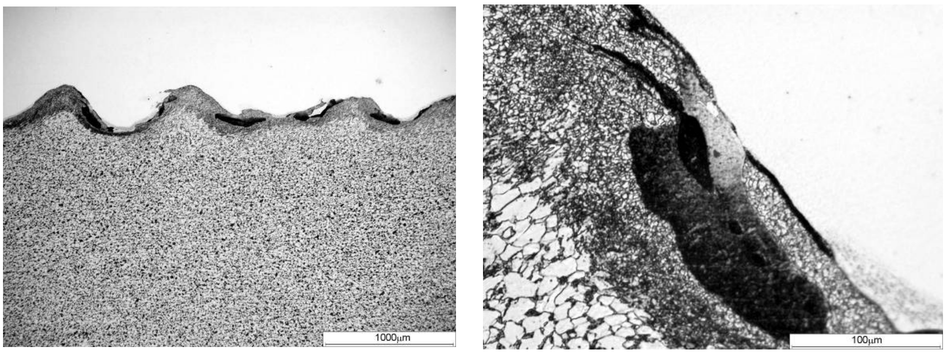

Fig. 3. Microstructure of clad-substrate interface after 100 thermocycles: a) magn. 100x, b) magn. 1000x

a) b)

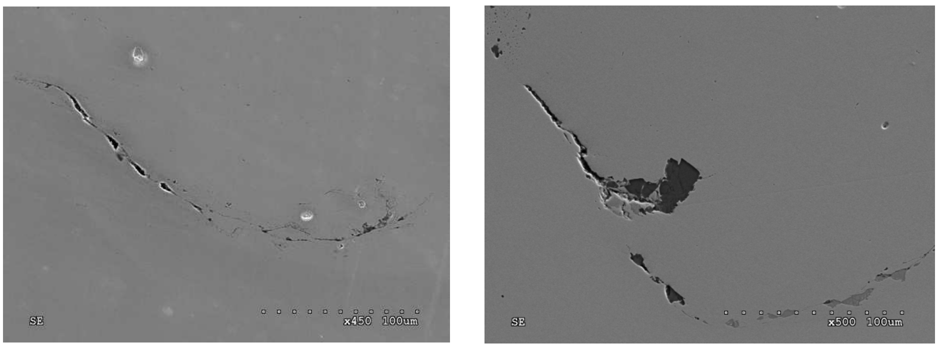

Fig. 4. SEM images made in the spots of increased ultrasonic signal amplitude: a) sample after 30 thermocycles, b) sample after 100 thermocycles

The line-based analyses of chemical composition (Fig. 6), carried out in a direction perpendicular to the micro-cracks, show that it runs along the base-cladding joint. Also, the presence of a transition zone between the base and the cladding materials can be observed. The diagram shows an increasing content of Cr and decreasing of Fe.

a) b)

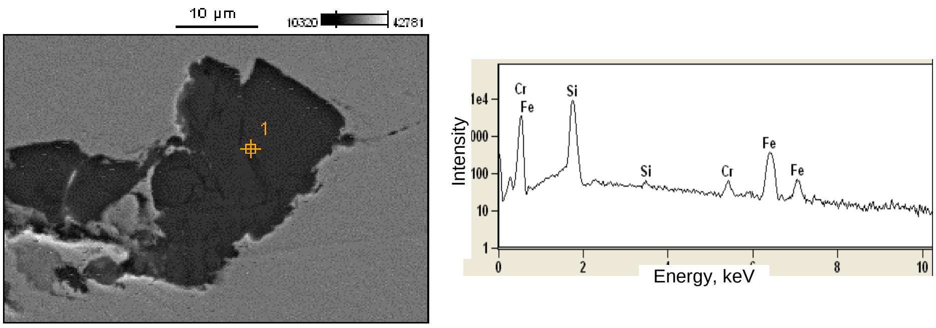

Fig. 5. Non-metallic inclusion promoting microcrack nucleation (a) and its EDS analysis (b)

a) b)

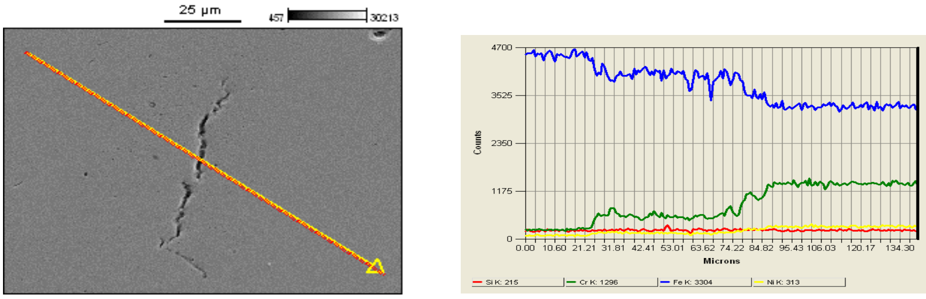

Fig. 6. STEM image (a) and EDS line scan conducted in the perpendicular direction through the microcrack (b)

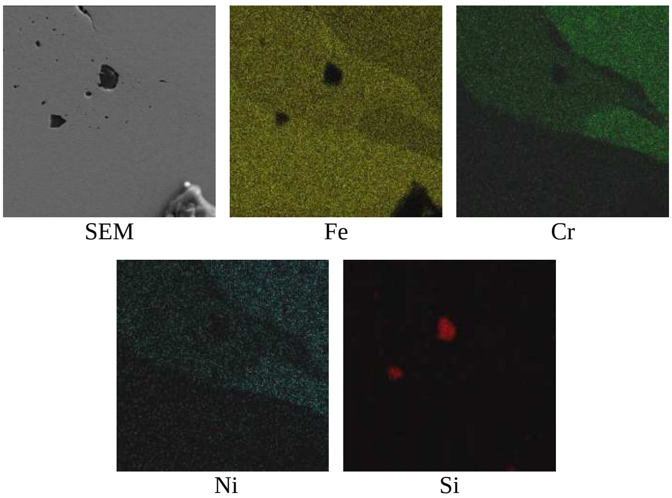

Fig. 7. The surface distribution of the alloying elements in transition zone in the joint area

The presence of a transition zone in the joint area is more visible in the element mapping made by the EDS method (Fig. 7). The changes of colour saturation indicate changes of content of an element. Silicon (Si) rich inclusions are clearly visible within the transition zone, which confirms that their origin (sand particles).

4. Conclusions

The ultrasonic defectoscopy tests performed and microscopy/microanalyses tests revealed the presence of micro-cracks, pores, and non-metallic inclusions rich in silicon, within the area of joint of the 13CrMo4-5 steel sheet (base) and the 304L austenitic steel (cladding), in the samples subjected to hydrogen oversaturation (thermocycling).

The tests prove that the purity of the joint produced using the explosive method may have a significant impact on the behaviour of clad sheets exposed to contact with gaseous hydrogen.

The results obtained indicate that with properly selected measurement settings the ultrasonic defectoscopy can be used to detect early stages of hydrogen degradation and allows an assessment of the degree of hydrogen degradation of the sheets with austenitic steel cladding.

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