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**NANOBAINITIC STRUCTURE RECOGNITION AND CHARACTERIZATION USING TRANSMISSION ELECTRON MICROSCOPY**

**ROZPOZNAWANIE I CHARAKTERYZACJA STRUKTURY NANOBAINITYCZNEJ ZA POMOCĄ TRANSMISYJNEJ MIKROSKOPII ELEKTRONOWEJ**

Various transmission electron microscopy techniques were used for recognition of different kinds of bainitic structures in 100CrMnSi6-4 bearing steel. Upper and lower bainite are morphologically different, so it is possible to distinguish between them without problem. For new nanobainitic structure, there is still controversy. In studied bearing steel the bainitic ferrite surrounding the retained austenite ribbon has a high density of dislocations. Significant fragmentations of these phases occur, bainitic ferrite is divided to subgrains and austenitic ribbons are curved due to stress accommodation.
*Keywords*: transmission electron microscopy, nanobainite, bearing steel

W celu rozpoznania i scharakteryzowania poszczególnych morfologii bainitycznych w stali łożyskowej 100CrMnSi6-4 zastosowano różne techniki transmisyjnej mikroskopii elektronowej. Rozpoznawanie bainitu górnego i dolnego nie nastręcza problemu, ze względu na ich zróżnicowane morfologie. W przypadku bezwęglikowego nanobainitu, ciągle jeszcze wiele jest kontrowersji. W badanej stali łożyskowej ferryt bainityczny otaczający wstęgi austenitu szczątkowego cechuje się dużą gęstością dyslokacji. Obydwie fazy wykazują znaczną fragmentację; ferryt bainityczny podzielony jest na podziarna a wstążki austenitu ulegają wygięciu w wyniku akomodacji naprężeń.

The bainitic transformation in steels has been extensively studied, however it is still controversial whether it proceeds by a diffusional [1-2] or shear (displacive) [3-4] or diffusional-displacive mechanism [5-6]. There are in detail many elements to the controversy surrounding the mechanism of formation of bainite until now.

In recent years Bhadeshia, Caballero, Garcia-Mateo and coworkers [7-12] developed new kind of bainitic structure named Nanobain. Low-temperature bainitic microstructure can be obtained in high-carbon Si-rich steels by isothermal transformation for a long time (1-3 weeks). This resulting carbide-free bainitic microstructure consists of plates of bainitic ferrite, which are just 20-40 nm in thickness, dispersed in a residue of carbon enriched retained austenite. The achieved combination of mechanical properties is excellent, with strengths in the range 1.6-2.5 GPa with a hardness of about 650-700 HV, and toughness of 30-40 MPa/m$^2$, depending on the transformation conditions [12]. It was very inspired to many researches and a lot of work was done during last decade to achieve nanostructured bainitic steel with such good properties [13-15]. The improvement in toughness reached in high silicon bainitic steels is attributed to the replacement of brittle interlath cementite of the upper conventional bainite structure by interlath films of softer retained austenite. Carbide precipitation can be suppressed during isothermal holding by adding the right amount of silicon as an alloying element. The microstructure is carbide-free, not only because Si retards the precipitation of cementite from austenite due to its low solid solubility in the cementite crystal structure, but also because a substantial quantity of carbon is trapped at accommodation twins and dislocations in vicinity of the ferrite-austenite interface [ 16]. However, despite the high Si content in the nanostructured bainitic steels (*sim*1.5 wt.%), evidence of $Fe_3C$ carbide formation has recently been found using advanced microscopic techniques, including Atom Probe Tomography [17]. A higher volume fraction of clusters and carbides were formed after the isothermal transformation at 200°C for 10 days than after transformation at 350° C for 1 day [18].

So, the question is, if it really carbide-free microstructure? What is the difference between dense lamellar pearlite and nanobainite?

## 1. Material and methodology of investigations

The chemical composition of the steel used in this investigation was Fe 0.93-1.05%C 0.45-0.75%Si 1-1.2%Mn 1.4-1.65%Cr (wt.%). This commercial steel is widely used in industry for bearings, so it is expected that enhancing properties by nanostructurization will extend applications of this very promising material. Studies of phase transformations occurring in these steel have been performed by dilato-

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metric measurements with the use of the Bähr's DIL805L dilatometer, in order to accurately design suitable heat treatment procedures. Specimens were austenitized for 30 minutes at 930°C and then isothermally transformed at 320°C, for 5 hours and slow cool-down in ambient temperature. The isothermal holding time enabled the total completion of the bainitic transformation. For comparison, incomplete transformation was performed (90%) and lower austenitizing temperature (850°C/260°C-lower bainite) or isothermal holding at 680°C (pearlitic microstructure).

TEM specimens were prepared from dilatometric heat-treated 3 mm rods. The foils used for the TEM were cut into 0.2 mm thick slices, mechanically thinned to 0.07 mm and then twin-jet electropolished to perforation using a Struers-Tenupol equipment with a mixture of 5% perchloric acid in glacial acetic acid. Microstructure observations were carried out on a JEOL JEM 3010 transmission electron microscope (TEM) operated at 300kV.

## 2. Results and discussion

Nanostructured bainite was observed after isothermal treatment in 320°C (Fig. 1). A nanometric bainitic structure observed in studied steel fulfilling the nano-crystallinity criteria: the plate width for both phases was well below 100nm (bainitic ferrite: 30-50nm, retained austenite: 14-20nm). For proper estimation of volume fraction of nanobainitic structure more than 60 images of microstructure was recorded around the thin foil perforation in each sample. From systematic observations it was concluded, that nanobainitic structure is dominant in all the areas, achieving more than 80% of the volume. Low Mag mode was very useful in this experiment due to visibility of extended areas with neighboring prior austenite grains. In that way not only local arrangement of nanobainitic structure was observed but also the connections between the prior austenitic grains. Crystallographic relationship between ferrite and austenite was determined using superimposed selected area diffraction patterns in proper orientation of both phases. The orientation relationship between ferrite and austenite was very close to Nishiyama-Wassermann in studied nanobainitic structure.

In the case of well developed nanobainitic structure carbides were not observed, or only sporadically. The amount of carbon and chromium in this steel favor carbides precipitation (for bearings it is appreciable). The amount of silicon in this steel is not sufficient to successfully avoid carbides abundance.

These carbides are not completely dissolved during austenitizing, because of chromium enrichment. It was observed, that in many cases, cementite carbides inhered from austenite are semicoherent with surrounding matrix and smoothly embedded without structural discontinuity (Fig. 2a). So, for this steel the terminology "carbide-free bainite" is through only for well developed nanostructured bainite. During prolonged holding secondary precipitation can also occur (Fig. 2b). These carbides are hidden in the microstructure because of very small size below 5nm. Short range diffusion to dislocation core is sufficient for decorating dislocations with fine carbides. Because of very small size, similar interplanar spacings and small volume fraction these clusters/nanocarbides are invisible on selected area electron diffraction, the spots are very weak.

a/ b/ c/

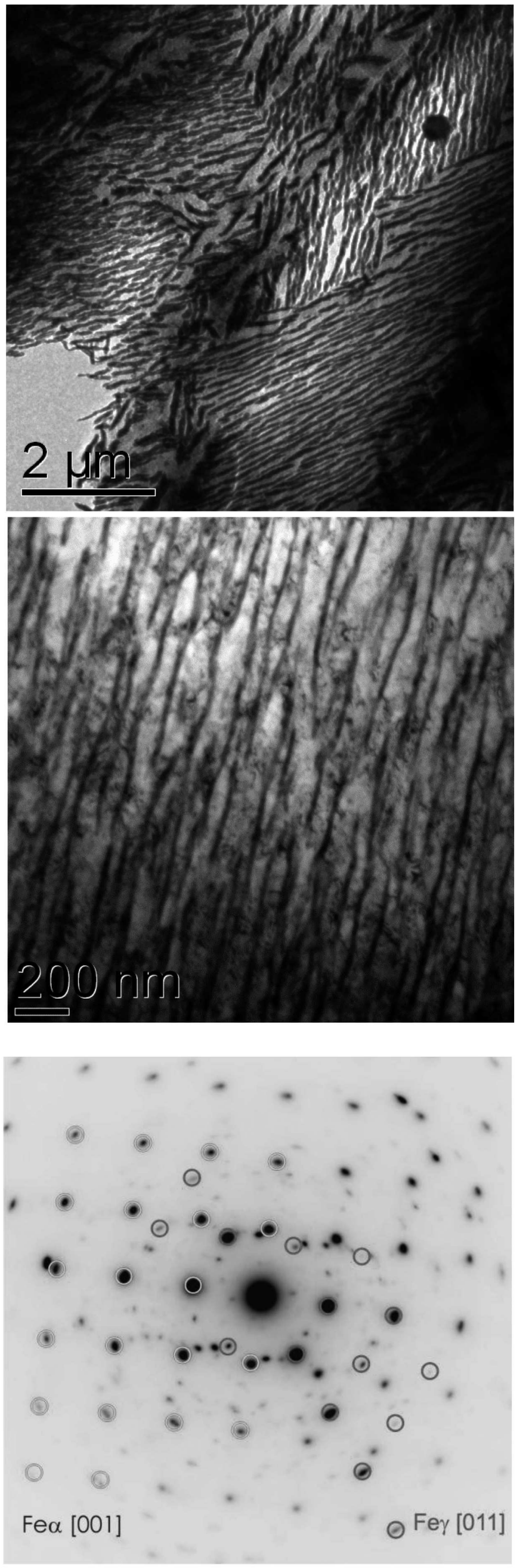


Fig. 1. Transmission electron micrographs of nanobainitic microstructure obtained at 320°C in Low Mag (a) higher magnification (b) and (c) selected area electron diffraction from carbide-free nanobainitic structure with Nishiyama-Wassermann orientation relationship

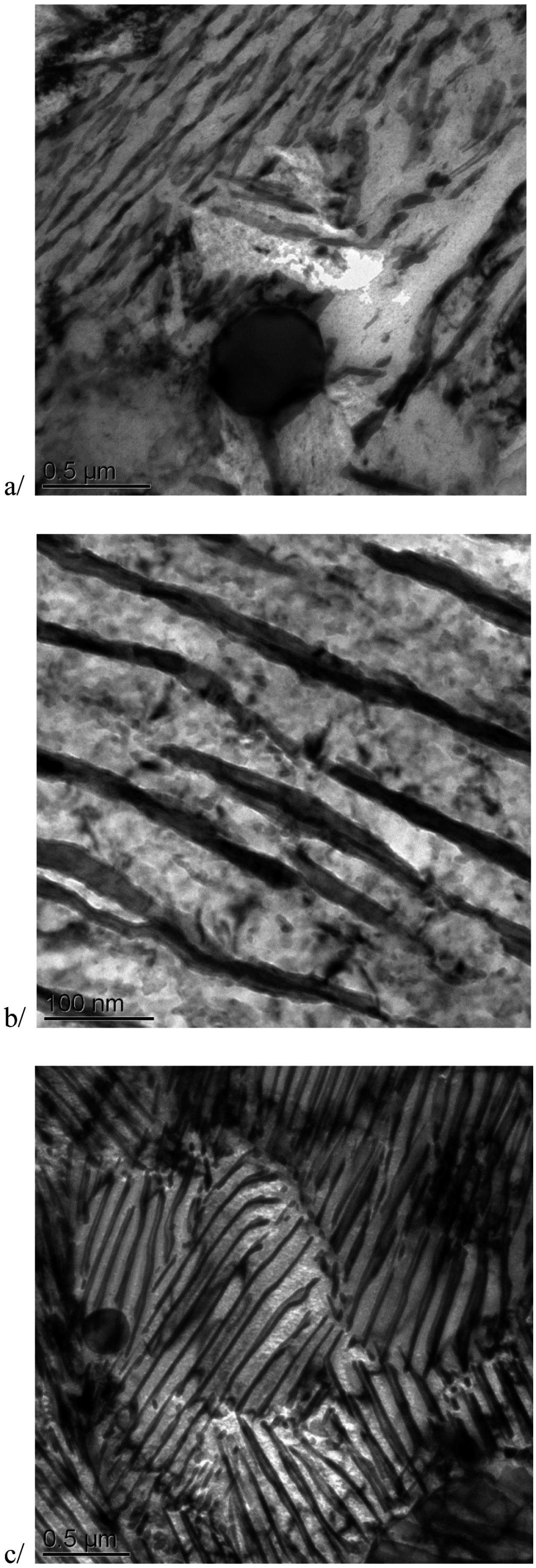


Fig. 2. TEM microstructure of 100CrMnSi6-4 bearing steel after isothermal quenching; (a) at 320°C for 6 h, (b) at 320°C for 4h, (c) at 680°C for 20 minutes

The second intriguing question was about similarity of nanobainitic structure to dense lamellar pearlite. The smallest pearlite lamellae for our steel were in the range 120-160 nm (Fig. 2c). The largest bainitic ferrite plates and retained austenite films were near this range. Looking at these microstructures in low magnification TEM or using SEM the mistake is possible. But looking carefully in TEM at higher magnification with proper alignment and contrast enhanced with objective aperture, the differences are evident (Fig. 3). The most dominant difference is due to significant density of dislocations for nanostructured bainite. Transformation dislocations associated with front of the transforming parent phase to transformation product are characteristic for displacive and for diffusional-displacive transformation. In the area of bainitic ferrite the density of dislocations are higher (Fig. 3a). Plate of bainitic ferrite is divided to subgrains with additional dislocations on the subboundaries. In the vicinity of retained austenite to ferrite interface these dislocations are clearly visible.

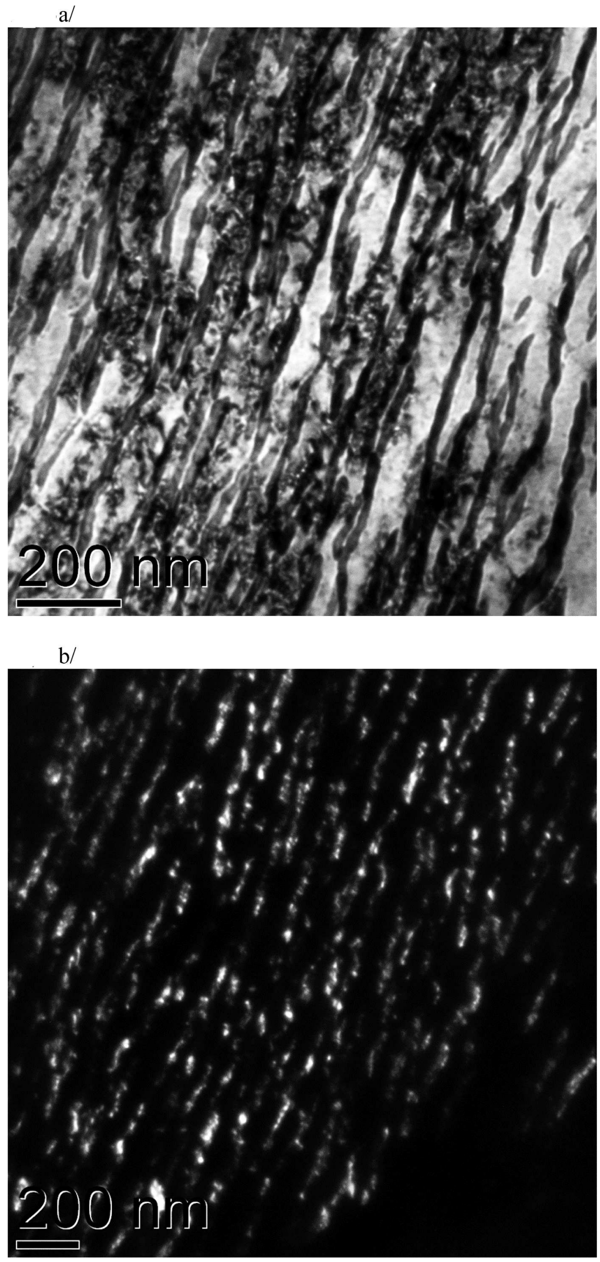


Fig. 3. Transmission electron micrographs of nanobainitic microstructure obtained at 320°C, (a) bright field, (b) dark field with (200) austenite spot

Pearlitic transformation is diffusional, so the area of ferrite between cementite lamella is clear, nearly without dislocations.

In our steel nanostructured bainite is a little different than we can find in the microstructure presented by Bhadeshia, Caballero, Garcia-Mateo and coworkers [19]. Instead of interpenetrated retained austenite film and bainitic ferrite plates we have opposite morphology: retained austenite ribbon/serpentine inside bainitic ferrite matrix (Fig. 3). Additionally, wider ferrite plates are divided to subgrains and retained austenite ribbon is strongly deformed, fragmented to finer segments and twins. The curvature of retained austenite ribbon is in wavy manner. This behavior is connected with stress accommodation and can be explained with theory of stress induced interaction developed by Khachaturyan [20]. Another difference in morphology it is the absence of blocky austenite. The benefit of this is manifested in reduction of shape deformation in final product after applied heat treatment.

The results of mechanical tests for 100CrMnSi6-4 steel with a nanobainitic structure after industrial heat treatment [21] are very promising.

## 3. Summary and conclusions

Various transmission electron microscopy techniques were used for recognition of different kinds of bainitic structures in 100CrMnSi6-4 bearing steel after isothermal quenching. A nanometric bainitic structure was observed in studied steel, fulfilling the nano-crystallinity criteria: the plate width for both phases was well below 100nm (bainitic ferrite: 30-50nm, retained austenite: 14-20nm).

The orientation relationship between ferrite and austenite is very close to Nishiyama-Wassermann in studied nanobainitic structure. The ribbons of austenite and bainitic ferrite appear as packets of smaller sub-units. In studied bearing steel the ferrite surrounding the austenite ribbon has a high density of dislocations.

Significant fragmentation of both phases occur, bainitic ferrite is divided to subgrains and austenitic ribbons/lamellae are curved due to stress accommodation.

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