

Electrolytic Phase Extraction in Stabilised Austenitic Cast Steel

Renata CHYLIŃSKA, Malgorzata GARBIAK*, Bogdan PIEKARSKI

Szczecin University of Technology, Al. Piastów 17, 70-310 Szczecin, Poland

Received 31 May 2005; accepted 01 July 2005

The study discusses the choice of electrolytes and current parameters used in the anodic polarisation-based process of electrolytic extraction, applied in order to isolate the phases which precipitate in creep-resistant 0.3C-30Ni-18Cr cast steel during annealing. The conditions of the extraction process were evaluated, taking into consideration the effectiveness of this extraction and the results of an X-ray phase analysis of the isolates.

Keywords: anodic polarization, phase isolation, Fe-Ni-Cr cast steel.

1. INTRODUCTION

Identification of phases in solid specimens by means of an X-ray phase analysis is possible only under the condition that the quantitative content of the examined phases is high enough in an alloy. If it is too low, it should be raised by an indirect method. In such cases usually the method of electrolytic extraction is applied [1].

The separation of phase constituents by an electrolytic extraction consists in selective digesting of the matrix in properly chosen environment, using an electrochemical process. In heterogeneous alloys, each phase is characterised by its own polarisation curve. The dissolution rate of a given phase depends on the composition of electrolyte and on the conditions of electrolysis, current density included [1, 2]. Phase precipitation from the matrix is, specially in the case of austenitic cast alloys, the process very complicated and requiring strict observation of the conditions of electrolysis and correct choice of the electrolyte. This is mainly due to the specific character of as-cast structures (their dendritic form mainly) as well as a corrosion resistance of the matrix [2].

In this study, taking as an example the creep-resistant 0.3 % C – 30 % Ni – 18 % Cr cast steel, the electrolytes and current parameters chosen for an electrolysis to achieve identification of carbides and intermetallic phases precipitating during annealing of the alloy have been described.

2. MATERIAL AND EXPERIMENTAL

The studies were made on samples of dimensions 10 × 30 mm, prepared from the creep-resistant 30 % Ni – 18 % Cr cast steel with additions of niobium and titanium (Table 1).

Before the investigation was started, the samples had been annealed at a temperature of 850 °C for 100 hours. After annealing, the samples were cooled in air, and then their surfaces were ground with an 800 abrasive paper.

The microstructure of the examined cast steel consisted of the co-existing austenitic matrix and precipitates of the phases present on both grain boundaries and inside

the grains (Fig. 1) [3]. The morphology of the precipitates was of a very complex nature.

Table 1. Chemical composition of the tested alloy, wt% [3]

C	Mn	Si	S	P	Cr	Ni	Nb	Ti
0.29	1.02	4.36	0.007	0.015	17.8	29.3	1.59	1.19

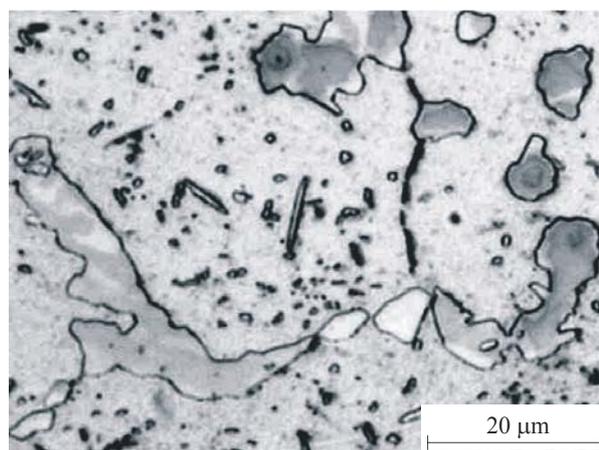


Fig. 1. Examples of macrostructures; etched reagent of the following composition: 10 g $K_3Fe(CN)_6$, 10 g KOH and 100 ml C_2H_5OH

Besides the large, primary precipitates, present mainly in the interdendritic spaces, the alloy matrix included at least two types of the secondary precipitates. Those were fine globular precipitates as well as large, oblong needle-like ones. The contrast of colours, visible on the photographs of microstructures (Fig. 1) in large precipitates, is most probably an indication of their heterogeneous composition.

Basing on the data published in literature, it was decided to use in the investigation electrolytes of the chemical compositions given in Table 2.

To determine the conditions under which the processes of an electrolytic extraction should be conducted, the curves of anodic polarisation were plotted for all the electrolytes, using an ATLAS 9431 potentiostat.

Adequately prepared cast steel samples were immersed in an electrolyte solution at a temperature of 25 °C, mixed with a magnetic stirrer. Having determined the

*Corresponding author. Tel.: +48-91-4494263; fax.: + 48-91-4494263.
E-mail address: odlew1@ps.pl (M. Garbiak)

stationary potential characteristics of each measurement, the polarisation was made within a range of the values from stationary potential up to 2000 mV. The readout density was 10 mV with the potential changing at a rate of 10 mV/s. Calomel electrode was used as a reference material. The curves of anodic polarisation plotted for the examined cast steel in individual solutions of electrolytes are shown in Figure 2.

Table 2. Chemical composition of electrolyte (E) solutions

E. No.	Composition	Ref.
1	5 g C ₂ H ₂ O ₄ , 200 cm ³ HCl, 1000 cm ³ H ₂ O	[1]
2	3 g C ₂ H ₂ O ₄ , 100 cm ³ HCl, 900 cm ³ H ₂ O	[3]
3	100 cm ³ HCl, 900 cm ³ C ₂ H ₂ OH	[1]
4	95.8 cm ³ H ₂ SO ₄ , 3.8 g NH ₄ SCN, 1000 cm ³ H ₂ O	[4]
5	10 g (NH ₄) ₂ SO ₄ , 20 g C ₄ H ₆ O ₆ , 970 cm ³ H ₂ O	[5]

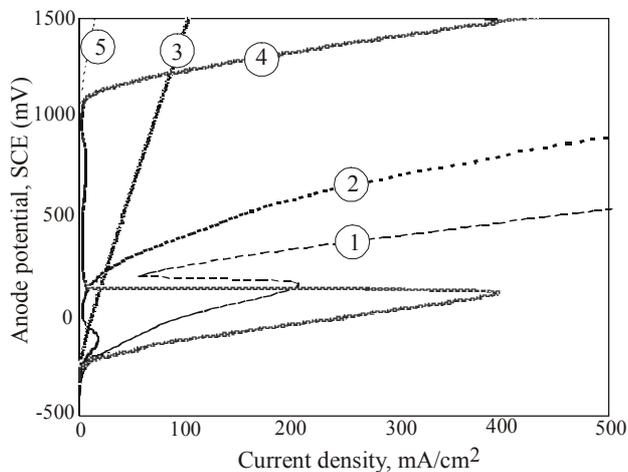


Fig. 2. Anodic polarization curves in tested electrolytes presented in Table 2

An analysis of the plotted curves indicates that in the case of solutions nos. 1, 2 and 4 it has been possible to match the electrochemical conditions in a way such as to make the austenitic matrix digest completely, leaving in an isolate the phase constituents typical of cast steel. On the contrary, in solutions nos. 3 and 5, within the investigated range of the current voltage values, no clearly marked areas of an active and passive state have been observed to exist (the process of austenite digestion did not take place).

In the process of cast steel digestion it has been decided to use a cathode made of an acid-resistant steel sheet and, to check the current parameters, anodic polarisation was carried out in respect of this electrode. Figure 3 shows an example of the polarisation curves of cast steel in electrolyte No. 1 in respect of the calomel electrode (SCE) and steel electrode (FeE). In all electrolytes, the polarisation curves were shifted upwards in respect of the steel electrode by a constant value of the anodic potential, with critical current density value remaining the same. The values of the critical currents read out from the plotted curves and the corresponding anodic potentials in the examined electrolytes are compiled in Table 3. Basing on the collected data, the parameters of the

electrolysis were selected and used next for the extraction – Table 4. To prove how significant is the effect of the current density on the volume of the isolate, specially in the case when the alloy includes a small amount of the fine-dispersed phases [3], it has been decided to use in the case of electrolytes No. 1 and 4 the current of both low (electrolytes No. 1 a and 4 a) as well as high (electrolytes nos. 1 b and 4 b) density.

Table 3. Electrochemical parameters in electrolytes

E. No.	Open circuit potential mV SCE/FeE	Critical potential mV		Critical current density, mA×cm ⁻²	
		SCE	FeE	SCE	FeE
1	-391/-67	161	490	207	207.4
2	-366/2	-118	236	18.2	18.7
4	-310/70	121	-350	397.2	343.6

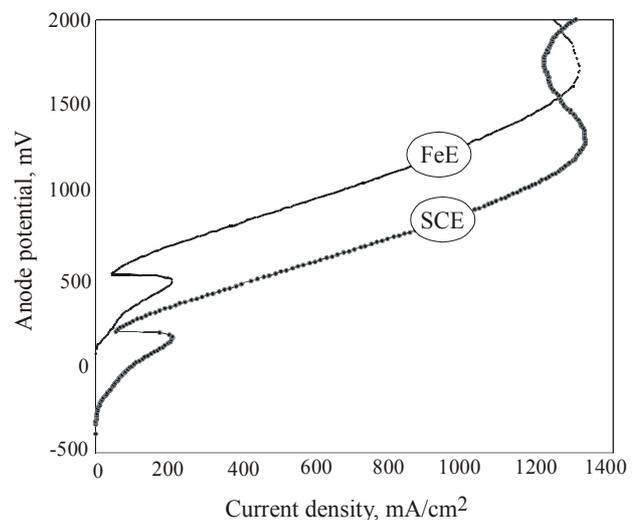


Fig. 3. Anodic polarization curves in electrolyte No.1, relative to SCE – standard calomel electrode, and to FeE – ferrous electrode

Table 4. Conditions and results of selective dissolution

E. No.	Current density, mA×cm ⁻²	Time, h	Weight of extraction residues, g	Fraction of residues, %
1	1a	15	0.2919	11.74
	1b	150	0.0907	10.13
2	15	24	0.1946	11.11
4	4a	15	0.1494	10.00
	4b	150	0.1187	10.22

All the processes of extraction were conducted in a similar way. The samples, after having been thoroughly cleaned and dried, were weighed at an accuracy of up to ±0.1 mg. The sediment obtained from this operation was thoroughly rinsed with ethyl alcohol, spinned and dried at a temperature of 70 °C. The rinsed and dried sample residue and the isolate were weighed once again. From the weighed fractions the percent content of the isolates was calculated.

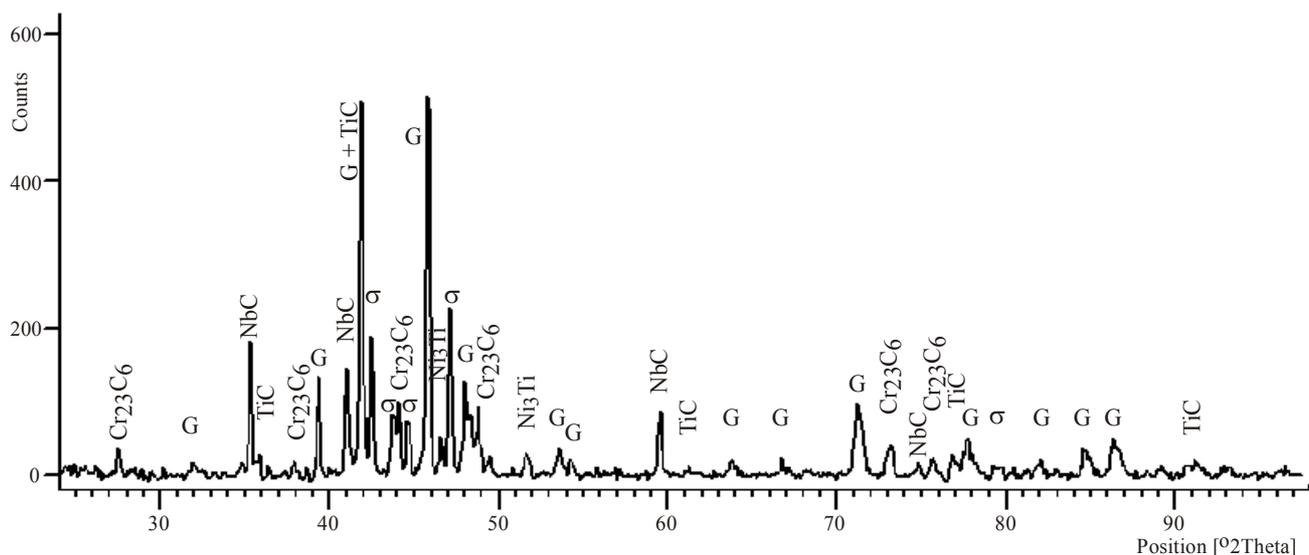


Fig. 4. X-ray diffraction pattern from residues obtained in electrolyte No. 2

Every process was repeated three times. The differences in a volume of the isolates obtained from the secondary isolations did not exceed 7 %. The mean values (in %) calculated from the volume of the obtained isolates are compiled in Table 4.

The phase constitution of the isolates was examined and determined by means of an X-ray phase analysis made on a Philips X'Pert PRO diffractometer (a $\text{CuK}\alpha$ type of radiation). Figure 4 shows as an example some results of the X-ray phase analysis of an isolate obtained from extraction made in electrolyte No. 2. In all electrolytes the following phases were identified: phase G (in this case it can be given the symbol of $\text{Ni}_{16}(\text{Nb,Ti})_6\text{Si}_7$ [3]), straight carbides NbC and TiC, and chromium carbide of an M_{23}C_6 type. Additionally, in isolates from electrolytes No. 1, 2 and 4 a, the presence of Ni_3Ti and σ phases was traced. At the same time, none of the diffraction patterns revealed the presence of peaks coming from austenite, which proves that the cast steel matrix must have been fully digested and passed to electrolyte.

3. DISCUSSION OF RESULTS

The results of both electrolytic extraction and X-ray phase analysis suggest that obtaining an isolate which would correspond, both quantitatively as well as qualitatively, to the real phase constitution of the examined alloy is a task very difficult and time-consuming. The first criterion in evaluating the efficiency of a given electrolyte in extraction of the alloy phase constituents is the volume of the obtained isolate. The results compiled in Table 4 show us that in this aspect the most effective electrolytes (for the specified conditions of an electrolysis) have been electrolytes nos. 1 a and 2. Yet, in both these cases, the time required to obtain an adequate volume of the isolate was very long.

It is true that in the isolates no such secondary products of electrolysis as chromium or iron oxides have been identified [2], the presence of which is, as a rule, undesired and proves that the process has been going on for a time definitely much too long. Nevertheless, in the studies when numerous samples are used, the duration of the process of isolation so long is not acceptable.

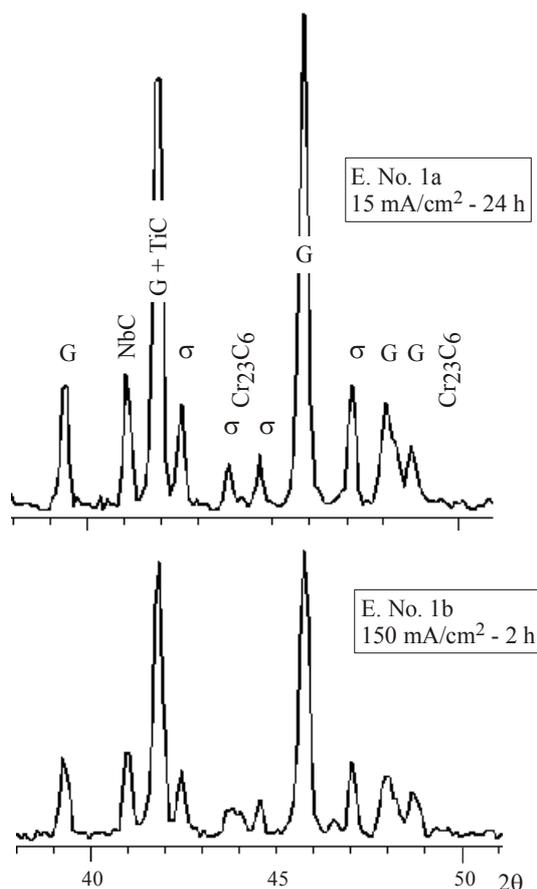


Fig. 5. X-ray diffraction spectra from residues obtained in electrolyte No. 1

Increasing the current density value considerably shortens the time of isolation (Table 4, E. No. 1 b), but in the example discussed here it also reduces the percent content of an isolate and, as a consequence, also the content of the individual phases. An approximate measure of this effect can be the reduced intensity of peaks coming from the individual phases (Fig. 5). At this stage of the research it is not possible to state whether the drop in the content of the individual phases in an isolate is of a selective character and means, first of all, the digestion in

electrolyte of fine-dispersed secondary phases, or if it also includes the digestion of large and massive phases of the primary origin, distributed along the grain boundaries (Figs. 1 and 6).

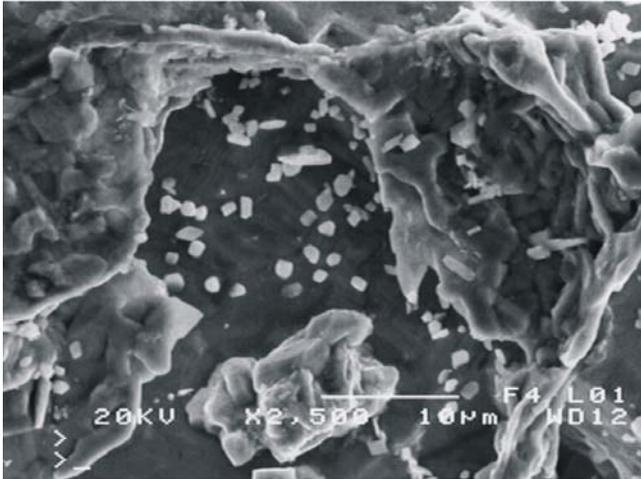


Fig. 6. SEM photographs of the sample after selective dissolution; electrolyte No. 1 b

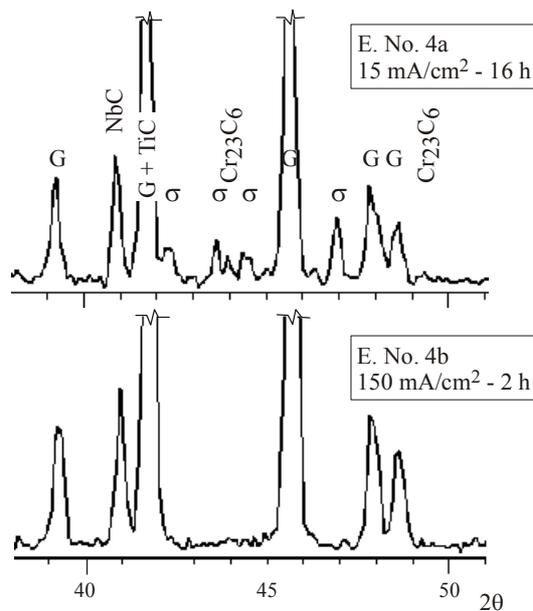


Fig. 7. X-ray diffraction patterns from residues obtained in electrolyte No. 4

On the other hand, the results of the measurements obtained for electrolyte No. 1 indicate that in the case when the research has as its main purpose only an identification of the phases present in cast steel, it is possible to apply with full success higher parameters of the current, since reducing the peak intensity does not necessarily mean that the possibility of an identification of all the phases present in cast steel must be less accessible, too. An assumption like this may, however, prove insufficient when studies on the run of the precipitation process are carried out in a time-temperature system. So, looking for a possibility of reducing the time of extraction without any harm to the quality of the obtained results, it has to be checked in what way the process output changes for current densities

comprised in a range of $15 \div 150 \text{ mA} \times \text{cm}^{-2}$. Likewise, it has to be emphasized that the next step in an evaluation of the reliability of conclusions drawn from the results of an experimental work should allow for a mass balance, that is, should also include a chemical analysis of the electrolytes and isolates. Compared with electrolytes nos. 1 and 2, electrolyte no. 4 is definitely much worse. This is proved by both the weight of the obtained isolate (Table 4) and by the result of an attempt to reduce the time of process duration by raising the value of the current density (Fig. 7). On the diffraction pattern there are peaks coming straight from the σ phase, which proves that during the process of electrolysis this phase has totally passed to electrolyte.

4. CONCLUSIONS

From the results of the conducted studies, aiming at an extraction of carbides and intermetallic phases present in the stabilised austenitic 0.3 % C – 30 % Ni – 18 % Cr cast steel, using various electrolytes and changing the conditions of electrolysis, it follows that the most efficient has proved to be an electrolyte of the following composition: 5 g $\text{C}_2\text{H}_2\text{O}_4$, 200 cm^3 HCl, 1000 cm^3 H_2O .

The obtained results also show us that, while using an electrolytic extraction for isolation of the phases precipitating in austenitic cast steel during annealing process, it is necessary to apply an individual approach to each object of the studies. The results of similar work done by other authors can only be used as guidelines in planning of own experiment.

Acknowledgments

A research work financed from the resources of the Polish State Committee of Scientific Research in years 2004 – 2007 as a research project.

REFERENCES

1. **Kliaczko J. A. et al.** Theory of Electrochemical Phase Analysis of Alloys (Issledovania po teorii elektrokhimicheskovo fazovovo analiza splavov) *Zav. Lab.* 24 (11) 1958: pp. 1308 – 1314 (in Russian).
2. **Barcik J., Fyda D.** Electrolytic Isolation of Carbides and Sigma Phase from Austenitic 25 % Cr-20 % Ni Steel (Elektrolityczna izolacja węglików i fazy σ ze stali austenitycznych 25% Cr-20 % Ni) *Prac. Nauk. Uniwersytetu Śląskiego* № 63 Katowice, Poland, 1974: pp. 51 – 61 (in Polish).
3. **Garbiak M., Piekarski B.** Identification of Phases in Stabilised 30%Ni-18%Cr Cast Steel *Acta Metallurgija Slovaca* 1 2004: pp. 822 – 824.
4. **Gill T. P. S., Gnanamoorthy J. B.** A Method for Quantitative Analysis of Delta-ferrite, Sigma and M_{23}C_6 Carbide Phases in Heat Treatment Type 316 Stainless Steel Weldments *Journal of Materials Science* 17 1982: pp. 1513 – 1518.
5. **Li R. B. et al.** Isolation and Determination for δ , γ' and γ'' Phases in Inconel 718 Alloy *Scripta Materialia* 46 2002: pp. 635 – 638.