MICRO-ORIENTATION STUDY OF SENSITISED AUSTENITIC STAINLESS STEEL USING ELECTRON BACKSCATTERED DIFFRACTION IN SEM

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Electron Backscattered Diffraction (EBD) technique was employed to study the relationship between grain boundary sensitisation and grain boundary types present in nitrogen-added AISI 316LN austenitic stainless steel heat-treated at 800 °C, varying time at this temperature in the range of 1 minute to 100 hours. In comparison to the basic state no changes neither in grain orientations nor in grain boundary types were observed. Twin boundaries were found in all samples with the highest frequency and only small occurrence changes. CSL designation mode also showed only little influence of heat treatment on distribution of CSL boundaries present. Additionally, on the base of misorientation measurements of 50 grooved boundaries, a preferred attack of high angle boundaries (30–55°) was noted.

K e y w o r d s: austenitic stainless steel, sensitisation, EBSD, CSL boundaries

ŠTÚDIUM MIKROORIENTÁCIE V SCITLIVENEJ AUSTENITICKEJ NEHRDZAVEJÚCEJ OCELI VYUŽITÍM DIFRAKCIE SPÄTNE ODRAZENÝCH ELEKTRÓNOV V REM

Difrakcia spätne odrazených elektrónov sa použila na štúdium vzťahu medzi scitlivením a typmi hraníc zŕn prítomnými v austenitickej nehrdzavejúcej oceli AISI 316LN s prídavkom dusíka, žíhanej pri 800 °C od 1 minúty do 100 hodín. V porovnaní so základným stavom sa nepozorovali žiadne zmeny v orientácii zŕn ani typov hraníc zŕn. Vo všetkých vzorkách boli dvojčatové hranice najpočetnejšie, len s malými zmenami ich výskytu. Taktiež CSL zobrazovanie preukázalo malý vplyv žíhania na typ prítomných CSL hraníc. Na základe dodatočného merania dezorientácie 50 naleptaných hraníc sa zaznamenalo prednostné napádanie veľkouhlových hraníc zŕn (30–55°).

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1. Introduction

Austenitic stainless steels are the most widely used stainless steels, constituting 70–80 % of stainless steel production. With excellent corrosion resistance and mechanical properties in the range from cryogenic to elevated temperatures, they are choice materials for food, chemical, petrochemical, thermal and nuclear power industries [1].

It is well known that the common factor affecting performance of austenitic stainless steels in such environments and the most reason of their service failure is the development of intergranular corrosion or intergranular corrosion cracking due to the formation of chromium-rich $M_{23}C_6$ carbides at grain boundaries.

There are various methods available for eliminating these phenomena [2, 3]. In last years an increased attention has been directed to alloying austenitic stainless steels with nitrogen. Replacing carbon by nitrogen has certain advantages since nitrogen is a stronger austenite stabilizer with a greater solubility than carbon. It is a potent solid-solution strengthener [4] and, in particular, it is known to increase the resistance of these steels to sensitisation treatment and to shift TTS (time--temperature-sensitisation) curves to the right on the time scale, which suppresses the intergranular corrosion [5].

Electrochemical and electron-probe experiments of sensitised stainless steels have shown that the development of intergranular corrosion is not the same on all grain boundaries. The sensitisation and precipitation of chromium rich carbides or other secondary phases will occur first on the highest energy interfaces (random grain boundaries), then on recognizable special (lower energy) boundaries such as non-coherent twin interfaces. Low Σ boundaries (like coherent twin boundaries) resist corrosion, and precipitation and sensitisation will thus occur at last on these boundaries [3, 6].

The aim of this investigation was to study the relationship between grain boundary sensitisation and grain boundary types present in nitrogen-added austenitic stainless steel after homogenization and sensitisation heat treatment using EBSD.

2. Application of EBSD

One possibility to study variations of grain boundary character in polycrystalline materials is the use of Electron Backscattered Diffraction (EBSD) technique. EBSD is now a well developed experimental technique, which can be achieved easily in a standard scanning electron microscope with EBSD equipment, namely by focusing the incident electron beam on a highly tilted bulk specimen (usually 70°) and capturing backscattered electrons as diffraction pattern using phosphorus screen and high-sensitive CCD camera. These patterns contain Kikuchi bands produced by lattice planes, which satisfy the Bragg condition. The orientation of the crystal irradiated is determined from the position of these diffraction bands. After scanning a particular sample area point-to-point the individual grains are recorded and misorientation between adjacent grains can be calculated easily. Information details of the grain boundary geometry, e.g. if high or low angle or 'special' type are thus gained [7], and their contribution to various intergranular degradation phenomena can be studied.

3. Experimental

3.1 Heat treatment

Material used in this study was AISI 316LN austenitic stainless steel. Its chemical composition is given in Table 1. Rolled austenitic stainless steel plate 12 mm in thickness was first solution annealed at 1050 ℃ for 1 hour and then water cooled. Specimens of $12 \times 8 \times 20$ mm were prepared from this plate to study intergranular corrosion. The sensitising treatment at 800 ℃, followed by water quenching, was subsequently given to these samples, varying time at this temperature. The labelling of samples used according to the increase of annealing time is listed in Table 2.

Table 1. The chemical composition of AISI 316LN steel [wt.%]

C	Cr	Ni	N	Mo	Mn	Si	S	P
0.02	17.39	12.27	0.018	2.13	0.082	0.047	0.001	0.024

In order to compare changes involved during annealing with respect to the initial steel state and to monitor possible anisotropy due to rolling and recrystallisation, three surfaces of basic state specimen were also analysed. Table 3 shows marking of basic sample surfaces regarding the rolling direction (RD) and rolling plane (RP).

3.2 Sample preparation

For EBSD measurements from former samples 3 mm thick specimens were cut, parallel to the surface 3 (Table 3). All samples were at first grinded with emery papers and then electrolytically polished in Struers A2 electrolyte (78 ml perchloric acid, 120 ml distilled water, 700 ml ethanol and 100 ml buthylglycol) at 29 V for 10 sec.

To develop the microstructure, samples were electrolytically etched in 10 % oxalic acid aqueous solution at a current density of 1 A/cm^2 for 1 minute.

Table 2. Labelling of annealed samples

Sample indication	Time of annealing – 800 °C
C51	1 min
C54	30 min
C55	1 h
C58	10 h
C59	20 h
C50	50 h
C5	100 h

Table 3. Labelling of basic state samples

Sample indication	Sample position
S1	„longitudinal cut“ – parallel to RD, perpendicular to the RP
S2	„surface cut“ – parallel to RP
S3	„transversal cut“ – perpendicular to RD

3.3 EBSD conditions

Individual EBSD measurements were carried out in scanning electron microscope Zeiss DSM 962 fitted with 'CHANNEL+' instrumentation made by HKL Technology. Following operating parameters were taken: accelerating voltage 20 kV and probe size about 70 nm, working distance (distance objective-sample surface) was 20 mm; for austenite detection 4–6 Kikuchi bands were used, taking the edges of the bands. Mean angular deviation during indexing was set to be $\leq 1.3°$.

4. Results

The basic information about the character of microstructure and tendency of material toward development of grain boundary sensitisation for all samples was obtained from pre-study using corrosion test ASTM A262-A, which provided the background information for subsequent EBSD evaluation. Nevertheless, it is necessary to note that sensitisation of AISI 316LN at 800 °C occurred first for sample treated 20 hours.

4.1 EBSD analysis

Individual EBSD samplings were carried out for each sample from areas close to the top and bottom as well as from the middle region. For measurements in outer sites magnification 200× and step size 2 μm were chosen; for internal sites – magnification 500× and step size 1 μm. In order to obtain good statistics of grain boundary types when time at sensitisation temperature is varied, 4 EBSD samplings per sample were performed.

EBSD analysis for all samples showed the presence of cubic texture with only slightly oriented grains of very variant grain size and a preponderance of twins, Fig. 1. No difference in grain orientations between basic and annealed states of the steel was observed, Fig. 2.

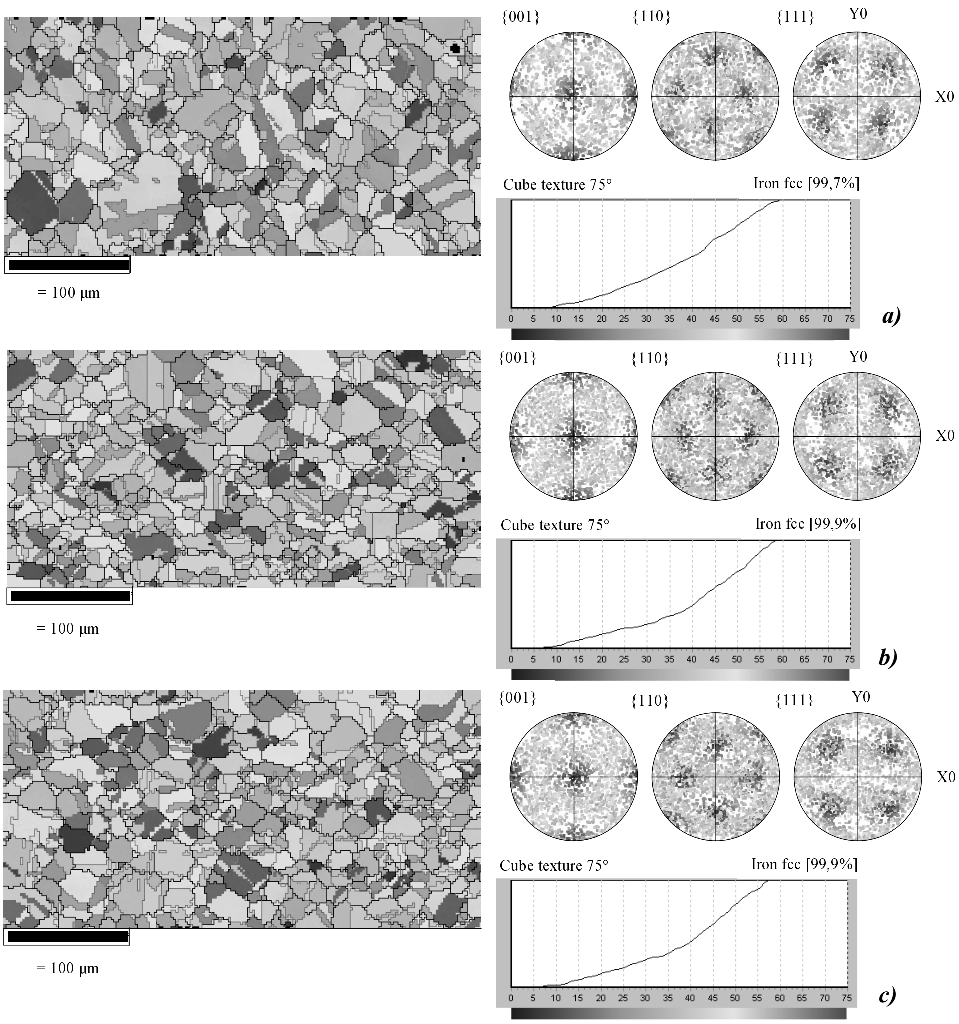

Fig. 1. Examples of orientation maps and pole figures from basic state specimens: a) S1; b) S2; c) S3; with colour coding done with the deviation angle from ideal cube orientation (axes of unit cell are parallel to sample coordinate system axes) using a rainbow scale.

4.2 Grain boundary classification

The elementary classification of grain boundary types can be directly depicted by basic colouring in orientation maps. With regard to the print, there is obscured grain boundary depiction in Figs. 1 and 2. Following colours for grain boundaries present were chosen: low angle boundaries up to 10° – dark grey, high angle bound-

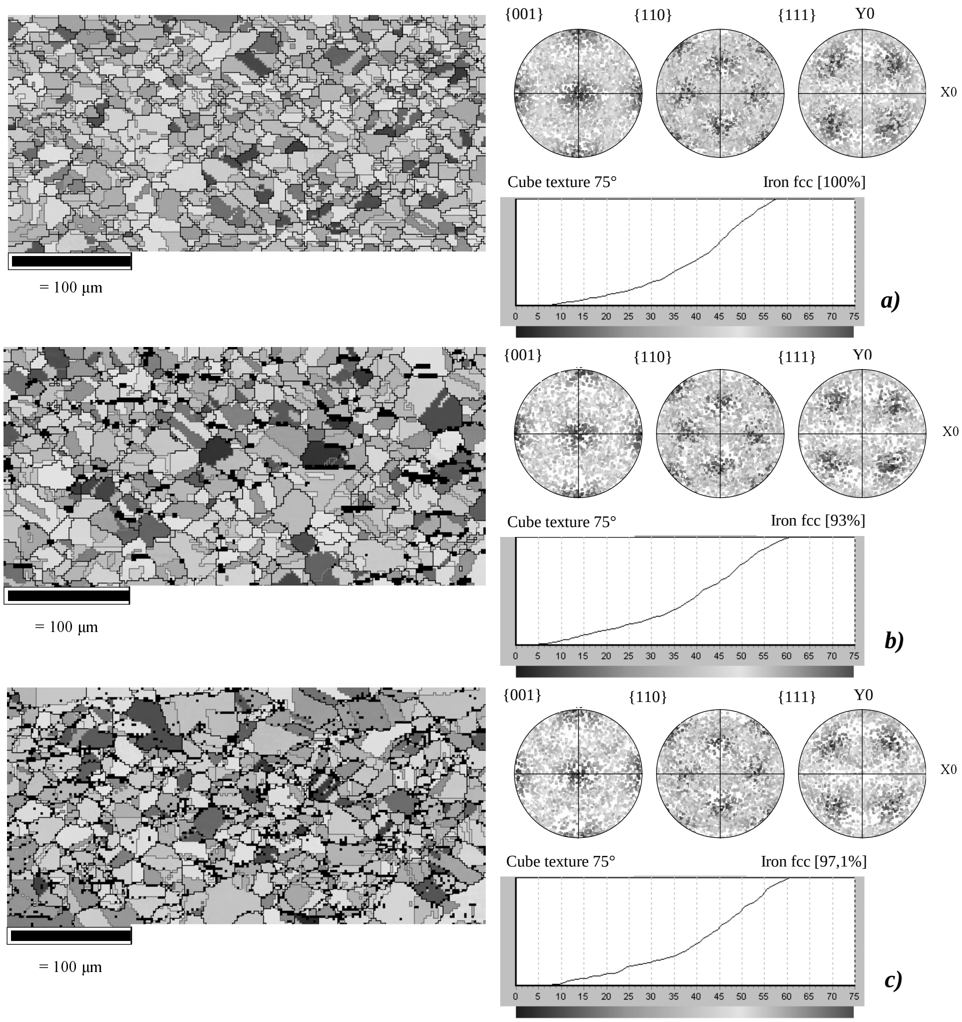

Fig. 2. Examples of orientation maps and pole figures from annealed samples: a) C54; b) C58; c) C5; with colouring as in Fig. 1.

aries up to 55° – black and grain boundaries with misorientation angles > 55° – grey colour.

The representation of particular families of grain boundaries as a function of its occurrence frequency in basic state sample is illustrated in Fig. 3. From the plot a similar accentuated presence of twin boundaries with peak maximum at 59.5° is evident. Compared to other surfaces, the highest relative frequency of these grain

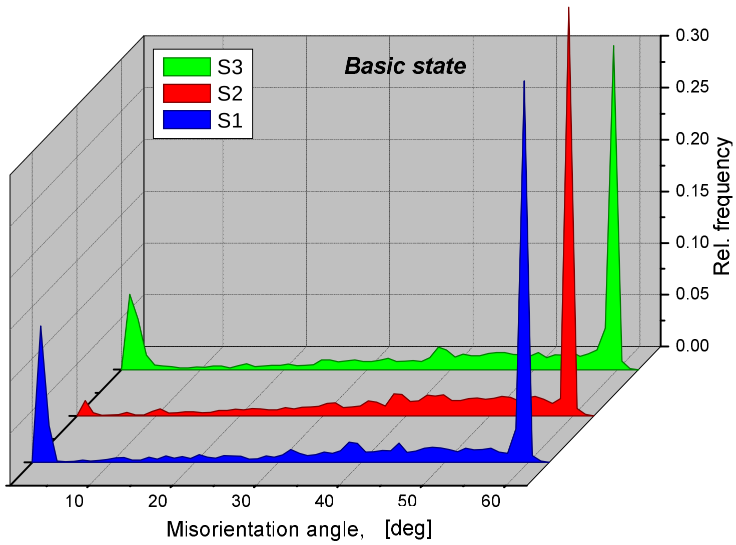

Fig. 3. The distribution of grain boundaries in basic state samples.

Table 4. Fractions of individual types of grain boundaries in investigated samples, mean values of four maps [%]

Sample	< 10°		< 57.5°		> 57.5° (twins)
	< 1.5°	others	< 55°	others	
S1	13.16	4.6	38.2	3.25	40.8
S2	1.47	1.54	50.24	4.7	42
S3	7.29	7.94	43.83	4.7	36.25
C51	1.805	3.57	55.83	1.15	37.65
C54	4.26	2.47	52.28	0.5	40.5
C55	2.04	1.74	50.78	4.5	40.95
C58	2.08	1.68	46.89	2.24	47.11
C59	8.25	7.94	39.72	4.9	39.2
C50	3.44	2.42	46.75	4.85	42.55
C5	1.81	3.18	44.26	4.75	46

boundaries was recorded for S2, parallel to rolling direction.

In S1 and S3 a conspicuous increase of low angle boundaries content with peak maximum 1.5° is seen, while their presence in direction parallel to rolling was suppressed down to 1.5 %. The rest of boundary families was composed of high

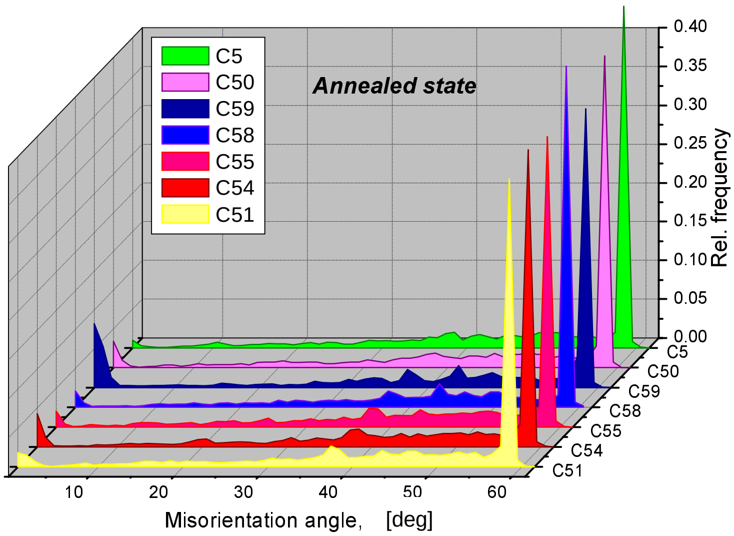

Fig. 4. The distribution of grain boundaries in annealed samples.

angle boundaries, with its slightly increased amount from misorientation angles about 39°. Variations in content of the individual grain boundary types are listed in Table 4.

Annealing at sensitisation temperature introduced no changes in grain boundary types in comparison to initial state (Fig. 4). The holding time variations afford only modifications in relative frequency of strong twin boundary peak at angle 59.5°. The highest amount of twins was observed for samples C58 and C5, the lowest one for sample C51 (Table 4).

The content of 1.5° low angle boundaries with correlation to basic state decreased, with maximum value for specimen C59, and for other samples was only up to 4 %. There was observed also a slight increase of high angle boundaries content in the angle interval of about 39° to 55°.

In order to have better understanding of relationship between crystallographic grain boundary types present and intergranular attack, exact misorientation angles for 50 attacked grain boundaries in sensitised C58-C5 samples using Channel 5 were also measured.

As evident from Fig. 5, the intergranular attack occurred preferably at high angle boundaries, with misorientation angles in the range of 30–55°. In the case of samples C59 and C5, grain boundaries with misorientation angles > 20° were also attacked. There were detected only few grooved low-angle and twin boundaries for

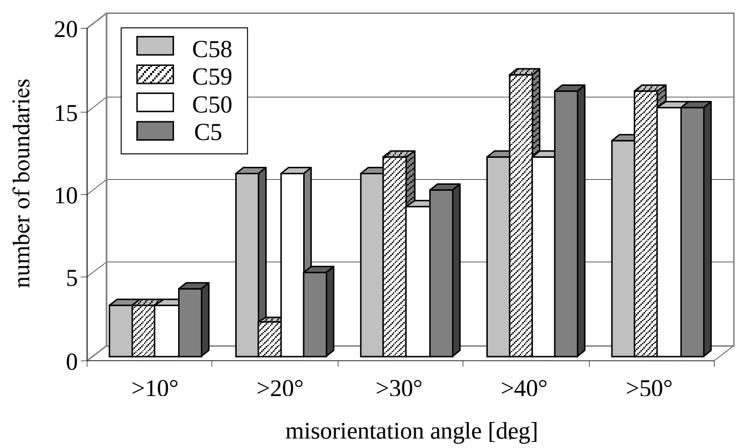

Fig. 5. The distribution of grain boundary types in attacked samples.

each sample. The fraction of attacked twins was roughly proportional to that of low angle boundaries and is involved in the last column.

4.3 Application of CSL theory

Automated electron diffraction techniques allow not only boundary misorientations to be obtained, but subsequently also categorized according to the CSL system [8]. CSL model defines periodicity, i.e. degree of fit between two lattices, which constitute the boundary. Using this model it is possible to divide boundaries

Table 5. The population of CSLs in AISI 316LN, mean value [%]

Sample	CSL boundary		
	Σ3	Σ9	Σ29a
S1	40.45	2.195	–
S2	41.5	2.41	–
S3	37.7	2.215	–
C51	40.2	2.375	1.13
C54	41.9	2.615	–
C55	40.05	2.4	–
C58	46.35	2.28	2.05
C59	40.5	2.045	2.64
C50	42.55	2.2	–
C5	46.2	2.12	–

into 3 categories: low angle (up to 15°), CSL and random, i.e. high angle non-CSL boundaries [9].

Table 5 shows results from the CSL grain boundary evaluation. All samples – basic state as well as the annealed ones – had a large proportion (> 40 %) of $\Sigma 3$ boundaries and a lower extent of $\Sigma 9$s. The remaining CSLs were not present at levels above 1 %, except $\Sigma 29a$, which content was in three cases of annealing state in the range of 1.13 to 2.64 %.

5. Discussion

After solution annealing, the investigated AISI 316LN stainless steels had a twinned microstructure, without stronger preferred orientation of grains and any grain orientation differences relative to rolling direction (Fig. 1). Comparing to maps obtained from annealed samples, there was no time depending change in grain orientation character and also grain size (measured also from EBSD maps). As evident from Fig. 2, a great spread of grain sizes for all annealed samples was kept.

With regard to observed grain orientations, annealing time did not introduce any changes in type of grain boundaries. For basic state as well as for all annealed samples, the maximum occurrence frequency of twin boundaries was recorded, with irregular amount modifications according to annealing time. Except twins, the second large group possesses high angle boundaries of similarly distributed misorientations, with their slightly increased amount in the range of 39° to 55°.

As shown by measurement of misorientations of 50 grooved boundaries, just this misorientation range seems to be the most crucial for grain boundary precipitation and sensitisation present. On the other side, twins and also low angle boundaries have a superior resistance to sensitisation. There were only few attacked boundaries of these types for each analysed sensitised sample, and their attacked proportion remained nearly constant in all cases. To conclude an exact relation between grain boundary types and sensitisation at chosen temperature, it is desirable to analyse a higher amount of attacked boundaries than was presented. Despite of this, the obtained results of misorientation measurements showed tendency to the attack of high angle boundaries, which well corresponds to the results documented elsewhere [6, 10].

Very popular for grain boundary classifying and determination of special boundaries is the CSL model. Presence of high proportion of special CSL boundaries in materials is desirable because in general intergranular degradation processes are supposed to minimize on it [8].

The application of CSL designation to the obtained maps confirmed for all samples a large fraction of twin boundaries (in CSL notation – $\Sigma 3$), with a good value fit to the twin proportion measured from accumulated histograms (Tables 4, 5). Also noted increased amount of about 39° high angle boundaries was found to correspond to the observed Σ9 boundary fraction. Consequently, it was revealed that increasing annealing time had a little effect on the statistical spread of CSL's (Table 5) and showed only slight evolving of grain boundary population toward a higher proportion of special grain boundaries.

6. Conclusions

The investigation of tendency to intergranular corrosion of AISI 316 LN nitrogen-added austenitic stainless steel, focused on the relationship between grain boundary sensitisation at 800 ℃ and grain boundary types present, was carried out by means of Electron Backscattered Diffraction technique.

The main conclusions are:

• Orientation mapping of samples confirmed observations of almost untextured, twinned microstructure. There were no differences between statistically determined orientation of grains in basic state and annealed samples.

• Between classes of recorded grain boundary types, the twin boundaries (59.5°) had the maximum frequency in the basic state samples. The highest amount of twin boundaries was observed in the plane parallel to the rolling plane. The fraction of high angle boundaries with angles between 39–55° in all three surfaces was increased.

• In annealed states, irrespective to time of holding, families of grain boundaries were markedly represented by the same types as in the case of basic samples.

• Measurements of misorientation angles of 50 grooved grain boundaries showed preferred attack of high angle boundaries in the range of misorientation angles of 30–55°, only for samples C59 and C5 it was also recorded for boundaries with angles $> 20°$. The attack of twin and low angle boundaries was negligible compared to the attack of other types of boundaries.

• Application of CSL theory confirmed strong presence of twin boundaries for all samples. There was only a little effect of annealing treatment on CSL types present.

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