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ATOM PROBE FIELD ION MICROSCOPY CHARACTERIZATIONS OF VVER STEELS

M.K. Miller, R. Jayaram, P.J. Othen+ and G. Brauer*

Metals and Ceramics Division,
Oak Ridge National Laboratory,
Oak Ridge, TN 37831-6376, USA

+Department of Materials, Oxford University,
Oxford, OX1 3PH, UK

**KAI Inc. Berlin at Research Center Rossendorf Inc.,*
Dresden, Germany

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Abstract

An atom probe field ion microscopy (APFIM) characterization of Soviet types 15Kh2MFA Cr-Mo-V (VVER 440) and 15Kh2NMFA Ni-Cr-Mo-V (VVER 1000) pressure vessel steels has been performed. Field ion microscopy has revealed that the lath boundaries in unirradiated VVER 440 and VVER 1000 steels are decorated with a thin film of brightly-imaging molybdenum carbonitride precipitates and some coarser vanadium carbides. Atom probe analysis has revealed significant enrichments of phosphorus at the lath boundaries.

Introduction

One of the main concerns of a nuclear power system is the mechanical integrity of the pressure vessel over its service life. It is extremely important to understand and be able to predict the changes in the microstructure that occur during service since the reactor is typically designed to operate at approximately 290°C for several decades. In order to determine these changes, the microstructures of both pre-irradiated and post-irradiated material must be fully characterized. Experience with these types of complex commercial materials has clearly demonstrated that no single microanalytical technique provides a sufficient or complete description of the microstructure. Therefore, multiple direct and indirect techniques must be used. These techniques include optical microscopy to identify the coarse features in the microstructure such as inclusions and characterize the general microstructure and high resolution techniques such as transmission electron microscopy (TEM) and atom probe field ion microscopy (APFIM) to characterize the fine scale and atomic scale features. In addition to these direct techniques, indirect methods such as small angle neutron diffraction (SANS) and positron annihilation (PA) can provide valuable information. However, both these indirect methods rely on the direct information provided particularly by the atom probe field ion microscope to ensure correct interpretation of their data.

Over the last few years, several studies have been performed where these multiple techniques have been applied to characterize the microstructures of pressure vessel steels used in nuclear reactors. However, most of the steels studied to date have been of the same general type and therefore their compositions have not differed significantly from one another. Therefore, to ensure that the features found in these pressure vessel steels are general in nature and not specific to a particular class of steel, it is advantageous to characterize different types of steels. One significantly different candidate is the high strength low alloy chromium-molybdenum-vanadium type of steel used in Soviet VVER 440 and VVER 1000 nuclear reactors.

The specifications for these chromium-molybdenum-vanadium 15Kh2MFA and 15Kh2NMFA steels (1) together with the ASTM specification for A533 type B steel (2) are given in Table I. The chromium and vanadium levels are lower and the nickel level is significantly higher in the 15Kh2NMFA steel specification than in the 15Kh2MFA steel specification. The range in molybdenum level is slightly lower in the 15Kh2NMFA steel specification. The carbon, manganese and silicon specifications are the same in both steels. It should also be noted that the maximum permissible levels for phosphorus and sulphur are lower in the 15Kh2NMFA steel. The phosphorus and sulphur specifications are also lower than those quoted (0.035% P max. and 0.040% S max.) in the ASTM standard specification for A533 type B pressure vessel steel. However, the currently available commercial limits for A533 type B steel (0.012% P and 0.015% S) are lower than both in the ASTM specification and in the steels used in the VVER 440 and VVER 1000 reactors (1). It should also be noted that both the Soviet and Western types of steel contain copper and other elements as impurities.

Table I. Specifications of 15Kh2MFA (VVER 440) and 15Kh2NMFA (VVER 1000) chromium-molybdenum-vanadium and A533 type B pressure vessel steels. The values are given in weight percent.

Element	15Kh2MFA (VVER 440)	15Kh2NMFA (VVER 1000)	A533 type B
Chromium	2.5 - 3.0	1.3 - 2.3	-
Molybdenum	0.6 - 0.8	0.5 - 0.7	0.45 - 0.60
Vanadium	**0.25 to 0.35**	**0.10 max.**	**-**
Nickel	**0.4 max.**	**1.0 - 1.5**	**0.40 - 0.70**
Manganese	0.3 - 0.6	0.3 - 0.6	1.15 -1.50
Silicon	0.17 - 0.37	0.17 - 0.37	0.15 - 0.40
Carbon	0.13 - 0.18	0.13 - 0.18	0.25 max.
Phosphorus	0.025 max.	0.020 max.	0.035 max.
Sulphur	0.025 max.	0.020 max.	0.040 max.

Since the nominal compositions of these chromium-molybdenum-vanadium steels are significantly different from the pressure vessel steels previously examined with the atom probe field ion microscope, the main emphasis of the first phase of this project is to determine the similarities and differences between these Soviet type steels and their Western counterparts such as A533 type B and A302B type steels in their pre-irradiated condition. It is planned to extend this project to examine of neutron-irradiated material in the next phase of this project. It should be noted that this atom probe field ion microscopy investigation is part of a larger multi-national program involving other techniques including transmission electron microscopy (3), small angle neutron scattering (4) and positron annihilation (5-8).

Experimental

The compositions of the two 15Kh2MFA Cr-Mo-V steels (VVER 440) and one 15Kh2NMFA Ni-Cr-Mo-V steel (VVER 1000) used in this study are given in Table II. These three steels were fabricated in 8 kg laboratory melts and differ primarily in the copper, nickel and vanadium contents. The copper and vanadium levels are significantly lower and the nickel level is significantly higher in the VVER 1000 steel. The two 15Kh2MFA steels differ primarily in the copper level. The copper level in the VVER 440 C steel is substantially lower (0.12% Cu) than in the VVER 440 E (0.30%Cu).

Table II. Composition of the three VVER pressure vessel steels used in this investigation. The balance of these compositions is iron and the results are given in atomic percent.

Element	VVER 440 C	VVER 440 E	VVER 1000
Chromium	2.51	2.77	2.48
Molybdenum	0.41	0.39	0.34
Vanadium	**0.25**	**0.33**	**0.11**
Copper	**0.12**	**0.30**	**0.05**
Nickel	**0.07**	**0.07**	**1.15**
Manganese	0.28	0.36	0.41
Cobalt	0.01	0.01	0.01
Silicon	0.24	0.36	0.49
Carbon	0.67	0.67	0.79
Nitrogen	0.07	0.07	-
Phosphorus	0.032	0.032	0.016
Sulphur	0.048	0.052	0.009

Prior to examination in the atom probe field ion microscope, the steels were heat treated. The 15Kh2MFA (VVER 440) steels were austenitized for 1 h at 1000°C, oil quenched and then aged for 10 h at 700°C and air cooled to room temperature. The 15Kh2NMFA (VVER 1000) steel was austenitized at 920°C, water quenched and then aged at 650°C, air cooled, aged 25 h at 620°C plus 20 h at 650°C and finally furnace cooled to room temperature. All materials were examined in the unirradiated condition.

The microstructural characterizations were performed in the Oak Ridge National Laboratory (ORNL) energy-compensated atom probe field ion microscope (9). Full details of this technique and its applications may be found elsewhere (10-12). All field ion images were recorded with neon as the imaging gas and with a specimen temperature of 70 K. Atom probe analyses were conducted with a specimen temperature of 60 K to minimize preferential evaporation and retention artifacts (10). Transmission electron microscopy characterizations were performed with Philips EM400T/FEG and CM30 electron microscopes operated at 100 and 300 keV, respectively.

Results and Discussion

The general microstructures of the 15Kh2MFA (VVER 440) and 15Kh2NMFA (VVER 1000) steels are shown in the optical micrographs in Figs. 1 and 2, respectively. The microstructure of the 15Kh2MFA Cr-Mo-V steels was found to be tempered martensite and approximately 10% bainite whereas the 15Kh2NMFA Ni-Cr-Mo-V steel was a mixture of tempered martensite and approximately 30% bainite. The prior austenite grain boundaries are clearly distinguished in the micrograph of VVER 1000 steel shown in Fig. 2. The details of these microstructures have been discussed previously by Törrönen (3) and therefore will not be presented here. A high number density of coarse precipitates and some inclusions were also evident in these optical micrographs.

Higher magnification micrographs of the general microstructure of the 15Kh2MFA (VVER 440) steel taken in the transmission electron microscope are shown in Fig. 3. The coarse precipitates were identified from selected area electron diffraction as M_7C_3 carbides. These carbides were blocky and exhibited a characteristic faulted structure as shown in Fig. 4. The size of these precipitates ranged from 60 to 300 nm in the VVER 440 E material and from 60 to 500 nm in the VVER 1000 steel. These carbides were observed both at grain boundaries and in the interior of the grains. Energy dispersive x-ray analysis with the use of the transmission electron microscope revealed that the metallic content of these chromium-rich carbides in the VVER 440 E steel was approximately 40 to 60 at. % Cr, 3.1 to 3.5% V, 1.5 to 2.6% Mo, balance Fe. Many of the field ion specimens exhibited darkly-imaging carbides in the images. An atom probe analysis of one of these precipitates in the VVER 440 E steel revealed a composition of 37.6 ± 1.7 at. % Cr, 22.7 ± 1.4% Fe, 3.5 ± 0.6% Mo, 2.7 ± 0.6% V, 0.6 ± 0.3% Mn, and 33.0 ± 1.6% C. No nitrogen, nickel, silicon or copper was observed in this precipitate. This composition and imaging behavior is consistent with a chromium-rich M_7C_3 carbide. The size of this coarse precipitate could not be estimated in the field ion image since it exceeded the field of view of the microscope. In addition to these coarse carbides, some finer (~10 nm diameter) approximately spherical MC carbides were also observed by the transmission electron microscope in the matrix of the VVER 440 E steel as shown in Fig. 5.

The compositions of the matrix of the VVER 440 E and VVER 1000 steels as determined in the atom probe are summarized in Table III. It should be noted that these compositions are from the matrix and do not contain contributions from small precipitates or the boundaries. Due to the fragile nature of these materials, the compositions quoted are a consolidation of the data obtained from several specimens into a single composition for each material. The error bars are based solely on the counting statistics of the individual atoms. These preliminary results indicate that the matrix of both steels is significantly depleted in chromium and vanadium and is consistent with the presence of the chromium-rich M_7C_3 carbides and vanadium carbide MC precipitates. A significant depletion of copper was also observed in the matrix. An energy dispersive x-ray analysis with the use of the transmission electron microscope revealed an local enrichment of copper at a grain boundary and suggests that some copper precipitates had formed. This behavior is consistent with the relatively long aging time at 600 to 700°C, the solubility limit of copper in the matrix at these temperatures (13), and with the copper precipitation observed at grain boundaries in A533B type steels during the stress relief heat treatment (11,12,14). Further investigation is required to confirm this observation.

Table III. Composition of the matrix determined by atom probe microanalysis. The balance of these compositions is iron and the results are given in atomic percent.

Element	VVER 440 E	VVER 1000
Chromium	1.59 ± 0.08	0.88 ± 0.08
Molybdenum	0.44 ± 0.05	0.39 ± 0.05
Vanadium	0.20 ± 0.03	0.03 ± 0.01
Copper	0.04 ± 0.02	0.01 ± 0.01
Nickel	0.17 ± 0.03	1.29 ± 0.10
Manganese	0.17 ± 0.03	0.47 ± 0.06
Cobalt	0.02 ± 0.01	0.01 ± 0.01
Silicon	0.22 ± 0.03	0.84 ± 0.08
Phosphorus	0.005 ± 0.005	0.02 ± 0.01

A field ion micrograph of the VVER 440 C steel is shown in Fig. 6. These steels exhibited good quality images with many crystallographic planes evident (10). The brightly imaging spots in this micrograph are due primarily to molybdenum and silicon atoms in random solid solution in the matrix. All three of these materials proved to be extremely fragile in the field ion microscope and this behavior is generally associated with a brittle material.

A pair of field ion micrographs of a lath boundary in the VVER 440 E steel is shown in Fig. 7. The second micrograph was taken after a few atomic layers of material were removed from the specimen to reveal a different segment of the boundary. It is evident from both these micrographs that this lath boundary was decorated with an almost continuous brightly-imaging film of ultrafine precipitates.

A section of another boundary between two larger brightly-imaging precipitates in the VVER 440 E material is shown in Fig. 8. These brightly-imaging precipitates were lenticular in shape and had their major axis in the plane of the boundary. The thickness of these precipitates was approximately 10 nm. Atom probe selected area analysis identified these coarser precipitates as vanadium carbonitrides with a carbon to nitrogen ratio of approximately 2:1. In addition to vanadium, the metallic content of these V(C,N) precipitates contained substanitally less but still significant amounts of molybdenum, chromium and iron. This section of the boundary adjacent to these precipitates was also decorated with brightly-imaging ultrafine precipitates but the number density and coverage were significantly lower than in the previous example (Fig. 7).

A sequence of field ion images of a lath boundary in the 15Kh2NMFA (VVER 1000) steel is shown in Fig. 9. This boundary also exhibited the brightly-imaging precipitates although at a slightly lower coverage than in the boundary in the VVER 440 E material. A second sequence of field ion images of a section of a lath boundary in the vicinity of a coarse brightly-imaging precipitate is shown in Fig. 10. The extreme edge of this precipitate is at the edge of micrograph shown in Fig. 10(a). This sequence of micrographs was recorded after the removal of approximately 0.2 nm between each frame. As in the previous example in the VVER 440 E steel, a slightly lower coverage of brightly-imaging precipitates is evident near the coarse carbide.

Atom probe selected area analysis of these brightly-imaging precipitates in both 15Kh2MFA and 15Kh2NMFA materials revealed molybdenum, carbon and nitrogen atoms indicative of a molybdenum carbonitride precipitate. The extremely small size of the precipitates in this film (< 0.5 nm) precluded an accurate analysis of their composition. This precipitation is similar to that previously observed in both unirradiated (and neutron-irradiated) A533B and A302B steels (11,12,14,15). However, the extent of the coverage of these precipitates on the boundaries appears to be significantly higher in these VVER steels.

The levels of vanadium measured by the atom probe were similar for the matrix and the boundary. Both these values were slightly lower than the bulk composition as a consequence of the presence of the fine vanadium carbonitrides and the M_7C_3 precipitates. In contrast to the A533B type steels, no enrichment of nickel was observed at the boundaries in either VVER steel. The level of manganese was slightly higher (2.1 times the matrix value) at the boundary in the VVER 440 E steel but was not statistically different in the VVER 1000 steel. Similar small enrichments have been measured in A533B steels (12).

Atom probe analysis also revealed the presence of extremely high levels of phosphorus at these boundaries. Analysis of the boundary in the VVER 440 E steel shown in Fig. 7 revealed a phosphorus enrichment of approximately 52 times that of the matrix. Local enrichments of phosphorus of approximately 15.6 times the matrix analysis were measured for the boundary in the VVER 1000 steel shown in Fig. 9. However, a more extensive analysis of this boundary revealed some local inhomogeneities in the phosphorus level and yielded a slightly lower average enrichment of approximately 8.6 times the matrix level. The difference in enrichment measured between the two VVER alloys is probably related to the different concentrations of phosphorus in the initial bulk materials: the VVER 1000 steel having both a lower enrichment and a lower bulk level of phosphorus. These levels of phosphorus were substantially higher that those previously measured (12) in unirradiated A533B steels (typically 3.5x) or even neutron-irradiated A533B steel (typically 12.5x: fluence 1 x 10^{23} m^{-2} [E>1MeV]). It should be noted that all these enrichment factors assume that the phosphorus was constant over the entire volume collected. Despite the extremely small size of the probe aperture in the atom probe (typically 1 to 2 nm diameter), the volume analyzed will contain a substantial contribution from the surrounding matrix. If a width of a monolayer is assumed for the thickness of the segregated layer, then the actual enrichment factors should be approximately 5 times the values quoted above. These substantial phosphorus enrichments should be a serious cause for concern since it has been well established that phosphorus is a primary cause of temper embrittlement in steels.

Conclusions

A characterization of Soviet types 15Kh2MFA Cr-Mo-V and 15Kh2NMFA Ni-Cr-Mo-V pressure vessel steels that are used in VVER 440 and VVER 1000 reactors has been performed. Transmission electron microscopy revealed the presence of coarse blocky chromium-rich M_7C_3 carbides and 10 nm diameter vanadium carbides (MC). Field ion microscopy has revealed that the lath boundaries in these unirradiated steels are decorated with a ultrathin film of brightly-imaging molybdenum carbonitride precipitates and some coarser vanadium carbonitrides. Atom probe analysis has revealed significant enrichments of phosphorus at the lath boundaries.

Acknowledgments

The authors would like to thank K.F. Russell for her technical assistance. This research was sponsored by the Division of Materials Sciences, U.S. Department of Energy, under contract DE-AC05-84OR21400 with Martin Marietta Energy Systems, Inc. and through the Postgraduate Research Program administered by Oak Ridge Institute for Science and Education.

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Fig. 1. Optical micrographs of the 15Kh2MFA (VVER 440 C and E) steels. The microstructure is a mixture of tempered martensite and ~10% bainite. (Etchant: 2% nital).

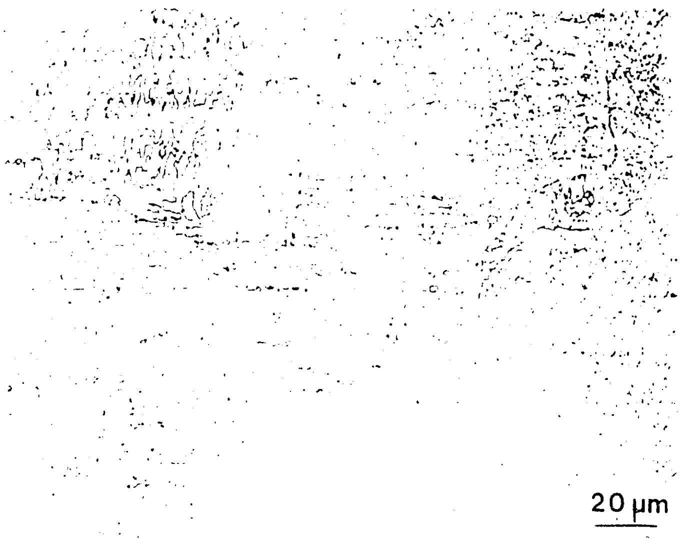

Fig. 2. Optical micrograph of the 15Kh2NMFA (VVER 1000) steel. The microstructure is a mixture of tempered martensite and ~30% bainite. (Etchant: 2% nital).

Fig. 3. Transmission electron micrographs of the general microstructure of the 15Kh2MFA (VVER 440 C and E) steels showing the coarse blocky M_7C_3 precipitates.

Fig. 4. Transmission electron micrograph of the general microstructure of the 15Kh2NMFA (VVER 1000) steel. The faulted nature of the M_7C_3 precipitates is evident.

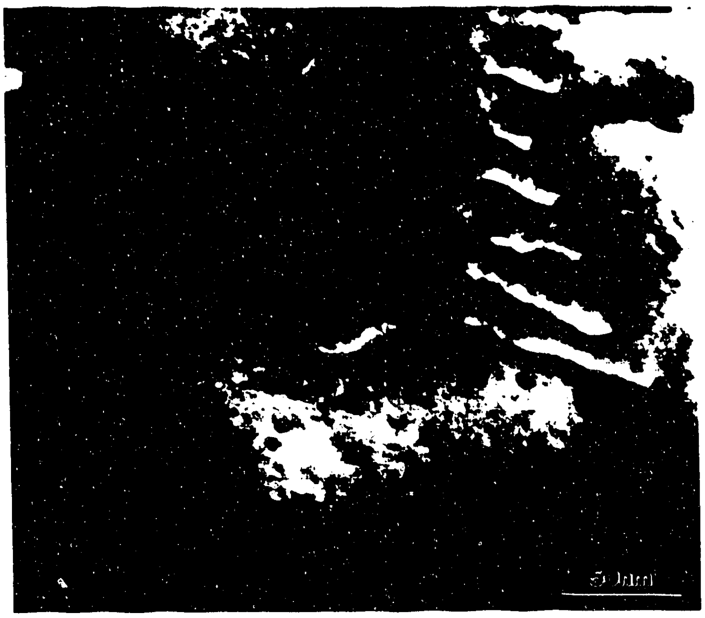

Fig. 5. Transmission electron micrograph of 10-nm-diameter spherical vanadium carbide precipitates in the matrix of the VVER 440 E steel.

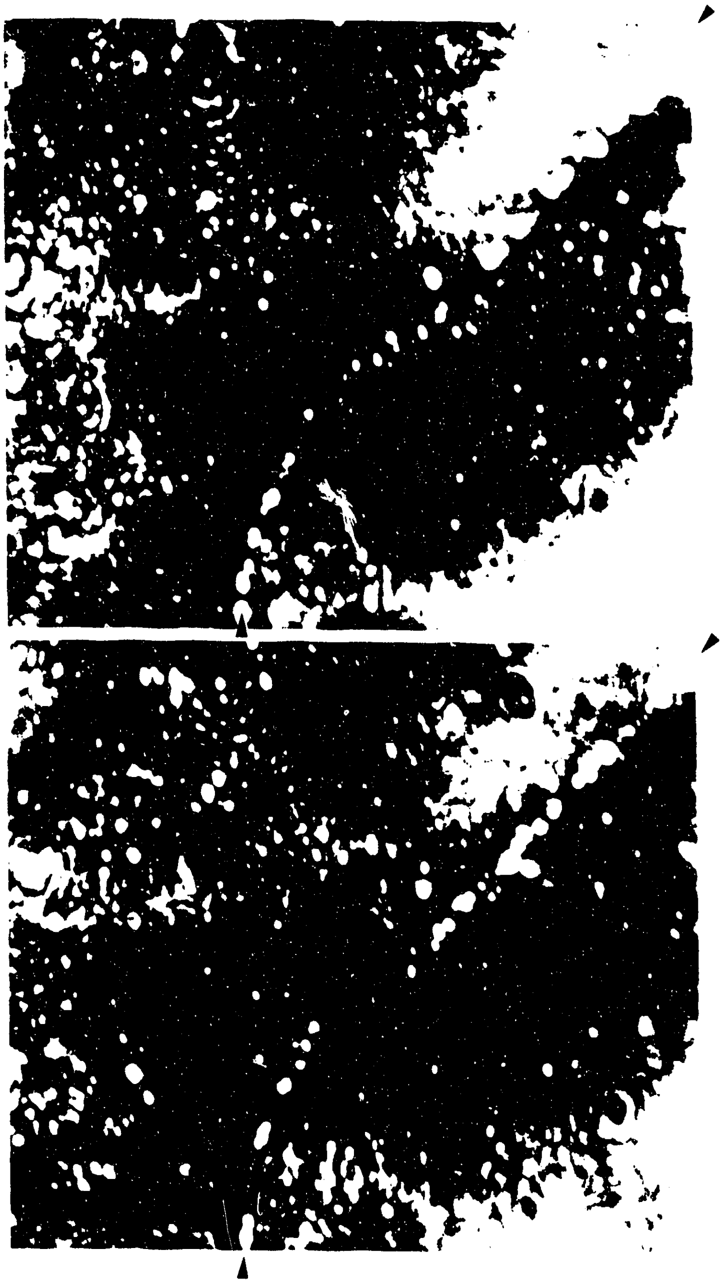

Fig. 7. Field ion micrographs of a lath boundary in the VVER 440 E steel. The boundary is decorated with a thin brightly-imaging film of molybdenum carbonitride precipitates.

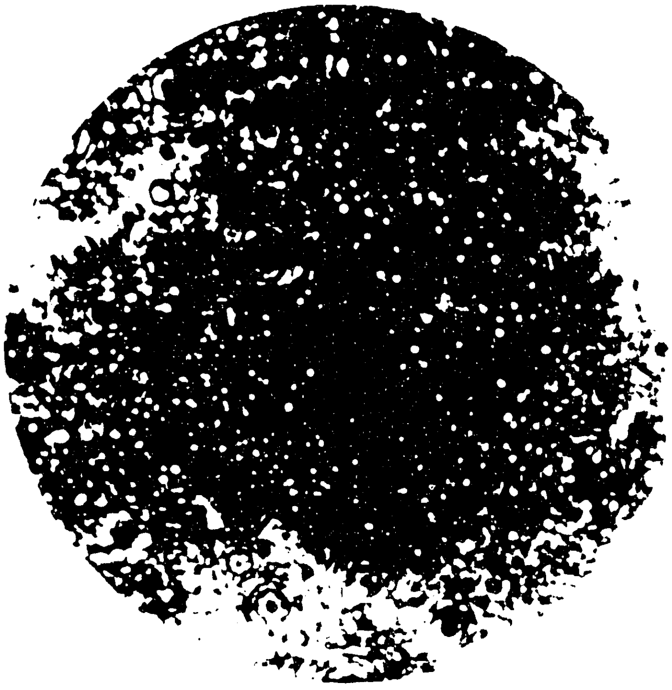

Fig. 6. Field ion micrograph of the matrix of the VVER 440 C steel. The bright spots evident in this micrograph are molybdenum and silicon atoms.

Fig. 8.Field ion micrographs of a section of lath boundary between two 10-nm-thick lenticular brightly-imaging vanadium carbonitride precipitates in the VVER 440 E material. The boundary is decorated with some ultrafine isolated brightly-imaging molybdenum carbonitride precipitates.

Fig. 9. Field ion micrographs of a lath boundary in the VVER 1000 steel. The boundary is decorated with a thin brightly imaging film of molybdenum carbonitride precipitates.

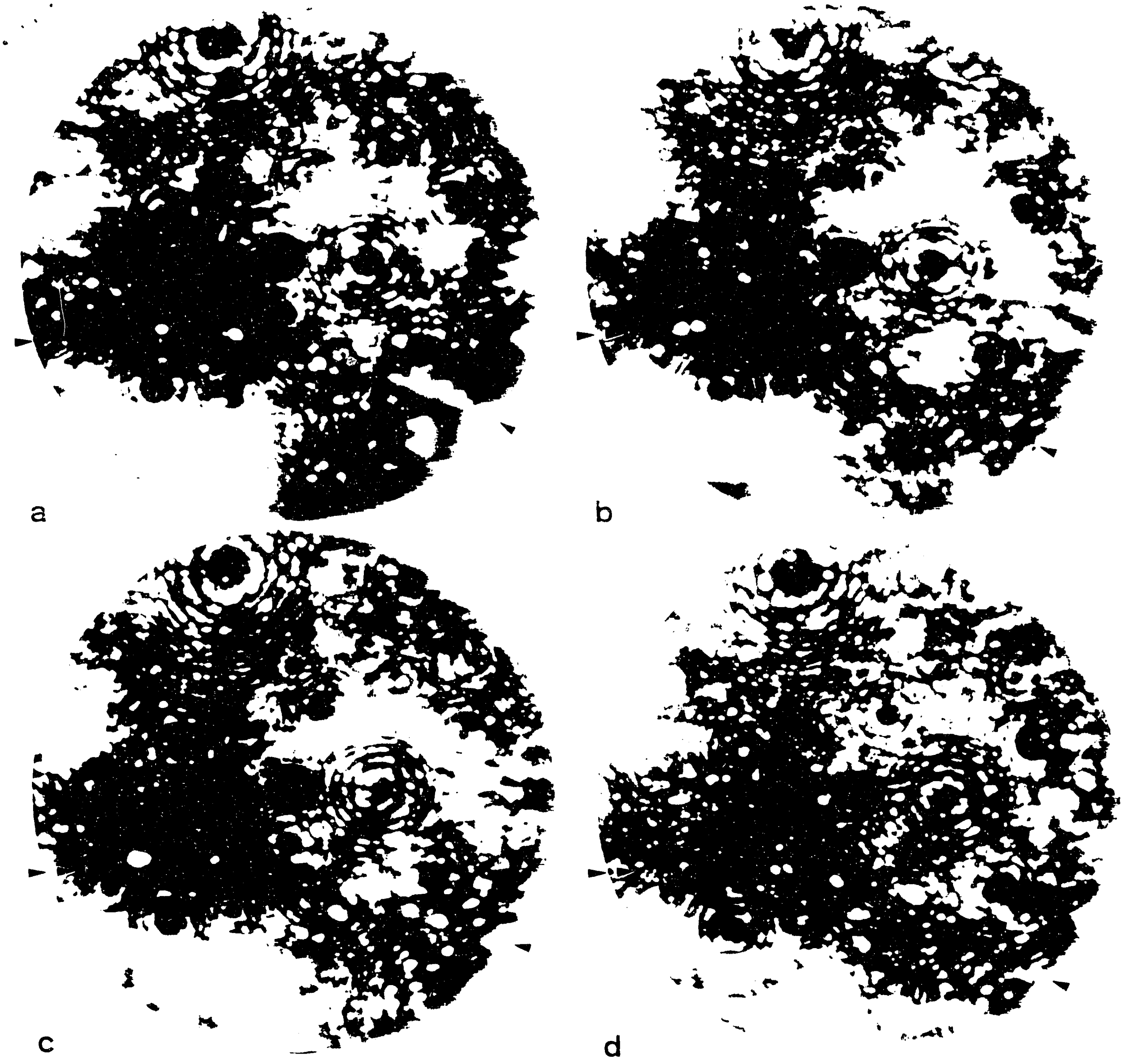

Fig. 10. Field ion micrographs of a section of lath boundary adjacent to a brightly-imaging vanadium carbonitride precipitate (lower right in a) in the VVER 1000 material. This sequence of micrographs was recorded after the field evaporation of approximately 0.2 nm between each micrograph. The coverage of ultrafine brightly-imaging molybdenum carbonitride precipitates near this coarse carbide was slightly lower than in sections of lath boundary removed from these coarse precipitates.

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