 https://doi.org/10.3311/PPme.23385

Periodica Polytechnica Mechanical Engineering, 68(1), pp. 38–43, 2024

Investigation of Spinodal Decomposition in Isothermally Heat Treated LDX 2101 type Duplex Stainless Steel at 475 °C

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Received: 07 September 2023, Accepted: 08 November 2023, Published online: 19 January 2024

Abstract

Spinodal decomposition of the ferritic phase, a thermally induced phase transformation process is studied in an LDX 2101 type lean-duplex stainless steel by different examination methods. This phase transformation in duplex stainless steels has special importance because it is responsible for the so called "475 °C embrittlement". This deterioration process causes a decrease in toughness and corrosion resistance. Fe-Cr alloys, thus several stainless steels, are susceptible to the spinodal decomposition at intermediate and low temperatures (<600 °C). Therefore, it is important to study this phenomenon in novel lean-duplex stainless steels as well. Our results revealed that spinodal decomposition occurs to a lesser extent in the studied type of lean-duplex stainless steel but its effect is not negligible in applications.

Keywords

lean duplex stainless steel, differential thermal calorimetry, X-ray diffraction, spinodal decomposition, magnetic measurements, thermoelectric power

1 Introduction

Duplex stainless steels (DSS) constitute a significant group of stainless steels with very attractive mechanical properties and corrosion resistance. These advantageous attributes are caused by a duplex microstructure which contains austenitic and ferritic phases in almost equal volumetric amount (50–50%). As a result of these special microstructure the duplex stainless steels have improved corrosion resistance, enhanced toughness, ductility, and weldability. The above mentioned nearly equal fraction of austenitic and ferritic phases is controlled by the appropriate addition of different alloying elements (e.g., Cr, Ni, Mo, N), while the carbon content is very low (<0.03%) [1].

The LDSSs are a novel subgroup of DSSs for cost-effective applications to replace higher grade standard and even super duplex stainless steels. They are considered lean because they contain lower amounts of the expensive alloying elements Ni and Mo, and higher Mn and N than higher grade duplex stainless steels. Their corrosion resistance is closer to the standard austenitic grades; however, their mechanical properties are excellent. Due to its good mechanical properties and excellent corrosion resistance, LDX 2101 type lean-duplex stainless steel (LDSS) is a material often used in engineering structures. It is often used in pipelines, heat exchangers, pressure vessels and chemical reactors in the petrochemical and pharmaceutical industries [2].

Spinodal decomposition is a mechanism that causes the spontaneous separation of a single phase into two phases without nucleation. The phenomenon is important in Fe-Cr systems, because all types of stainless steels contain a high amount of Cr [3, 4].

Due to the high quantity of alloying elements, undesirable secondary phases (e.g., α'/alpha prime, σ/sigma, χ/chi phases) can develop in machine components made from DSS exposed to higher temperatures (300–1000 °C). In this article, we deal with the α'-phase of them. This phase is formed when the ferritic phase undergoes a spinodal decomposition into a Fe-rich α- and a Cr-rich α'-phase. This process takes place between 300 and 600 °C and causes the so-called "475 °C embrittlement" effect.

Cite this article as: Berecz, T., Mészáros, I., Jenei, P. "Investigation of Spinodal Decomposition in Isothermally Heat Treated LDX 2101 type Duplex Stainless Steel at 475 °C", Periodica Polytechnica Mechanical Engineering, 68(1), pp. 38–43, 2024. https://doi.org/10.3311/PPme.23385

The presence of the α'-phase can result in the premature failure of DSS components in two different ways. On one hand, it is a harder phase which has a detrimental effect on ductility and toughness of DSS. It can drop the impact energy of corrosion-resistant steel from the original value of 140–150 J to less than 10 J [5]. On the other hand, α'-phase is rich in Cr, therefore its presence decreases the concentration of this element in the adjacent grains causing a reduction in the corrosion resistance [6–12].

In the case of Fe-Cr alloys, the spinodal curve in the phase diagram involves a concentration range of approximately between 20–30 and 78–82% [13, 14]. Therefore, an alloy with a Cr concentration between 20–30% can be sensitive to the degradation process due to spinodal decomposition. However, it is also known that nickel alloying reduces the tendency of the decomposition process [15]. The LDX 2101 type LDSS contains nearly 21% Cr and 1% Ni, which can be considered a borderline case based on the former.

The tests presented in this article were conducted to clarify to what extent the LDX 2101 type LDSS is prone to spinodal decomposition. The results of the test are important for all technical applications where LDX 2101 type LDSS is used at elevated temperatures.

In this paper we applied different examination methods to study the formation of α'-phase through spinodal decomposition and its effects on microstructure. These methods were magnetic, thermoelectric power (TEP), micro-hardness and X-ray diffraction (XRD) measurements.

Although many papers discuss the possible phase transformations in the newly developed DSSs by applying different kind of pre-treatments and testing methods, they mainly study the phase transformations at higher (700–1000 °C) temperatures. Only few studies can be found in which especially the spinodal decomposition is studied [10, 15].

The purpose of this paper is to facilitate a better understanding of the spinodal decomposition process in LDSSs. The results obtained can help to avoid failure occurrences in DSS engineering structures and they can be useful in creating methods for failure prediction.

2 Materials and methods

The experimental material was a commercially available LDX 2101 type LDSS (other standards: UNS S32101, EN Number 1.4162 [16]). The nominal composition of this steel is given in Table 1 [17]. The samples were isothermally heat treated at 475 °C for the ageing times of: 2, 4, 6, 48, 672 and 1008 hours to study the spinodal decomposition both in its earlier and later stages. The effect of this phenomenon was studied by differential scanning calorimetry (DSC), X-ray diffraction (XRD), TEP measurement (thermoelectric power), hardness testing, as well as AC and DC magnetic measurements.

Table 1 Chemical composition of the sample material (LDX 2101 type LDSS)

Element	Nominal (%)
Fe	71.45
Cr	21.5
Ni	1.5
Mo	0.3
Si	0.25
Mn	5
Cu	0.3
C	0.03
N	0.22

DSC is a thermoanalytical technique in which the difference in the amount of heat required to increase the temperature of a sample and the reference is measured as a function of temperature. Both the sample and the reference are maintained at nearly the same temperature throughout the experiment. DSC seems to be suitable to reveal phase transformations at different temperatures.

DSC examinations were performed by a Perkin-Elmer DSC2 (USA) type device to determine phase transformations in the untreated sample. Samples were heated from 100 °C to ~1100 °C with different heating rates (5, 10 and 20 °C/min) in argon atmosphere.

XRD measurements were performed on a SmartLab diffractometer (manufacturer: Rigaku, Japan) in the Bragg-Brentano geometry with a 1D D/Tex detector using Cu$K\alpha$ radiation. Diffractograms were evaluated with the PDXL2 program using ICDD-2018 database. For X-ray measurement the samples were grinded (P1200, P2000 and P4000), than electropolished using LectroPol-5 (Struers) with 20 V for 30 sec.

Hardness test is one of the most frequently applied methods for the approximate characterization of the mechanical strength of metals or alloys. Changes of the microstructure that are not related to the varying chemical composition (e.g., phase transformations) can usually be detected by hardness testing, because they usually affect mechanical strength. For these investigations a Vickers indentation micro-hardness tester was used (Buehler IndentaMet 1105, manufacturer: Buehler Ltd., USA). The tests were carried out on the polished surfaces of the samples with an applied load of 4.905 N (500 gF).

TEP or Seebeck coefficient of a material is a measure of the magnitude of an induced thermoelectric voltage in response to a temperature difference across that material. TEP measurement (due to its high sensitivity) is a very useful method to detect microstructural changes of alloys. This is because TEP depends on a material's temperature, crystal structure, its impurities and defects [18, 19]. TEP measurements were carried out by a Trivolt PK120 type TEP instrument on 100 × 4 × 4 mm samples, on their endpoints 15 and 25 °C temperatures.

Ferrite content of the samples was measured by a Fischer FMP30 type Feritscope. The magnetic coercivity was determined by a 1.106 type Förster coercimeter (Reutlingen, Germany) and an AC magnetometer-setup built in our department. Feritscopes are useful, portable tools for fast and non-destructive determination of ferrite content of ferrous alloys. It was calibrated with an etalon series before measurement.

The block scheme of our AC magnetometer can be seen in Fig. 1. This method is suitable to measure the hysteresis and normal magnetization curves of the specimen from which among others the maximal polarization, remnant induction, coercive field and initial permeability can be determined.

The yoke contains two symmetrical U-shaped laminated Fe-Si cores which closes the magnetic circuit. A digital function generator and a power amplifier produce sinusoidal excitation current at a frequency of 5 Hz. The driving coil and the pick-up coil are around the middle part of the sample. A 16-bit input-output data acquisition card accomplishes the measurements. The maximum excitation field strength was 12800 A/m. In this investigation 200 minor hysteresis loops were measured in case of each specimen. The normal magnetization curves which are determined from the peak points of the minor hysteresis loops gave the maximal polarization.

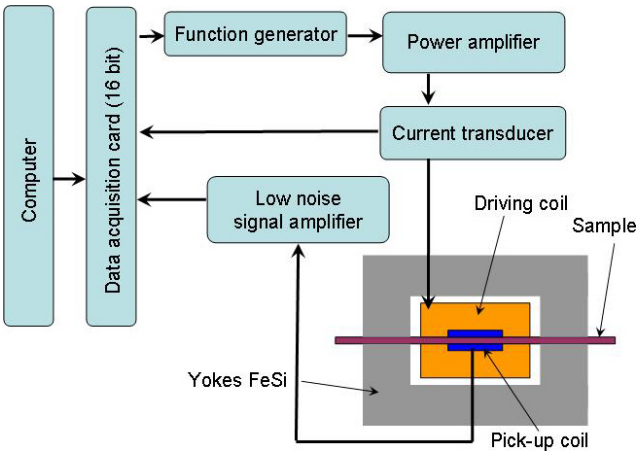

Fig. 1 Block scheme of the AC magnetometer

3 Results

3.1 DSC measurements

Results of DSC measurements on the untreated sample are shown in Fig. 2. Only one local minimum can be seen at the temperature ~540 °C which is assumed to indicate the spinodal decomposition of the ferritic phase. In order to identify this phase transformation, the above mentioned studies were performed. Formation of σ-phase between 800–900 °C due to the eutectoid decomposition of the ferritic phase into austenite and σ-phase ($\alpha \rightarrow \gamma + \sigma$) was not revealed.

3.2 Magnetic measurements

Results of magnetic measurements can be seen in Fig. 3. They show that ferrite content decreases due to ageing. This is presumably due to the formation of Cr-rich regions that are paramagnetic at room temperature [3, 10, 15]. On the other hand the coercivity of the ferrite increases during the ageing process which is a clear indication of the spinodal decomposition process.

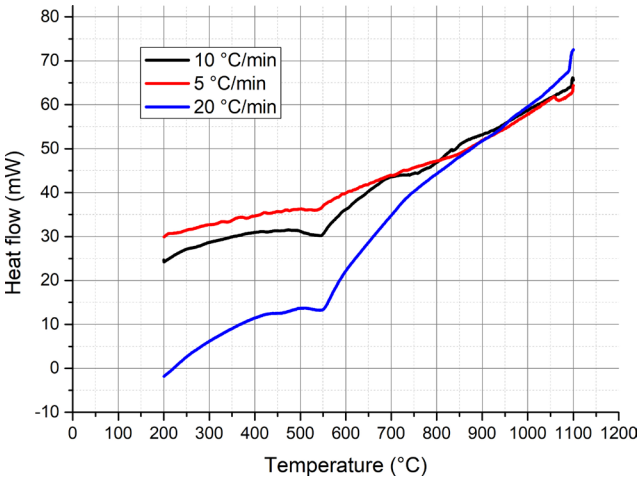

Fig. 2 DSC curves at different heating rates

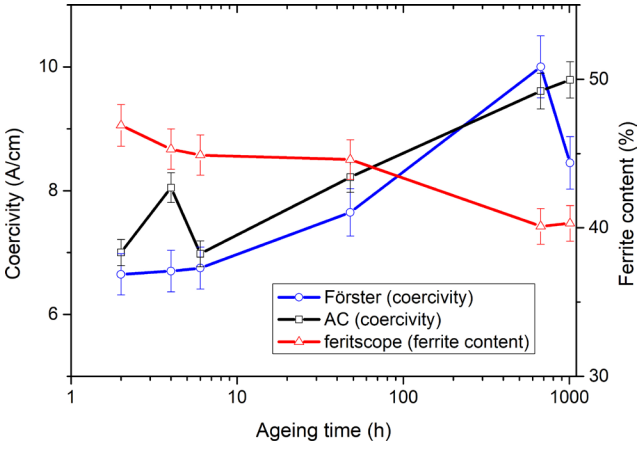

Fig. 3 Results of magnetic measurements. For the untreated sample, coercivity values measured by Förster coercimeter and AC magnetometer are: 6.6 A/cm and 7.59 A/cm; the ratio of ferrite content is 49.2%

As it was discussed previously the spinodal decomposition of ferrite produces Fe-rich α and Cr-rich α' grains in the size range of 10–50 nm. The α' ferrite grains behave as pinning sites for magnetic domain walls therefore the domain wall displacement becomes more difficult. It results the increase of the coercivity [20].

3.3 Hardness and TEP measurements

The results of the micro hardness and TEP tests can be seen on Fig. 4. Standard deviations of both hardness and TEP values are less than 2% of the values.

It shows that hardness of the heat-treated samples increased steadily due to the formation of α'-phase. This means 22% growth in hardness up to 1008 hours of ageing. Phenomenon of hardening due to spinodal decomposition in stainless steels can be explained on one hand by solution hardening, and by the fact that the hardness of pure Cr is much higher than that of pure Fe. [3] On the other hand, hardness can increase due to stress fields between Cr-rich α' and Fe-rich α zones that hinder the movement of dislocations [21]. However, with the increase of ageing time the growth of TEP is much greater than that of the hardness. It also refers to changes in microstructure.

3.4 XRD measurements

Fig. 5 shows the X-ray diffractograms for the as received and annealed samples. Diffraction peaks are symmetric, no satellite peaks were observed. According to the XRD measurements both samples consist of ferritic (PDF: 01-080-3816) and austenitic (PDF: 01-081-8775) phases.

Table 2 shows the intensity fraction and the lattice parameter of the two phases. The intensity fraction was determined as the ratio of the X-ray peaks area for the given phase and the area under the whole curve (after background subtraction) between 40–100°.

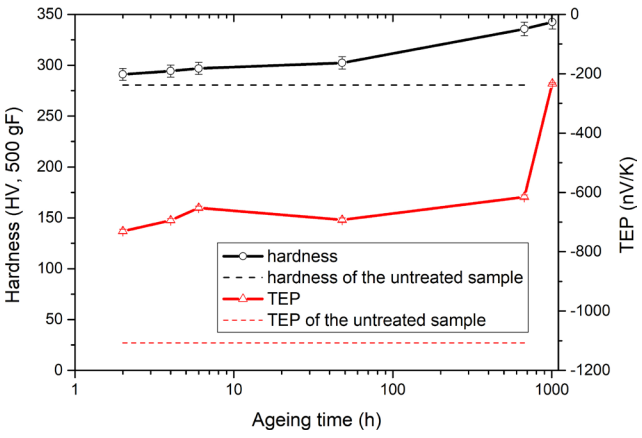

Fig. 4 Results of micro-hardness tests and TEP measurements

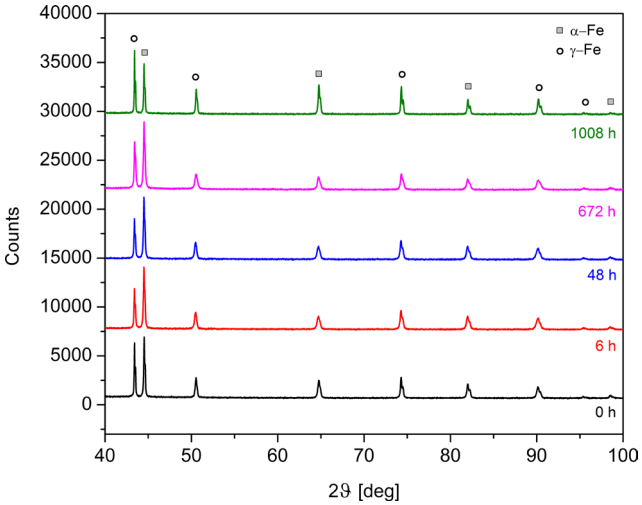

Fig. 5 X-ray patterns for the samples with different ageing time

The error of the intensity fraction was determined from the fitting error of the functions fitted to the peaks and the error of the lattice parameter was determined from the intercept error of the linear curve fitted to the Nelson-Riley plots.

A lattice parameter was evaluated from Nelson–Riley-plots. The data shown in Table 2 indicate that the phase fraction of the α-Fe and γ-Fe is not changing during the heat treatment, the lattice parameter is practically constant within the experimental error.

4 Discussion

As it was mentioned above, spinodal decomposition is carried out without nucleation. It means that in this kind of decomposition processes there are no sharp interfaces, but there are domains with different concentrations that are separated by diffuse interfaces [3, 4, 21].

It can be supposed that the formation of the α'-phase is mostly affected by the Cr diffusion within the ferritic phase forming Cr-rich and Cr-depleted zones through spinodal decomposition [22–24]. The increase in hardness can be explained by the presence of the Cr-rich zones, which have a higher hardness due to solution hardening.

These zones unfortunately cannot be revealed by XRD. Cr atoms in the lattice of Fe change the lattice parameter of ferrite according to Vegard's law. However, there is only a small difference between the lattice parameter of Cr and Fe: they are 0.29100 nm and 0.28665 nm, respectively [25]. Therefore, even though there is a Cr content difference of about 38 percentage point between the Cr-rich and Cr-depleted zones [25], the lattice parameters of these zones are so close to each other that they cannot be separated in the diffractogram. Therefore, XRD analysis was not able to detect the spinodal phase transformation in our investigation.

Table 2 Intensity fraction and the lattice constant of the α-Fe and γ-Fe phases

Ageing time [h]	0	6	48	672	1008
Intensity fraction of α-Fe	0.49 ± 0.02	0.48 ± 0.02	0.50 ± 0.02	0.48 ± 0.02	0.45 ± 0.02
Intensity fraction of γ-Fe	0.51 ± 0.02	0.52 ± 0.02	0.50 ± 0.02	0.52 ± 0.02	0.55 ± 0.02
Lattice parameter of α-Fe [nm]	0.28784 ± 0.00011	0.28769 ± 0.00006	0.28790 ± 0.00019	0.28792 ± 0.00017	0.28774 ± 0.00007
Lattice parameter of γ-Fe[nm]	0.36115 ± 0.00007	0.36098 ± 0.00002	0.36110 ± 0.00020	0.36100 ± 0.00030	0.36096 ± 0.00003

It was found that the proportion of the ferritic phase decreased, and at the same time the coercivity of the samples increased significantly. Both effects can be explained by the formation of the α'-phase as a result of the spinodal decomposition process. Since α'-phase contains about 67% Cr, it is not ferromagnetic [26]. On the other hand, the tiny, submicroscopic (10-50 nm) α'-phase grains act as anchoring sites for the magnetic domain walls, resulting in a significant increase in coercivity.

According to related studies ferrite decomposition is affected by lattice defects. Hättestrand et al found in SAF 2507 DSS that cold working has an influence on the de-composition of ferrite phase from nucleation and growth to spinodal decomposition, probably due to the increased dislocation density [27]. Hedström et al found that the presence of third elements (Ni, Cu) can shift the ferritic decomposition towards nucleation and growth. According to them, this can be explained by the presence of tiny precipitates that can promote nucleation and growth at grain boundaries as preferential nucleation sites [28].

5 Conclusions

In this study, we investigated the spinodal decomposition of the ferritic phase in LDX 2101 type LDSS with different examination methods, such as DSC, XRD, TEP, Vickers hardness test and magnetic measurements. This is particularly important because this alloy is close to the edge of the spinodal curve due to its 21% Cr content. That is, the LDX 2101 type LDSS appears to be a borderline case in which it is questionable whether there is a spinodal decomposition or not.

Our results are of practical importance, because it is known that the two-phase microstructure resulting from spinodal decomposition makes the alloy brittle and causes a significant deterioration of the corrosion properties. The performed tests proved that a spinodal decomposition process can occur in the LDX 2101 type LDSS, so it can be concluded that this alloy is sensitive to the deterioration processes associated with spinodal decomposition.

Among parameters of the aforementioned test methods, the coercivity and TEP, as structure-sensitive properties, as well as the content of ferromagnetic ferrite seem suitable for monitoring the spinodal decomposition process. Therefore, they can be characteristic indicators of test methods in the lifetime assessment that would be suitable for testing the progress of the process in structural elements made from DSS and exposed to heat in industrial conditions.

Acknowledgement

The authors express their thanks to Alajos Ö. Kovács technical assistant (Eötvös Loránd University, Department of Materials Physics) for DSC measurements and to Viktória Németh for English proofreading.

This research was supported by the János Bolyai Research Scholarship of the Hungarian Academy of Sciences, grant number: BO/00821/20/6.

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