XN9500245

SWELLING AND FRACTURING OF BORIDES UNDER NEUTRON IRRADIATION

by

A.G.KRAINY*, V.V.OGORODNIKOV**, E.U.GRINIK*,
L.I.CHIRKO*, A.A.SHINAKOV*

* DAEP Inst. for Nuclear Research NASU,
252028 Kiev, Prospect Nauki, 47, Ukraine

** Frantzevich Inst. for Probl. of Mat. Sci. NASU,
252180 Kiev, Krzhizhanovsky str., 3, Ukraine

ABSTRACT. The neutron irradiation of high temperature borides, which are a structural part of boron-contained reactor steels and other constructional materials, results in high internal stresses. This leads to considerable swelling and micro- and macrofracturing.

The results of direct investigations of boride destruction process under neutron irradiation over wide region of temperatures and fluences are generalized. The change of mechanism of radiation damage of borides within the temperature interval of 400-530 °C is discussed. The macrocracking with formation of annular and radial cracks is observed below this temperature region. The accumulation of microfractures and the process of gas swelling takes place at irradiation temperatures above 530 °C. The results obtained conform to resistometrical data. The effect of the high internal stresses is compared with external pressure.

The presence of borides can provoke erosion and corrosion of boron-contained reactor materials.

Keywords: swelling, fracturing, boride, fluence, macro- and microcracking, crumbling.

Boron-contained steels for using in nuclear technics can be prepared by usual or powder metallurgy methods. A combination of this methods allows to change the boron content in steels in wide limits with enveloping such spheres of applicationsas neutron shields, compensators of changing reactivity, control facilities, in which the high absorbing properties of ^{10}B nuclei are used. The solubility of boron in iron is very small, therefore boron in steels form high-boron phases. Steels of powder metallurgy preparation can contain not only borides of iron, but also borides of other transition metals, what gives additional possibilities for the achievement of disirable nuclear properties in composite m a terial. Behaviour of various borides under irradiation have a great influence on erosion and corrosion processes in reactor boron-contained constructional materials. In order to study the mechanisms of radiation damage of boron phases we carried out investigations of the swelling and fracture of a number transition metal borides in free state under reactor irradiation at various temperatures and neutron fluences.

The irradiation of refractory compounds with high hardness and brittleness results in micro- and macrofracturing specimens under the action of high internal stresses created by radiation defects [1-9]. In borides, the highest elastic stresses are created by the metal and boron atoms displaced to interstitial sites as well as by the radiogenic atoms of helium and lithium which arise as products of the nuclear reaction, $^{10}B(n,\alpha)^{7}Li$ [10,11]. The detailed investigation of kinetic and temperature regularities of the titanium diboride radiation damage was earlier carried out indirectly, namely, by means of the electric resistance measurements and analysis of resistance jump-like change when cracking the specimen [7,8,11,12].

The specimens of borides studied were produced by the hot pressing of the proper powders. After pressing, the specimens were cooled at the conservation of the ambient pressure in 10-15 minutes. The pressing temperature was tested pyrometrically. The form of specimens was cylindrical with 8 mm diameter and 10-12 mm length. For removing internal stresses, the specimens of borides were additionally annealed at 1500 ^{o}C for 2 h in vacuum.

The specimens were irradiated in the special channels placed in the reflector zone of research WWR-M reactor. The irradiation at 100^{o}C was carried out in the water-cooled channels, other irradiation temperatures were obtained in helium-cooled channels.

The dependence of volume change for the specimens of TiB_2 and its alloys with CrB_2 irradiated at the temperature $\sim 100^{o}C$ on the fluence of thermal neutrons is shown in Fig.1. As it is obviously clear from the fragments of microstructure presented in the figure, the volume change is accompanied by the formation and growth of cracks. The beginning of macrocracking is observed at the fluence $1x10^{19}$ cm^{-2}. The appearance of annular and radial cracks is typical for cylindrical specimens. They are observed visually and with optical microscope (the interval of fluences is $1\text{-}7x10^{19}$ cm^{-2}). Then the cracks gradually grow up with increasing fluence and form chips on separate parts of surface (interval of fluences is $0{,}7\text{-}1{,}3x10^{20}$ cm^{-2}). The subsequent irradiation (interval of fluences is $1{,}3\text{-}2{,}5x10^{20}$ cm^{-2}) results in the destruction of surface layer into splinters and its crumbling. The increase of fluence above $2{,}5x10^{20}$ cm^{-2} leads to the splinter crushing into the smaller fragments including the core. The investigation results of the radiation-damage resistance for a number of borides at the radiation temperature of $\sim 100^{o}C$ are summed in Fig.2. As compared with other borides (ZrB_2, HfB_2, CrB_2, Mo_2B_5, W_2B_5, $(Ti,Cr)B_2$ and LaB_6), titanium diboride has the highest resistance to destruction into splinters (fluence is $2x10^{20}$ cm^{-2}). The beginning of marked macrocracking of different borides is observed in a rather narrow interval of fluences ($0{,}3\text{-}1x10^{19}$ cm^{-2}). ZrB_2, Mo_2B_5 and $(Ti_{0,9}Cr_{0,1})B_2$ have the lowest radiation damage resistance. In these borides, the surface cracks penetrate into the central part of specimen and cleave it into the splinters. So the fragmentation of splinters begins earlier in them (fluence is $2x10^{19}$ cm^{-2}).

According to fig.3, the temperature dependence of the macrovolume change of TiB_2 specimens has non-monotonic character. The volume change after irradiation to the fluence of $7x10^{19}$ cm^{-2} is 3% at the low irradiation temperature (~ 100 ^{o}C).
The volume change is reduced to 2% at the irradiation temperature of 400-530 ^{o}C and increased again to 3% at 680 ^{o}C. Such nature of dependence has been proved by the repeated measurements.

The nature of boride radiation damage is changing with the temperature increase. Together with the volume change of

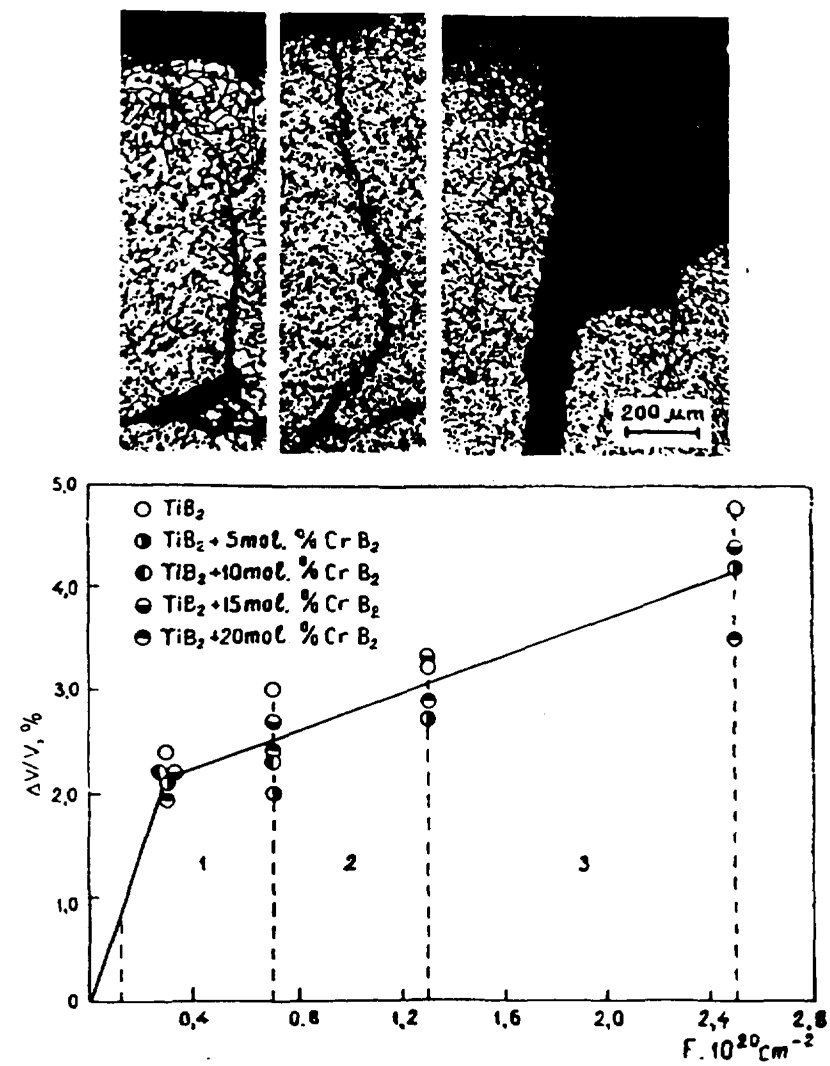

Fig.1.The change of macrovolume $\Delta V/V$ and damage character of microstructure for TiB_2 and its alloys with CrB_2 as function of thermal neutron fluence at the temperature of ~ 100 °C.

1 - Annular and radial cracks
2 - Opening of radial cracks and cleavage
3 - Severe fracturing and crumbling of surface layer

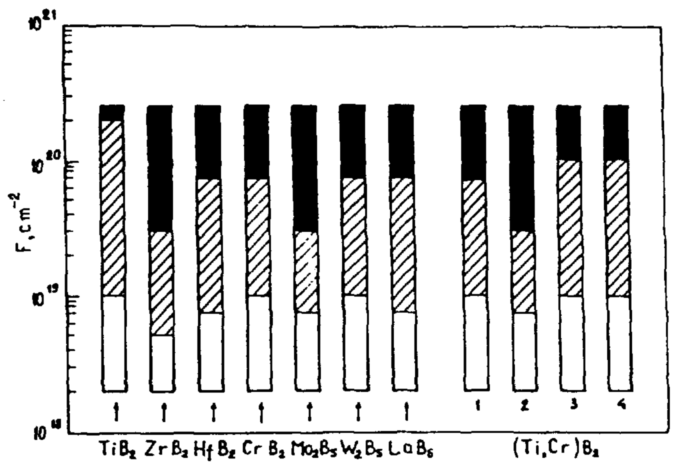

Fig.2 - Damage degree of specimens of hot pressed borides of transition metals

1 - $TiB_2 + 0,05CrB_2$; 2 - $TiB_2 + 0,10CrB_2$;

3 - $TiB_2 + 0,15CrB_2$; 4 - $TiB_2 + 0,20CrB_2$.

■ - heavy demages;

▨ - weak damages;

□ - damages are absent or very weak.

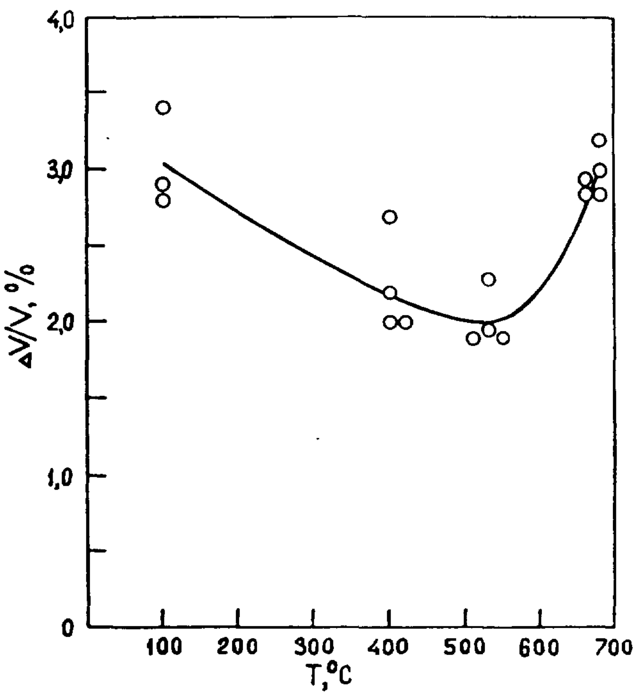

Fig.3 - Dependence of TiB_2 macrovolume ΔV/V upon the irradiation temperature for thermal neutron fluence of $7{,}0 \times 10^{19}$ cm^{-2}.

TiB_2 specimens to 3% (Fig.3) the average degree of macrodamage (according to the scale of radiation-damage resistance in Fig.2) is observed at irradiation temperature of ~100 °C and fluence of $7x10^{19}$ cm^{-2}. The considerable progress in annular and radial fracturing with appearance of separate chips on the surface coresponds to this degree (Fig.1). The increase of irradiation temperature to 400 °C leads to considerable decrease of the fracture opening and to the absence of macrocracks in TiB_2 specimens. Neither chips nor macrofractures are observed in titanium diboride specimens at the irradiation temperature of 530 °C and 680 °C and fluence of $7x10^{19}$ cm^{-2}. Only separate microcracks are found on the joints of grains in surface layer by means of optical microscope.

The damage accumulation in TiB_2 with increase of fluence over $7x10^{19}$ cm^{-2} at different temperatures is characterized by the following data. The intensive macrocracking and macrodestruction of specimens is going on at ~ 100 °C (Fig.1,2). The rate of formation and growth of macrocracks is sharply lowering at 400 °C. The specimens survive intact up to fluence of $2,5x10^{20}$ cm^{-2}. An excess of this fluence leads to appearing small chips and gradual crumbling surface layer. The transition from macroscopic nature of damage to microscopic one is near completed at 530 °C. Above this temperature the accumulation of damages go on at the expence of increasing concentration of microcracks, which are uniting into network and making the specimen as weakcoupled fragments. The specimens of TiB_2 irradiated to the fluence of $2,5x10^{20}$ cm^{-2} at > 530 °C have external integrity, however their surface layer has no mechanical strength and represents loosely bounded powder which splits under weak mechanical action. It is repeatedly observed in the process of unloading the irradiated containers. The microscopic nature of damage is preserved at 680 °C but the process of destruction is going much slower. At the same time the black points identified as gas micropores are detected with optical microscope.

These processes of macro- and microdestruction investigated in detail in titanium dyboride are typical for all borides. Some distinctive features were marked at the low-temperature irradiation (~100 °C). In some borides (TiB_2, $(Ti,Cr)B_2$, CrB_2, HfB_2, LaB_6), macrodestruction has initially enveloped only surface layer; in others (ZrB_2, Mo_2B_5, W_2B_5) the macrofractures arising on the surface have penetrated right away into all depth. In addition, the temperature of transition from macro- to microdestruction has rather varied for different borides. The macrodestruction was not detected in borides VB_2 and NbB_2, irradiated at such high temperature, as 800-900 °C (fluence was $1x10^{20}$ cm^{-2}).

Comparison of results obtained by the direct investigations of structure damage and fracture in boride specimens with the corresponding indirect data obtained by resistance measurements has shown the good agreement between them. According to the generalized scheme of TiB_2 radiation damage (indirect data, Fig.4), there are three temperature regions with different damage mechanisms:

1 - low-temperature one ($T < 400$ °C) with the mechanism of "hard" swelling, macrocracking and destruction into the splinters,

2 - middle-temperature one ($T = 400-1200$ °C) with the mechanism of microcracking, weak gas swelling and gradual destruction,

3 - high-temperature one ($T > 1200$ °C) with the intensive gas swelling without destruction.

In the frame of this classification, the direct investigations at the irradiation temperature of ~ 100 °C and 400 °C are related to low-temperature region whereas these at 530 °C and 680 °C are related to middle-temperature one. The change of damage mechanism takes place at the temperature range 400 to 530 °C), which is proved by $\Delta V/V(T)$ dependence (Fig.3) and by the described data of visual observations of changing radiation damage character as the irradiation temperature is increased.

Compare the dose stages of damage, determined visually and resistometrically. As it is shown in [11], the accumulation of damage has three stages in the low-temperature region:

(1a) - the concentration increase of own and additional (radiogenic) interstitial atoms, the progress of shear stresses on

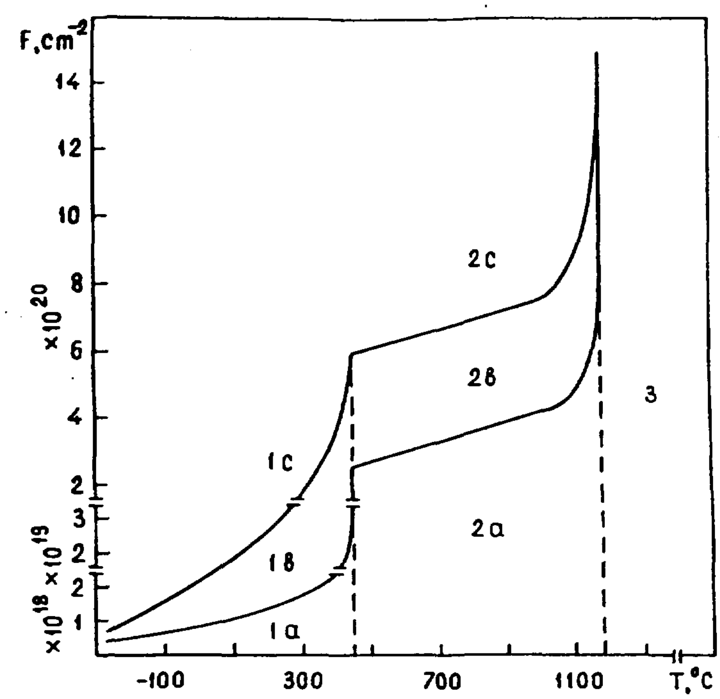

Fig.4 – General scheme of radiation damage and destruction of titanium diboride under neutron irradiation.

the boundaries between the crystallites;

(1b) - the formation of single cracks and their gradual union into main fracture;

(1c) - the cleavage of specimens into parts which further cleave into smaller fragments up to dimensions corresponding to the total destruction (Fig.4).

At the irradiation temperature of $\sim 100\ ^{o}C$ the fluence of $1x10^{18}\ cm^{-2}$ is upper limit of stage (1a). The stage (1b) covers the fluence range $1x10^{18}$ to $1x10^{19}\ cm^{-2}$. The stage (1c) takes place above $1x10^{19}\ cm^{-2}$. In Fig.2, the fluence range $1x10^{18}$ to $1x10^{19}\ cm^{-2}$ for titanium diboride is marked as the region of weak destruction or absence of visual damages, which is related with (1b) stage in [11]. Note that small single cracks are difficult to detect by the investigation of macrostructure fragments while the resistometry fixes them safely by jumps of electric resistance. The destruction of mean degree is observed over the fluence range $1x10^{19}$ to $2x10^{20}\ cm^{-2}$, the character of which is shown in Fig.1. At that state, the formation and the cleavage of splinters of surface layer up to 2 mm deep really take place - stage (1c). The total destruction of surface layer (macrodestruction) is observed at the fluence of $2\text{-}2{,}5x10^{20}\ cm^{-2}$.

In accordance with the scheme, the change of damage mechanism at 400-530 ^{o}C leads to transition from macrocracking to microcracking and to considerable shift of stages (1a), (1b), (1c) to higher fluence region: (2a), (2b), (2c). This is confirmed by direct observation stated in the previous section. The irradiation at 680 ^{o}C shifts the stage of intensive macrocracking (initiated by gas swelling) to the fluence range 2 to $6x10^{20}\ cm^{-2}$. The microdestruction of borides corresponds to the upper limit of this range according both to direct and indirect data.

Comparing the action of internal radiation stresses with mechanical loads, it should be noted that radiation-initiated stresses are analogous as a first approximation to external all-round extending stresses. In spite of radial symmetry of appearing stresses, the deformation is irregular through the stress concentration on grain boundaries and increase of shift components. The additional nonuniformity in stresses and deformations arises because of the nonuniform burning of ^{10}B nuclei.

The stress concentration becomes apparent especially at the low irradiation temperatures when the posibilities of stress relaxation are very limited.Under this condition, there is only possibility of considerable stress relaxation that is macrocracking. The role of relaxation mechanisms without fracturing increases as the temperature rises. At a low temperature, they consist in small shifts of atoms near lattice knots, some deformation of unit cells, position changes of defects, such as interstitial atoms and etc. After that, the shift mechanism of line relaxation joins. The activation mechanisms of defect annealing play the defining role at higher temperatures. Defect in question are own and admixture (radiogenic) interstitial atoms, vacancies both in metal and in metalloid sublattices. Then the cooperative mechanisms become significant: migration of grain boundaries, recrystallization, creep and finally, self-deffusion which ensures all stress relieving without destruction, namely by means of mass diffusion transfer in the mechanical stress field.

As found by direct observations (visual and microscopical), there are three temperature regions of the radiation damage of refractory borides. The low-temperature region is characterized by macrocracking (up to 530 °C for TiB_2). In the middle-temperature region, microcracking and gradual destruction takes place (530...1200 °C for TiB_2). The high temperature region is characterized by gas swelling without brittle fracturing (above 1200 °C for TiB_2).

The low-temperature region (1) is most carefully studied. It may be separated into three stages. First stage (1 a) includes gradual accumulation of point defects, which cause the increase of normal and shear stresses (up to $1x10^{19}$ cm^{-2} for TiB_2). Second stage (1b) consists in the formation of radial and annular macrocracks in the surface layer of specimens ($1x10^{19}...1x10^{20}$ cm^{-2} for TiB_2). Third stage (1c) is accompanied by the severe fracture of surface layer and penetration of cracks into the core of specimens (above $1x10^{20}$ cm^{-2} for TiB_2).

Concrete temperature and fluence ranges of radiation damage for different borides somewhat change depending on their chemical composition and crystal structure, what is noted in the previous pages.

Observed effects are explained by the accumulation of radiation defects in the crystal structure, as well as by transmutations of ^{10}B nuclei, which take place preferentially at the surface of specimens.

The carried out investigations of the swelling and fracture of borides under neutron irradiation lead to conclusion that steels with borides as a structural part will be undergone to high internal stresses on the interphase boundaries. As a result, micro- and macrofractures can arise at this boundaries with a possible consequence of the increasing erosion and corrosion of steels. The increase of steel swelling can be also observed because of enhancement of boride particles volume, their fracture, as well as penetration of helium atoms in metal matrix from boride dispersion. Nevertheless there are possibilities to increase the resistance of boron-contained constructional materials against neutron irradiation by changing boride phase tipe, its concentration and other parameters of compositions.

References

[1] Kovalchenko M.S., Ogorodnikov V.V., Rogovoy J.I., Krainy A.G. Radiation Damage of refractory Compounds, Moscow, Atomizdat, 1979.

[2] Keilholtz G.W., Moore R.E., Osborne M.F. Nucl. Applic., Vol.4, 1968, pp.330-336.

[3] Goltsev V.P. Effect of Irradiation on Absorbing Materials, Minsk, Nauka i tekhnika, 1975.

[4] Samsonov G.V., Kovalchenko M.S., Ogorodnikov V.V., Krainy A.G. Atomnaja Energia, Vol.24, 1968, pp.191-192.

[5] Ogorodnikov V.V., Murzin L.M., Krainy A.G. In book "Radiation Effects of Mechanical Properties Change of Engineering Materials and Methods of Their Research". Kiev, Naukova dumka, 1976, pp.89-97.

[6] Ogorodnikov V.V., Kovalchenko M.S., Krainy A.G., Koliada V.M.

Atomnaja Energija, Vol.23, 1967, pp.341-342.
[7] Topchan L.S., Naskidashvily I.A., Ogorodnikov V.V. Atomnaia Energija,Vol.42, 1977, pp.226-228.
[8] Murzin L.M., Ogorodnikov V.V., Kelim V.D., Atomnaja Energija, Vol.54, Issue 2, 1983, pp.118-122.
[9] Kovalchenko M.S., Ogorodnikov V.V., Krainy A.G., Atomnaja Energija, Vol.21, Issue 6, 1966, pp.470-475.
[10] Ogorodnikov V.V. Voprosy atomnoj nauki i tekhniki. Series on Radiation Damage Physics and Radiation Material Science, Issue 1(4), 1977, pp.100-106.
[11] Murzin L.M., Ogorodnikov V.V., Metallophysica, Vol.8, 1986, pp.96-101.
[12] Topchan L.S., Naskidashvily I.A., Ogorodnikov V.V. Atomnaja Energija, Vol.54, Issue 2, 1983, pp.118-122.