A R C H I V E S O F M E T A L L U R G Y A N D M A T E R I A L S
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SYNTHESIS OF NANOPARTICLES IN THE FERRITE OF DUCTILE IRON

SYNTEZA NANOCZĄSTEK W FERRYCIE ŻELIWA CIĄGLIWEGO

This article presents preliminary results of the processing and microstructural evolution of ductile cast iron modified by an addition of vanadium. The main goal of this work was to investigate the possibility of precipitation of vanadium carbides in the ferritic matrix of ductile cast iron giving rise to its properties improvement. The proposed research was based on similar approach known for precipitation hardened steels, however, only occasionally applied in cast iron. The involved procedure comprised soaking the ductile iron at the temperature closed to solidus (1095°C) for 100 h, cooling down to 640°C, holding on at this temperature for 16 h and cooling again to room temperature. Such heat treatment led to dissolving of existing (primary) vanadium-rich carbides and further their reprecipitation in the dispersed form. The precipitation processes were examined by light, scanning and transmission microscopy. It was shown that next to dispersed vanadium-rich carbides with an average size of 50 nm, extremely small (on the order of 1 nm) precipitates were also revealed. These minute precipitates were found in all examined areas; they produced images in transmission electron microscope characteristic for coherent precipitates as well as gave extra spots on selected area diffraction patterns. Also, other particles, with similar size to VC precipitates, however enriched with Mg and O, were found but less frequently. The investigation showed that it is feasible to age-harden ductile iron by introducing vanadium and carry out a proper heat treatment.

Keywords: ductile iron, particle hardening, vanadium carbides, titanium nitrides

Zaprezentowana praca obejmuje wstępne wyniki badań nad wytwarzaniem i rozwojem mikrostruktury ciągliwego żeliwa, którego skład chemiczny został wzbogacony przez dodatek vanadu. Głównym celem pracy było przebadanie możliwości wydzielania węglików vanadu w osnowie ferrytycznej żeliwa ciągliwego i tym samym przyczynienia się do poprawy własności żeliwa. Zaproponowane badania opierały się na zjawiskach znanych w stalach umacnianych wydzieleniowo, lecz tylko sporadycznie wykorzystywanych w żeliwach. Zastosowana obróbka cieplna żeliwa obejmowała wyżarzanie w temperaturze bliskiej solidusu (1095°C) przez 100 godzin, ochłodzenie do 640°C, wytrzymanie w tej temperaturze przez 16 godzin i studzenie razem z piecem. Taka obróbka cieplna doprowadziła do częściowego rozpuszczenia się pierwotnych węglików bogatych w wanad i ich ponownego wydzielenia się w formie dyspersoidu. Procesy wydzielania badano technikami mikroskopii świetlnej oraz elektronowej – skaningowej i transmisyjnej. Wykazano, że oprócz dyspersyjnych węglików wanadu, o średniej średnicy ok. 50 nm, występują jeszcze bardzo drobne wydzielenia o wymiarach rzędu 1 nm. Te niezwykle drobne wydzielenia znajdowano we wszystkich analizowanych obszarach ferrytu; obrazy z elektronowego mikroskopu transmisyjnego wykazywały charakterystyczne cechy dla cząstek koherentnych, a na selektywnych dyfrakcjach elektronowych występowały dodatkowe refleksy. Badania wykazały, że możliwym jest umocnienie ferrytu żeliwa ciągliwego, przez dodatek wanadu i zastosowanie odpowiedniej obróbki cieplnej.

1. Introduction

Ductile iron is a valuable structural material, which depending on its matrix (ferritic, ferritic-perlitic, ausferritic, bainitic or martensitic) offers a wide range of mechanical properties (Fig. 1), with simultaneously a good wear resistence and a good ability to absorb the mechanical vibration.

Considering these properties and production costs, it is apparent in many cases, that castings with nodular graphite can be the substitute to more expensive forged steels. Graphite in ductile iron becomes a ready source of carbon, which can be used during the phase transformation in solid state. According to the literature pertaining to solid state transformations in ductile iron [4,5], it is

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evident that very little attention was paid to improving ferritc matrix properties. Moreover, in spite of extensive research on precipitation hardening in steels, only a few attempts [6,7] have been made to apply a similar approach to ductile iron.

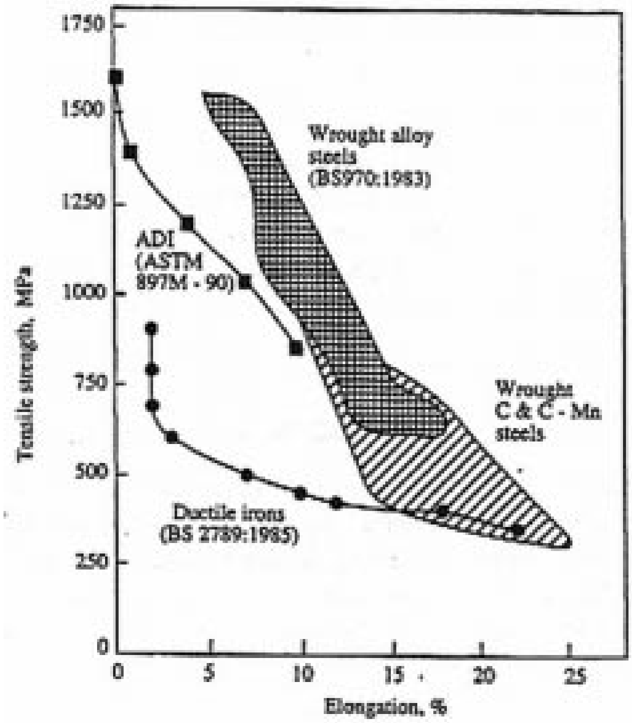

Fig. 1. Comparison of tensile properties of ductile iron and forget steels [1-3]

Particle hardening belongs to the most effective strengthening mechanism in metals. It was shown (Ref. [8]) that strengthening is obtained by "slip interference" within the grains due the "keying effect" of the dispersed hard particles, and that the effect increases with the fineness of subdivision of the hard constituent (for a given amount of the phase), further suggesting that the strengthening reaches the maximum at an intermediate particle size. With a given amount of precipitate, lager particles would have less-hardening effect because there would be fewer keys. In steels and in age-hardening non-ferrous alloys the particles are formed by precipitation from supersaturated solid solution, and this constitutes by far the most commonly used technique for producing a dispersed second phase.

The purpose of our research is to develop a method of nanoparticles synthesis in ferritic matrix of ductile cast iron, which are supposed to increase its strength without affecting notably its ductility. It is believed that the present study makes possible to work out new grades of ductile iron assigned to application to low temperatures, e.g. as parts of wind power-station, ships or oil platforms, used in an arctic climate.

2. Experimental procedure

The examined ductile iron with a target chemical composition (wt. %) of: C = 3.25%, Si = 3.0%, Mn = 0.13%, P = 0.024%. S = 0.013%, V = 0.08%, Ti = 0.013%, Nb = 0.001%, Mg = 0.04% and Fe – bal. was melt in a middle frequency induction furnace with 15 kg capacity. As a charge, the pig iron and ferro-vanadium 80 wt. % were used. The spheroidization was performed by bell method, i.e. overheating the bath to 1500°C, adding Fe-Si-9% Mg alloy and then applying an inoculation process by means of Foundrisil 75 containing Si = 73-78%, Ca = 0.75-1.25%, Ba = 0.75-1.25%, Al = 0.75-1.25%, Fe – bal. in quantity of 0.8% to all weight of the bath. The ductile iron was poured into the Y-shape sand molds.

The samples (15×15×6 mm) were cut out from Y-shape casting keel blocks and were capsulated in quartz tubes under vacuum for protection against their oxidation during further heat treatment. Two types of annealing heat treatment were used. Single stage annealing was used to study the dissolution kinetics of vanadium carbides. In this case, samples were subjected to the soaking at 1080°C for 1, 10 and 100 h, and at 1095°C for 100 h and quenching to room temperature. The as-cast as well as soaked and quenched samples were then prepared for optical metallography. Metallographic sections were mechanically polished and etched with the following solution (at boiling point) 28 g NaOH, 4 g KOH, 4 g picric acid and 200 g water. This etchant allowed vanadium carbide to be readily distinguished from other phases in as-cast samples. The change in volume fraction of coarse particles was determined using a Leica QWin quantitative analyzer, taking care to count sufficient number of particles to obtain statistically reliable results.

The reprecipitation of carbides was studied on samples annealed by two-stage process in which samples were subjected to the following heat treatment: soaking at 1095°C for 100 h, cooling down to 640°C, holding on at this temperature for 16 h and subsequently furnace cooling to room temperature. Such a heat treatment was aimed at producing VC dispersed precipitates. Following heat treatment the samples were examined by light, transmission and scanning electron microscopy (LM, TEM and SEM). The 3 mm disks for the TEM investigation were cut out from the bulk material while for LM and SEM study metallographic sections were mechanically polished in order to reveal compositional contrast (Z-contrast) formed by back scattered electrons (BSE). Light and scanning microscopy was aimed at revealing the distribution of graphite and other big particles. The 3 mm disks were ground down on sand papers and then electropolished by a Struers jet electropolisher in a solution of perchloric acid in acetic acid (1:10) at 10°C. Afterwards the disks were additionally thinned in an ion mill. Since perforation of disks during electropolishing resulted from kicking out big graphite particles a fairly thick specimen around the holes remained and thus the additional thinning was performed in an ion mill. In addition to thin foil examination carbon extraction replicas were prepared in order to analyze precipitates forming upon heat treatment.

The TEM investigation was carried out by means of a JEOL 2010 ARP analytical scanning transmission electron microscope operating at acceleration voltage of 200 kV. Imaging was performed by conventional transmission mode while for chemical analysis (X-ray Energy Dispersive Spectroscopy – EDS) the nanoprobe mode was utilized. The nanoprobe mode enabled to obtain electron probes approaching a few nanometers in diameter (practically about 10 nm because at smaller electron probes the number of X-ray counts is usually too low for analysis). The EDS analysis was performed by Oxford-Link system attached to the microscope. The Oxford-Link system was equipped with Si(Li) detector. This system detects all elements down to boron. In order to examine the crystallography of precipitates the Selected Area Diffraction (SAD) patterns analysis was also performed.

3. Results and discussion

The metallographic investigation of as-cast samples shows, that the microstructure contains nodular graphite and ferrite matrix with the large particles identified by EDS (in SEM) as primary vanadium-rich carbides VC (Fig. 2). The average size of primary vanadium-rich carbides was estimated on approx. 2 μm and volume fraction on 0.24%. The globular graphite particles were uniformly spread out through the sample (Fig. 3). The primary vanadium carbides, on the other hand, were sited rather within interdendritic areas (Fig. 2). The application of compositional contrast in SEM revealed also big Ti-rich particles (Fig. 4) being attributable to the unintended presence of 0.013% Ti in cast iron. However, the distribution of such particles was highly nonuniform; the particle formed colonies in one part of sample while in other parts such precipitates were absent (Fig. 4).

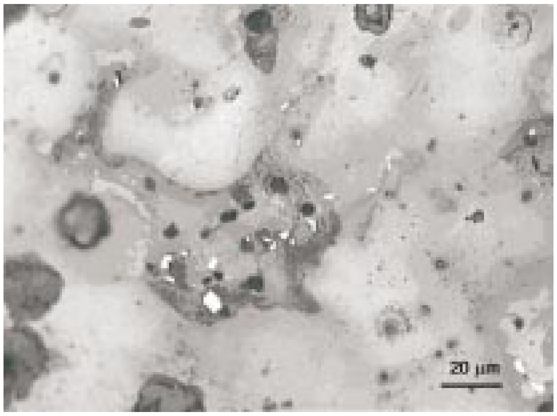

Fig. 2. A typical as-cast microstructure (vanadium-rich carbides are white)

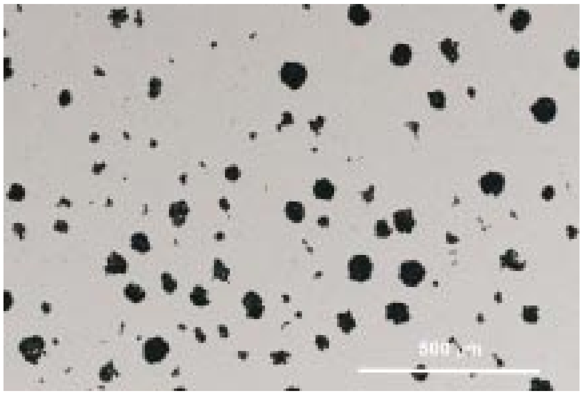

Fig. 3. Distribution of graphite particles; SEM BSE

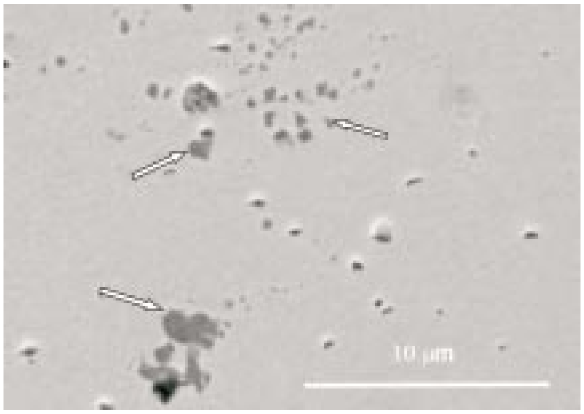

Fig. 4. Colonies of Ti-rich particles marked by arrows; SEM, compositional contrast

The presence of Ti-rich particles was also confirmed by examination of replicas in TEM (Fig. 5). The crystal structure of such particles, determined from selected area diffraction patterns, was f.c.c. and the measured lattice parameter 421.1 pm. Thus these particles were identified as titanium nitrides TiN (the lattice parameter for TiN found in Ref. [9] was 432.8 pm). The other type of particles found in as-cast microstructure constituted particles enriched with Mg and O (Fig. 6a,b); they probably appears as a consequence of inoculation process with Mg. The crystal structure of this phase was not identified yet. The size of these particles was similar to those enriched with vanadium or titanium but volume fraction seemed to be much smaller.

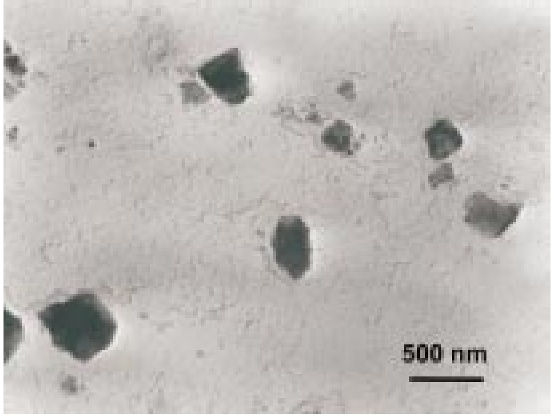

Fig. 5. TiN particles on a carbon replica

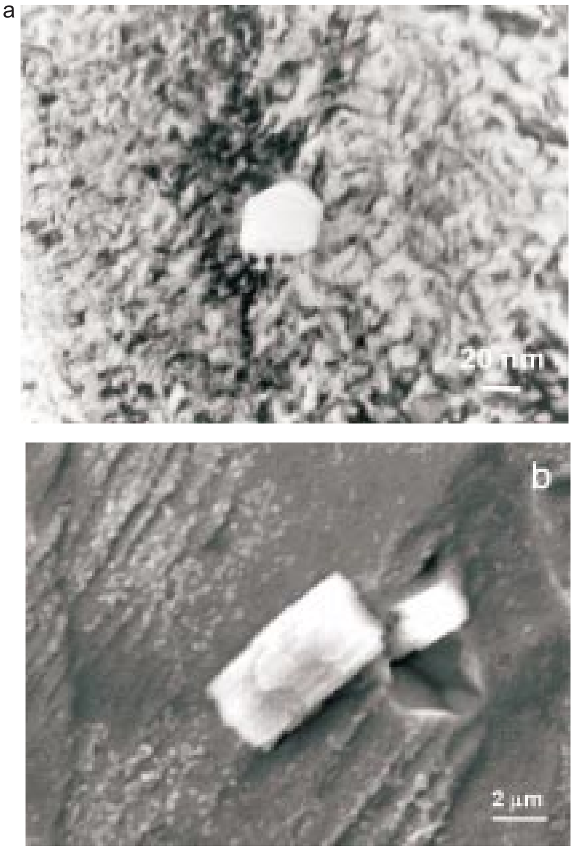

Fig. 6. Examples of a Mg-rich particle, a) TEM and b) SEM

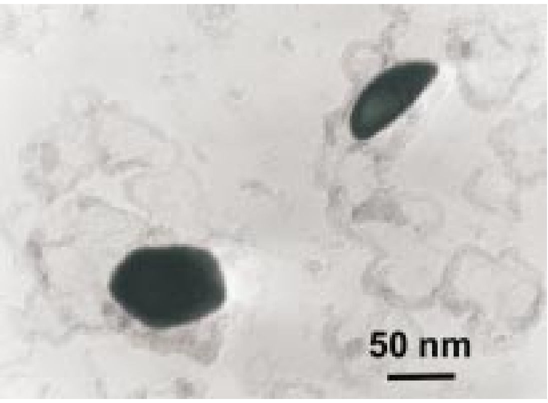

Fig. 7. VC particles on a carbon replica

Light as well as scanning microscopy investigation of heat treated samples showed that during soaking the size and volume fraction of V-rich particle changed, while other types of particles (Ti-rich and Mg-rich) were almost unaltered. Table shows heat treatment conditions matched with the fraction of vanadium carbides. The carbide volume fraction changed from 0.24% at as-cast condition to 0.11% after soaking at 1095°C for 100 h. At the same time the particle size changed from about 2 μm to about 1 μm.

Ageing at 640°C brought about reprecipitation of dispersed vanadium-rich carbides. Examination of carbon replicas permitted the small precipitates to reveal (Fig. 7). EDS analysis showed that vanadium was the main constituent element in these particles. The carbon content was not analyzed since a strong C peak from carbon support film overwhelmed the intensity coming from carbon tied to vanadium. The particle size fell into the range 10-100 nm with an average of 50 nm. The particles had usually rounded shape but sporadically small rods about 200 nm long were also observed. SADP analysis unequivocally showed that all V-rich particles exhibited f.c.c. crystal structure and thus were identified as VC-type carbide. The lattice parameter calculated from SAD pattern was 416 pm and was very close to that one cited in literature [9] (416.6 pm).

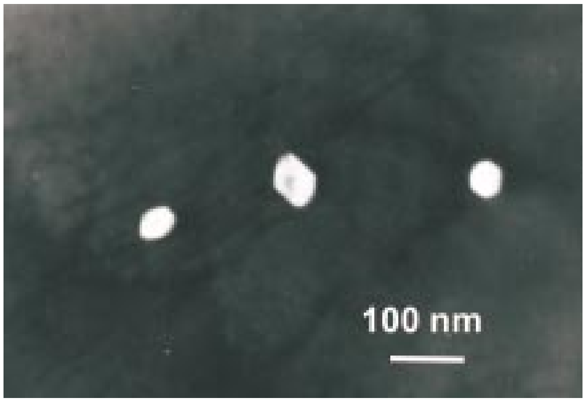

Fig. 8. TEM dark field image of VC precipitates

Thin foil examination confirmed results obtained from replicas. Predominant dispersed particles were identified by EDS and SADP as vanadium carbides (Fig. 8). Many of them were found on dislocations (Fig. 9). Titanium rich particles were found as well (Fig. 10). Investigation of thin foils also provided evidences for the presence of Mg-rich particles (Fig. 11). The size of these particles changed within broad limits: from a few nanometers to about 1 μm, however, majority of these particles exhibited size on the order of V-rich precipitates. The crystal structure of this phase has not been determined yet due to difficulties in obtaining sufficient

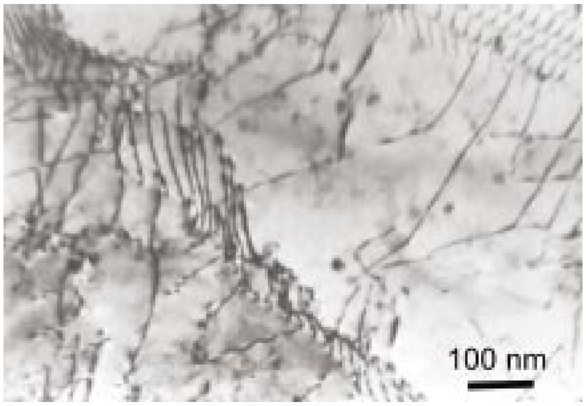

Fig. 9. VC precipitates on dislocations; TEM

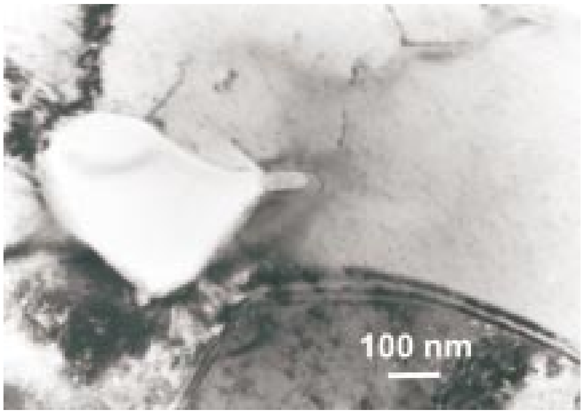

Fig. 10. TEM image of a TiN particle (white)

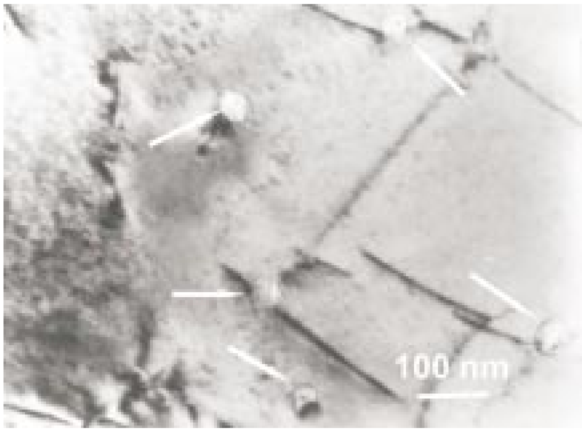

Fig. 11. Distribution of Mg-rich particles marked by arrows and extremely small precipitates on the left side of micrograph

number of SAD patterns (the particles appear almost out of diffraction condition irrespective of the specimen tilt).

The other important finding revealed by TEM was the presence of extremely small precipitates which occurred in all examined areas (Fig. 11, 12). The precipitates gave rise to typical type of contrast characteristic for large strain fields. Because of this strong contrast extending around precipitates, the particle size could not be determined precisely but it likely falls into the range 1-10 nm. The contrast appeared only at some specimen positions (specimen tilt angle) and produced some extra spots on SAD patterns (Fig. 12b). These relatively strong extra spots along with strain field contrast throughout the samples suggests fairly large volume fraction of these precipitates as well as their coherency with iron matrix. However, the data collected from the TEM investigation turned out to be not sufficient for identification of these precipitates.

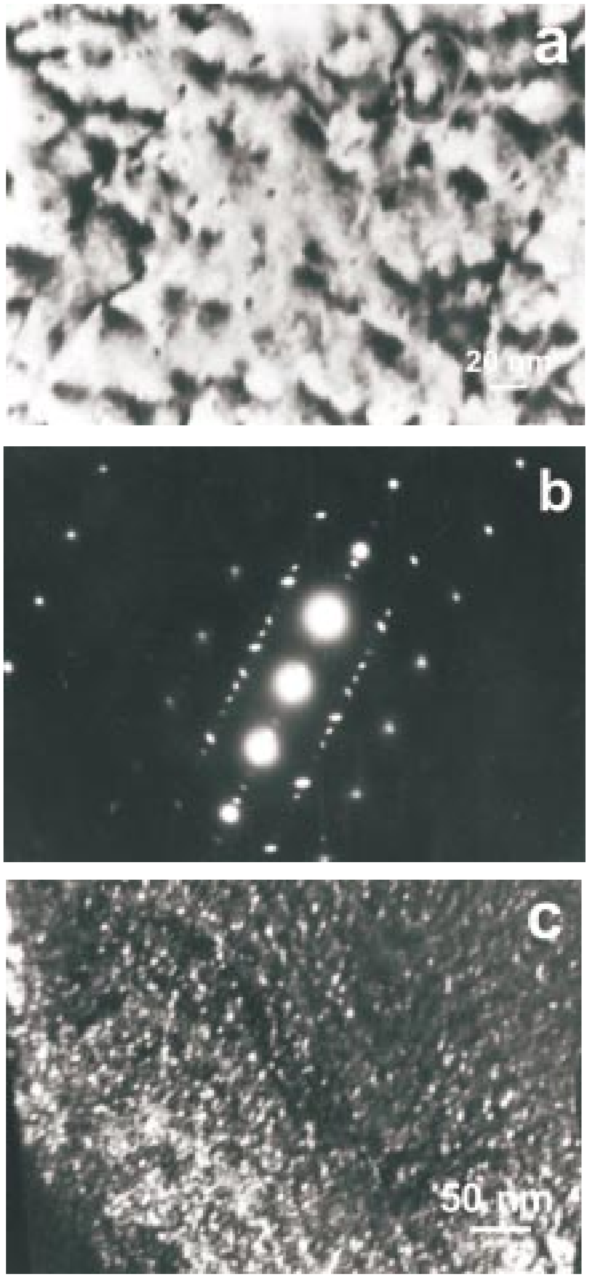

Fig. 12. a) Bright field image of dispersed precipitates; b) corresponding SAD pattern with extra spots coming from precipitates; c) dark field image of precipitates

When samples are heated up to 1080 or 1095°C, the ferritic matrix transforms to the austenitic one, and during the heating process the fraction and size of primary carbides decreased (Table), what confirms its solubility in the matrix. As a consequence, the carbon and vanadium contents in austenite rise up. According to Haskell [10], a maximum solubility of these elements in austenite increases with temperature. However, in samples austenitized at 1080 and 1095°C for 100 h, the coarse primary vanadium-rich carbides were still present. Isolated large primary vanadium carbides have negative effect on plasticity and impact toughness properties of ductile iron. It can be possible to claim, that during the first step of heat treatment it occurs an advantageous effect of their partial elimination. At the temperature of austenitization there is a certain maximum solubility of vanadium in austenite, above which the primary carbides do not further dissolve and this solubility should be the criterion of vanadium selection in cast iron. According to the first investigation, this maximum of vanadium content is approx. 0.04%.

TABLE

Soaking conditions and volume fraction of vanadium-rich carbides

No.	Time, h	Temperature, °C	Fraction of V-rich carbides, %
0	0	as-cast	0.24
1	1	1080	0.23
2	10	1080	0.18
3	100	1080	0.15
4	100	1095	0.11

During cooling the samples to the temperatures of austenite → ferrite transformation, the austenite become oversaturated with carbon and vanadium. A part of excessive carbon diffuses to graphite nodule increasing its diameter, and remaining part of carbon, together with solute vanadium, precipitate as vanadium-rich carbides. The precipitation of vanadium carbides in cast iron structures was also found in other works [7, 11].

4. Conclusions

1. It is feasible to age-harden ductile iron by introducing vanadium and heat treating close to solidus temperature for long time (100 h) and then ageing at elevated temperature (640°C).

2. The as-cast microstructure of examined ductile iron contains coarse primary vanadium carbides with approx. size of 2 μm and 0.24% fraction. During annealing at temperatures 1080-1095°C for 100 h the size and area fraction of these carbides decrease to approx. 1 μm and to 0.11%, respectively.

3. The SEM, thin foils and replicas investigation of ductile iron after two-stage heat treatment shows that the following types of particles were found in ferrite:

- big vanadium-, titanium-, magnesium-rich particles with approx. 2 μm size,
- vanadium carbides with an average size of 50 nm; the particles had usually rounded shape but sporadically small rods about 200 nm long were also observed. Many of them were found on dislocations,
- particles enriched with Mg and O with approx. 40 nm size,
- extremely small (approx. 1 nm size) precipitates which occurred in all examined areas.

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REFERENCES

[1] British standard specification for spheroidal graphite or nodular graphite cast iron, BS 2789, 1985.

[2] British standard specification for wrought steels for mechanical and allied engineering purposes, BS970, Part 1, 1983.

[3] American Society for Testing Materials: Standard specifications for austempered ductile iron castings (metric) ASTM, 1990.

[4] K. Bunin, J. Malinoczka, J. Taran, Metallurgia, Moskwa, 1969.

[5] G. Lesoult, J. Lacaze, Physical Metallurgy of Cast Iron, Scitec publications, Switzerland, 1997.

[6] X. Shen, S. Harris, B. Noble, Material Science and Technology, **11**, 893 (1995).

[7] M. Rezvani, R.A. Harding, J. Cambell, International Journal of Cast Metals Research, **11**, 401 (1999).

[8] J.W. Martin, Precipitation Hardening, Butterworth Heinemann, Oxford, 1998.

[9] H.J. Goldschmidt, Interstitial Alloys, Butterworth, 1967.

[10] D.R. Haskell, Introduction to Metallurgical Thermodynamics, 2nd edition, Hemisphere, 1981.

[11] J. Dawson, Vanadium in cast iron, 49 International Foundry Congress, Chicago, Apr. 1982.