Sample preparation vs quality of X-ray phase analysis results

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Abstract

In this study, taking as an example the creep-resistant austenitic cast steel, the results of the investigations were presented whose aim was to show what effect the specimen surface condition, discussed in terms of its roughness obtained by grinding, polishing with diamond paste, electrolytic polishing and etching, may have on the quality of results obtained by X-ray phase analysis. The preset goal has been achieved comparing the quantity and intensity of reflections on X-ray diffraction patterns obtained from the prepared specimens. The test material was cast steel containing (in wt.%): 0.29%C, 1.02%Mn, 4.36%Si, 0.007%S, 0.015%P, 17.8%Cr, 29.3%Ni, 1.59%Nb and 1.19%Ti, subjected to the process of annealing at a temperature of 850^oC for 100 hours. For identification of structural constituents by the technique of X-ray phase analysis, four solid specimens were prepared. Their surfaces were successively ground, polished, and subjected to electrolytic etching. The reference sample (isolate) was obtained by the method of electrolytic extraction. In solid material the following phases were identified: $Fe\gamma$, NbC and G; in the isolate additionally the presence of TiC, $M_{23}C_6$ and σ was reported. It has been proved that in the case of solid specimens partial identification of phase constituents may be carried out on surfaces subjected only to grinding with 600 grit abrasive paper without the need of any further preparation.

Keywords: Metallography; Creep-resistant austenitic cast steel; Additions of Nb and Ti; Phase identification.

1. Introduction

X-ray phase analysis is the tool commonly used in qualitative and quantitative analysis [1].

The samples for structure examinations are prepared from solid material in the form of flat specimens. However, the technique of their preparation should not cause distortions of the structural constituents, as these are, quite naturally, the prime object of examinations. Mechanical treatment of the specimen surface with abrasive paper of different grit size or with various sorts of diamond paste may introduce very serious changes to the existing state of stress, a consequence of which will be the change in the intensity of diffraction pattern lines. Non-uniform, and misadjusted to the sample hardness, force of clamping the specimen to the abrasive material creates a sub-surface layer of

plastic strain - known as Beilby layer. Electrolytic polishing does not as a rule cause such changes. To remove the distorted layer from the specimen surface, the specimen is etched with proper chemical reagent and next it is electrolytically polished. Through selection of the best current voltage and density, the time of polishing, and the temperature of electrolyte, it is possible to obtain the conditions under which the process of dissolving will provide a smooth and glossy surface. Polishing should not last for a time too long, because the specimen may pick up some hydrogen, which will change the parameters of crystal lattice in the examined material [1, 2]. The choice of proper technique of surface preparation in the examined material also improves the sensitivity and reliability of identification. All these operations raise the concentration of the phase identified in a mixture to a value such that obtaining of its diffraction pattern becomes finally

possible. To increase the concentration, the differences in physical and chemical properties of various phases are utilised. The operations usually consist in selective dissolving of phases carried out by chemical or electrochemical process [2].

In examinations of alloys, where solid samples composed of a matrix with relatively small amounts of other phases are used, selective etching of the matrix enables obtaining alien phases in concentrations and amounts suitable for X-ray phase identification. Unfortunately, the process of phase precipitation from the matrix is of a complex nature and as such requires the choice of best electrolyte and strict observance of the preset regime of electrolysis [1, 3].

Austenitic steel (cast steel) is a good example of complex alloys with different amount and size of precipitates [4÷7].

The aim of the present study was determination of an effect that preparation of the specimen surface may have on the quality of the results of a X-ray phase analysis carried out on the stabilised austenitic cast steel.

2. Test materials and methods

Tests were made on the cast steel of chemical composition given in Table 1. The keel blocks were annealed at a temperature of $850^{o}C$ for 100 hours; they were next cooled in air to serve as a starting product for cutting out of $\varnothing 10\times 30$ mm specimens. The cast steel microstructure is shown in Figure 1. From the results of microscopic observations of the cast steel structure it follows that, besides an austenitic matrix, it is composed of at least four types of the precipitates.

Table 1.
Chemical composition of the examined cast steel, wt %

C	Mn	Si	S	P	Cr	Ni	Nb	Ti
0.29	1.02	4.36	0.007	0.015	17.8	29.3	159	1.19
another: Al = 0.13, Cu = 0.21								

Front planes of the specimens were prepared for examinations by:
a - grinding with 600 grit abrasive paper,
b - grinding with 800 grit abrasive paper,
c -grinding with 800 grit abrasive paper and polishing with 9 μm diamond slurry,
d -grinding with 800 grit abrasive paper and electrolytic etching for 3 seconds; etching was made with a reagent of the following composition: 3g $FeCl_3$, 10 cm^3 HCl and 90 cm^3 C_2H_5OH,
e - grinding with 800 grit abrasive paper and electrolytic polishing.

Electrolytic polishing was carried out with A2 electrolyte made by Struers. The conditions of polishing were controlled through the choice of appropriate current voltage, and the time and intensity of electrolyte flow. For tests a LectroPol-5 apparatus made by Struers was used. The process parameters were as follows: voltage 3V, polishing time 25 seconds, temperature 22°C.

For identification of phase constitution a X'Pert PRO diffractometer (Cu tube; voltage 30 kV, current 40 mA) was used along with a X'Pert High Score program [9]. The measurements

were taken in the angle range 2θ from 30 to 100°. The results of a X-ray phase analysis are shown in Figure 2a÷e.

The results of this analysis prove that, besides austenite, two phases of plain carbides of the NbC type and phase G ($Ni_{16}(Nb,Ti)_6Si_7$) can be identified.

It has also been observed that the intensity of reflections from individual phases differs quite considerably and depends on the specimen surface condition (see: Figure 2a÷e). In this respect, the most legible seems to be the diffraction pattern of specimen a. To confront this observation with the true intensity of reflections present on diffraction patterns, the total number of fields under the peaks originating from individual phases was calculated, and the obtained values were next compared within the measurement results from a to d. In other words, a relative volume fraction of the identified phases was determined. For this purpose a relationship presented in [1] was used:

$$m_j = (m_w/k_j) \cdot (J_j/J_w) \qquad (1)$$

where:
m_j, m_w – mass fractions in the sample of phase j and reference phase, respectively,
J_j, J_w – diffraction reflection intensities for phase j and reference phase, respectively, expressed as a size of field under the peak,
k_j – ratio of the diffraction reflection intensities of the examined phase and reference phase at equal content of these phases in a sample.

According to relationship (1), the content of a given phase can be approximately determined from the intensity of reflections expressed as a size of field under the peak, providing it has been assumed that the value of k_j is relatively constant.

The reflections selected for analysis are compared in Table 2.

Table 2.
The examined reflections

Phase	2θ				
NbC	35.26	40.96	—	—	—
G	42.06	45.90	48.97	59.39	—
Feγ	43.60	50.84	74.84	90.76	96.30

The size of fields under the peaks was measured by a Profile Fit program [10]. In measurements it has been assumed that the sum of all fields under all peaks within the range 30÷100 2θ is 100%. On the other hand, the sum of fields under the individual peaks corresponding to a given phase determines the percent content of this phase. The results of a quantitative analysis of the phase content in the examined samples are shown in Figure 3.

From the results of calculations shown in this drawing it follows that, basically, they do not differ from each other within the range of an acceptable error. For consistent identification of phases present in cast steel, the cast steel matrix was subjected to a selective, electrolytic etching. Because of complex, multi-phase composition of the examined material (see: Fig. 1), the process of extraction required an optimum choice of both the electrolyte solution and process parameters. Detailed description of the selected electrolyte and current parameters is given in [8]. The results of X-ray phase analysis made on an isolate are given in Figure 2f.
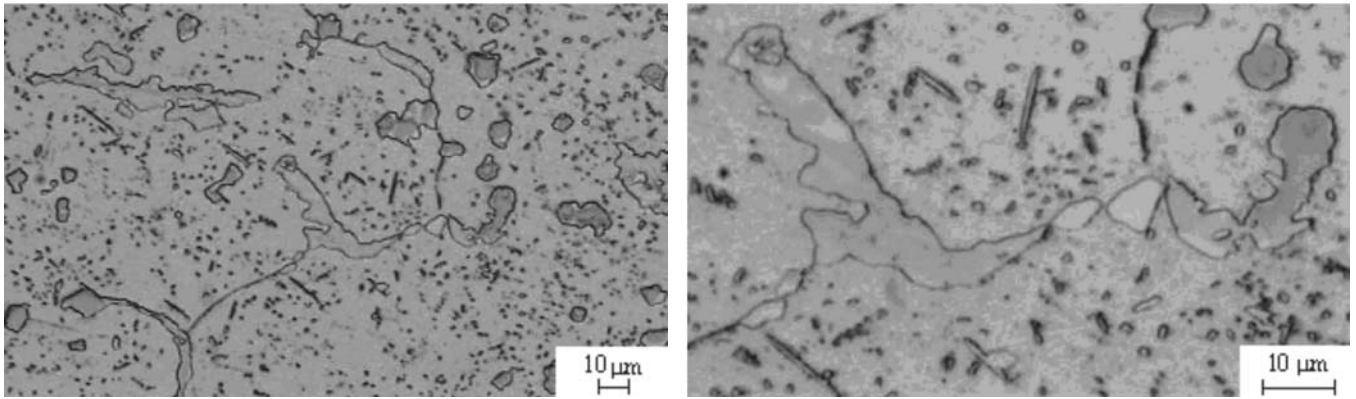
Fig. 1. Microstructure of the examined cast steel [6]
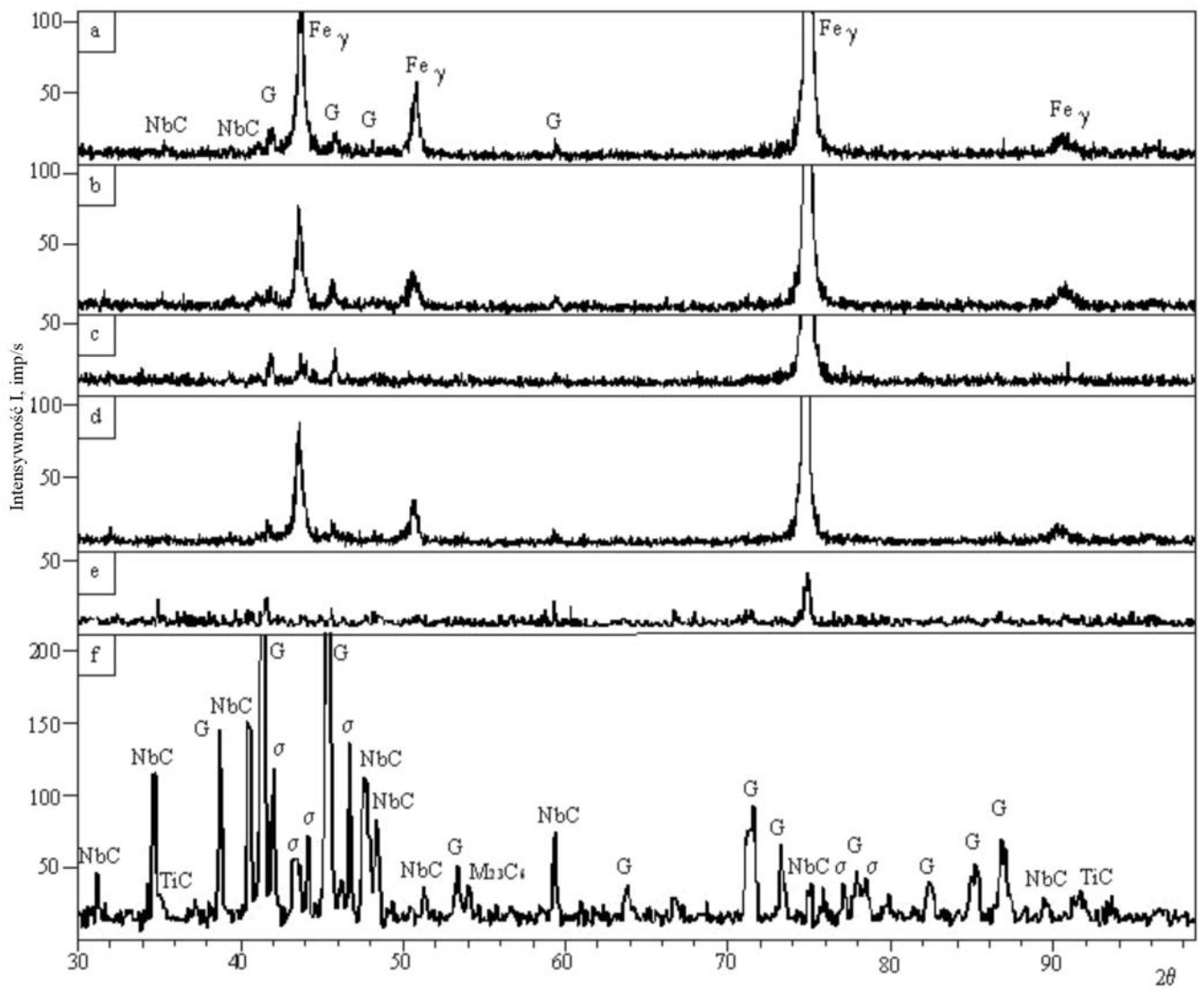

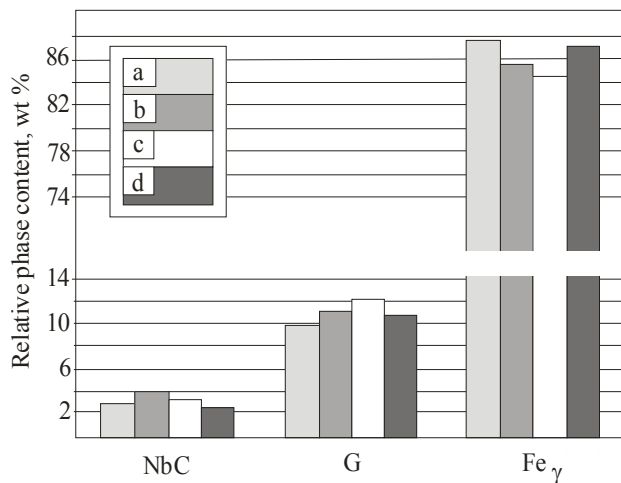Fig. 2. The results of X-ray phase analysis; for explanation of symbols see the text

Fig. 3. Comparison of relative phase content in individual specimens; for explanation of symbols see the text

The diffraction pattern reveals, besides two phases detected in solid specimens, also the presence of the next three phases. These are the phases of plain carbides of the TiC type, chromium carbide of the $M_{23}C_6$ type, and phase σ. No austenite or the secondary products of the process, like chromium oxides or iron oxides, have been identified in the isolate, which proves that the process of extraction has been carried out in a correct way.

3. Summary

The results of the investigations described in this study show the effect of solid specimen surface preparation on the quality of the X-ray phase analysis results.

In view of the fact that the identification of phase constitution carried out on solid samples, specifically on the samples taken directly from castings, cannot in most cases give a relevant and full answer [1], the results of the investigations presented here are but only a next proof of this statement, showing the restrictions that this examination carries with itself when applied to the stabilised cast steel of a 0.3C-30Ni-18Cr type.

The identification of the cast steel phase constituents made on specimens whose surface has been ground with 600 grit abrasive paper gives quantitative and qualitative information similar to that obtained on the specimens ground with a finer abrasive paper,

polished or etched (see: Fig. 3). In all these cases, the only constituents identified have been austenite, phase G and plain carbides of the NbC type. When the main phase (matrix) is masking the activity of other structural constituents, the best way of phase determination when phases are present in small amounts is, as proved by the results of this study, selective isolation of phase constitutents by the method of electrolytic extraction. After selecting an optimum solution of the electrolyte and parameters of the process of the matrix etching, an isolate has been obtained, which contained plain carbides of the NbC and TiC type, chromium carbide of the $M_{23}C_6$ type, and phases σ and G.

Acknowledgments

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