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Degradation of Creep Resistant Ni - alloy During Aging at Elevated Temperature Part II: Structure Investigations

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Abstract

The results of structure observations of Ni base superalloy subjected to long-term influence of high pressure hydrogen atmosphere at 750K and 850K are presented. The structure investigation were carried out using conventional light-, scanning- (SEM) and transmission electron microscopy (TEM). The results presented here are supplementary to the mechanical studies given in part I of this investigations. The results of study concerning mechanical properties degradation and structure observations show that the differences in mechanical properties of alloy subjected different temperature are caused by more advanced processes of structure degradation during long-term aging at 850K, compare to that at 750K. Higher service temperature leads to formation of large precipitates of δ phase. The nucleation and growth of needle- and/or plate-like, relative large delta precipitates proceed probably at expense strengthening γ'' phases. Moreover, it can't be excluded that the least stable γ'' phase is replaced with more stable γ' precipitates. TEM observations have disclosed differences in dislocation structure of alloy aged at 750K and 850K. The dislocation observed in alloy subjected to 750K are were seldom observed only, while in that serviced at high stress and 850K dislocation array and dislocation cell structure was typical.

Keywords: Ni-base superalloy, structure, SEM and TEM observations

1. Introduction

The results of mechanical properties investigation study presented previous in part I of these study showed that the degree of degradation of Ni-base subjected long-term influence of high pressure dissociated ammonia atmosphere at temperature 750K depend on the temperature and on the distance from the inner surface of high pressure chamber. The aim of study presented in this part is to look into structure of the alloy being studied to find out what caused the differences of mechanical properties observed during tensile strength, impact and hardness measurements. However, before start to describe the results of the investigations it would be helpful to bring some crucial information concerning precipitation hardening Ni-base superalloys. The strengthening of Ni-base superalloys arises from combined hardening mechanisms including: solid- solution atoms, precipitates and grain boundaries. Among them the most effective is precipitation hardening by coherent Ni_3M - type intermetallic phases: γ'' {Ni_3 (Nb, Ti, Al)} and γ' {Ni_3(Al,Ti)}[1]. Precipitation of γ'' phase characterizes with unique strengthening effect because of high coherency strain strengthening caused by large mismatch between them and γ matrix. However, γ'' intermetallic is meta-stable phase transforming to stable δ (Ni_3Nb) at high temperature, especially above 923K. Similarly γ' is also meta-stable phase which transforms to stable η (Ni_3Ti) phase during long time exposure at high temperature. Before it happen, long-term heating at high temperature lead to growth of γ'' and γ' precipitates which seriously degrade the strength of material. Many attempts were made to increase stability of the structure of Ni-base superalloys. One and relatively simple method is appropriate design of chemical composition described in elaborations [2, 3].

2. Experimental procedure

The specimens for structure observation were the same as those used in mechanical properties studies (see part I). The samples for optical metallography were cut from the chamber wall which plane to be studied perpendicular to the chamber axis. The specimens were grinded and polished using automatic Tenupol equipment. Finally the polished surface was etched with typical Ni alloys etchant. The metallography observations were carried out in Olympus IX-70 light microscope at different magnification. The most typical microstructures of the samples were registered with digital camera. For fractography observation the specimen taken at different distance from inner surface of the chamber, broken in tensile test were used. The fracture surfaces were observed in Zeiss scanning electron microscope (SEM) using secondary electrons (SE). For detailed structure investigations electron transmission microscopy (TEM) was applied. Thin foils were prepared from 3mm diameter rods which axis was oriented perpendicular with respect to the inner chamber surface. The rods were cut from the chamber wall using EDM method. First 0,1mm thin discs were cut from the rods at different distance from inner surface of the wall. Then the specimens were electro-polished with double jet method using Struers equipment and A8 solution. The TEM observations were carried out in JEM 1200 EX II Jeol transmission electron microscope working at acceleration voltage 1200 kV. Because of insufficient quality of thin foils some of them were additionally ion-polished with Gatan ion-milling equipment.

3. Results and discussion

As was said before, the structure investigations included conventional light, scanning and transmission electron microscopy observations. As a first the results of light microscopy studies are presented.

3.1. Metallography observations

In fig. 1 the microstructure of studied nickel base heat-resistant alloy after long-term aging at temperature 873 and 973K is presented. As can be seen the structure is quite different.

a.

b.

c.

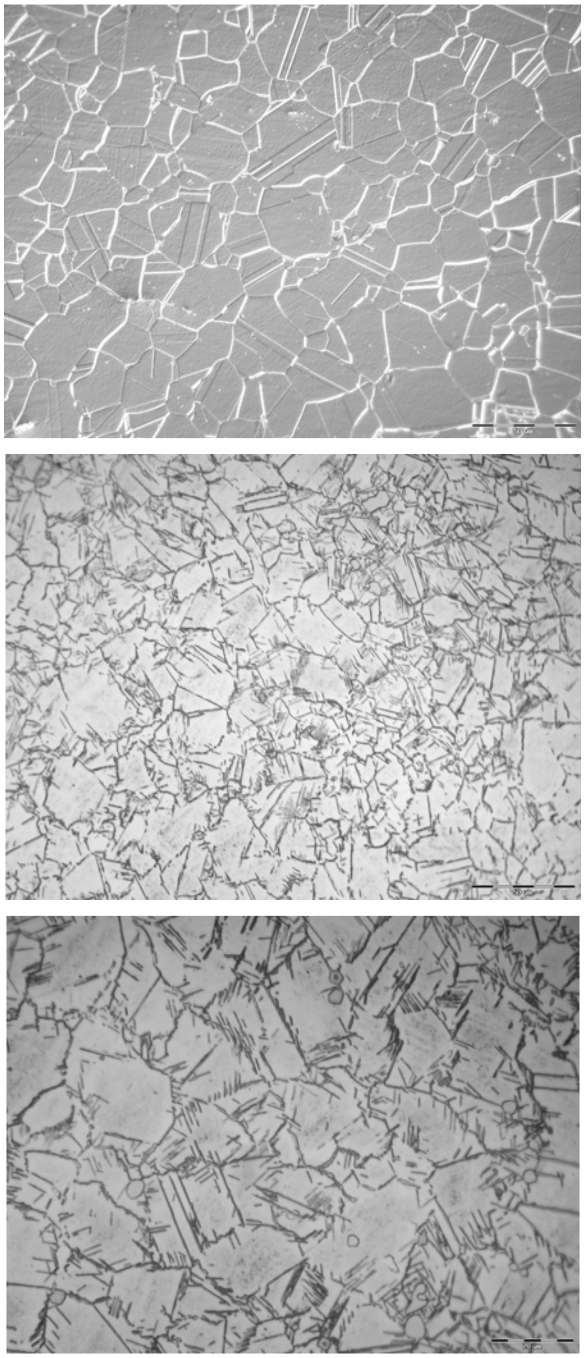


Fig. 1.The microstructure of the alloy after long-term aging at temperature: a - 750K (x500), b - 850K (x500), c - 850K (x1000)

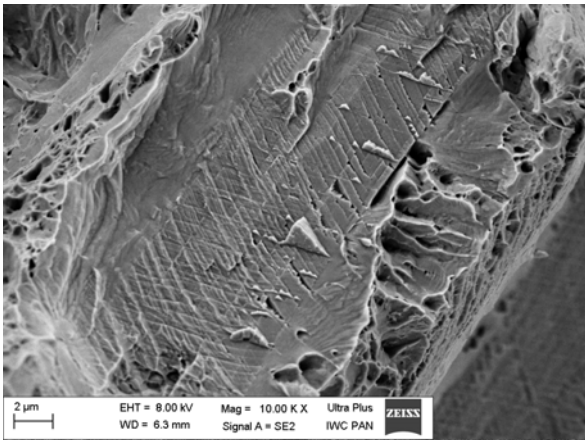
In all three photos (fig. 1 a-c) characteristic twins are visible. The difference between photos are relative large needle-shaped precipitates observed in specimen subjected long-lasting aging at temperature 850K (fig. 1b and c). It is obvious that because too small magnification and resolution obtainable in light microscope no ultrafine precipitates strengthening phases γ' and γ''are visible.

3.2. SEM investigations

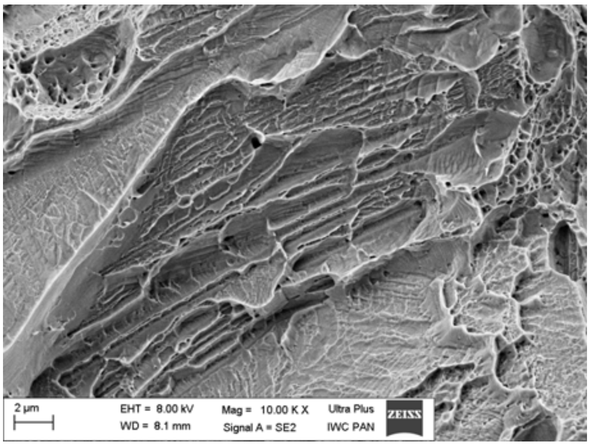
Fig. 2 and 3 show some examples of SEM investigations of the samples aged the same time but at different temperature. It is easy to see the different morphology of the fracture surface obtained in specimen broken in tensile test which were subjected long-term influence of high pressure of gaseous hydrogen and temperature. Before the results of SEM will be analyzed it would be convenient to introduce description of the specimen which included temperature and number indentifying the distance from inner surface. For example symbol 750 - x_1 denotes specimen aged at temperature 873K taken from place located at x_1 - 3,1mm while 850 - x_3 the specimen aged at 850K but cut from the place in the wall distanced x_3 = 16,3mm from inner surface of the cylindrical chamber.

Brief evaluation of the fracture surface morphology showed in fig. 2 and 3 lead to the conclusion that character of fracture was a mixed mode. However, it can be suggested that fracture surface of the specimen aged at higher temperature looks to be a little more ductile (fig. 3) compare to that showed in fig. 2.

a.



b.



c.

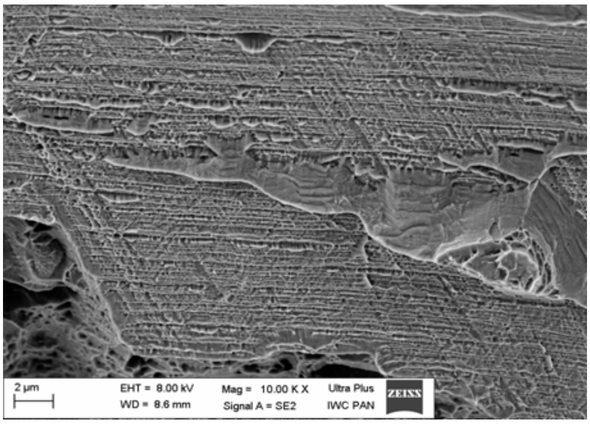
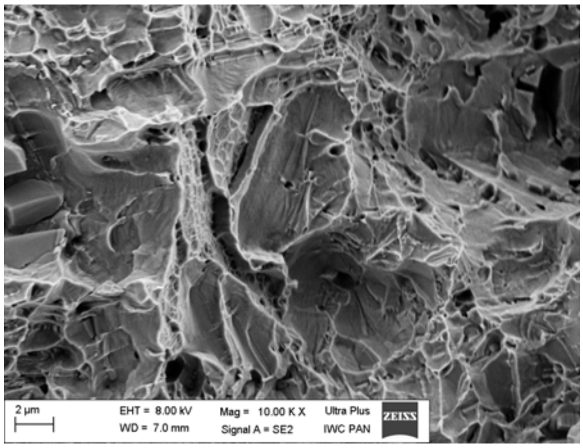


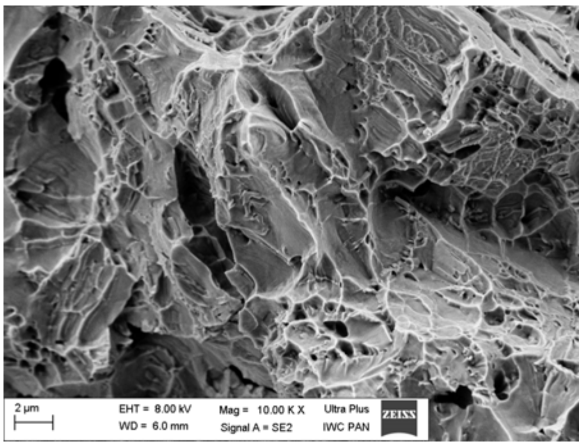
Fig. 2. The morphology of fracture surface of specimen aged at temperature 750K: a - sample 750-x_1, b - sample 750-x_2 and c - sample 750-x_3

If take a look a little closer a large flat planes can be recognized in first set of micrographs (fig. 2). There is no question that some of them are transgranular cleavage planes with the characteristic river pattern lines (bottom part of fig. 2b) [4].

a.



b.



c.

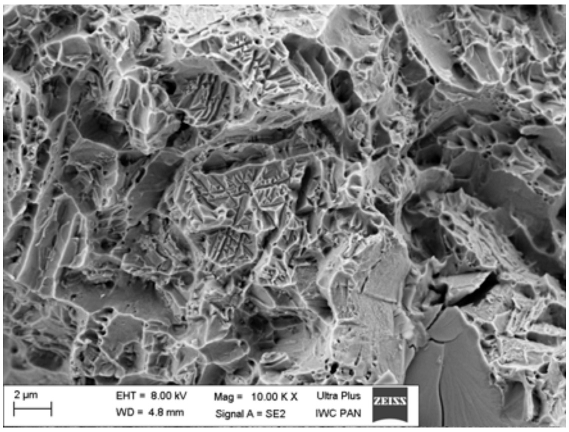


Fig. 3. The morphology of fracture surface of specimen aged at temperature 850K: a – spec. 850-x_1, b – spec. 850-x_2 and c – spec. 850-x_3

Besides in fig. 2a and b, small tongues typical for micro-twins are visible [4]. Except of these tongues, fine parallel intersecting lines can be identified in central part in fig. 2a. These can be interpreted as a slip steps formed by sliding dislocation emerging on the specimen surface during tensile test.

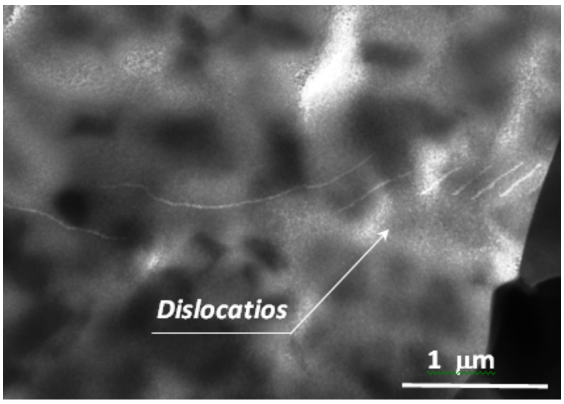
The fracture surface of specimens subjected to influence higher temperature is characterized with many relative deep dimples typical for ductile materials (fig. 3). Parallel to these dimples flat cleavage facets can be identified (see bottom right corner in fig. 3c). Moreover, broken brittle particles (see left side in fig 3a) and secondary cracks (fig. 3c) were also observed.

3.3. TEM observation

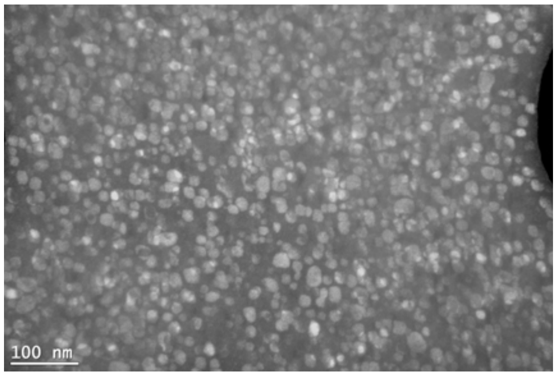
As a last the results of TEM observations are presented. Although preparation of thin foil is often very difficult, TEM is one the method only which assures magnification and resolution needed for revealing of nano-size precipitates and dislocation structure. Such difficulties concerned probably with non-uniform chemical composition of specimens we meat also in this studies.

The first three micrographs (fig. 4) show the most typical structure of the material after long-term aging at 873K taken from specimen at different distance from inner surface of the chamber.

a.



b.



c.

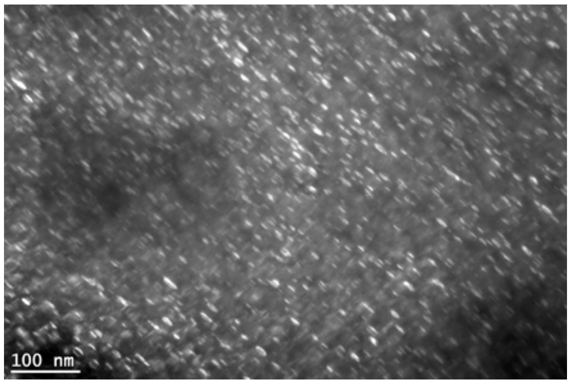
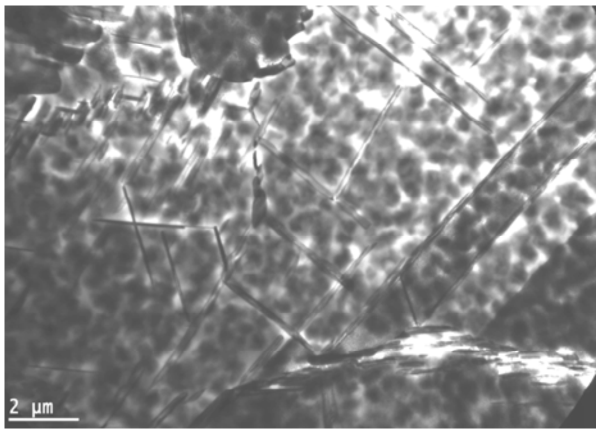


Fig. 4. The structure of alloy subjected to long-term aging at temperature 873K: a – spec. 750-1 (x150.000), b – spec. 750-2 (x250.000) and c – spec. 750-3 (x250.000)

In first photo (fig. 4a) weak beam dark field (WBDF) [5] micrograph showing a few dislocations is depicted. It should be noted that dislocations were rarely observed in this material, although the specimens were tilted in TEM in range of angles to bring the observed areas into correct Bragg condition assuring dislocation observations [6]. The next micrographs (fig 4. b and c) show very fine precipitate observed in dark field condition – DF [6]. In both pictures, size of precipitates is of about 30-50nm, which are probably γ” and γ’ mixtures. Some difference in shape of these precipitates follows from different orientation of disk shaped with respect to electron beam.

a.



b.

c.

d.

e.

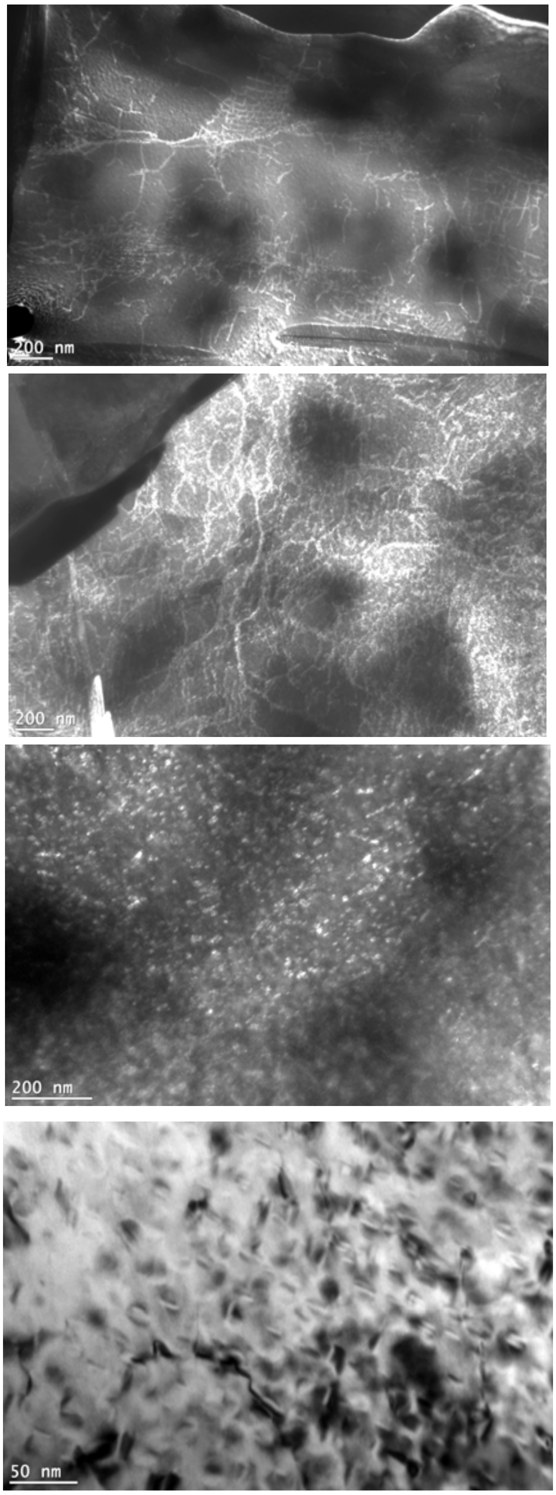


Fig. 5. The structure of the alloy to long-term aged at 850K: a – spec. 850-1 (x75.000), b – spec. 850-1 (x75.000), c – spec. 850-3 (x75.000), d - spec. 850-3 (x150.000) and e - spec. 850-3 (x500.000)

In next set of photos (fig. 5) the structure of alloy aged at temperature 850K is presented. It is easy to see that the structure of alloy aged at higher temperature is distinctly different from that aged at 750K. First of all large needle- or plate-like relative large precipitates are visible (fig. 5a). Contrary to the structure of alloy aged at temperature 750K where dislocation were rarely observed, here many dislocations forming array (fig. 5b) and dislocations cells structure (fig. 5c) are clear visible. Although the authors did not carried out qualitative assessment precipitation density it looks from fig. 5d that the density is lower compare to that observed in alloy aged at temperature 750K (fig. 4c). The last electron micrograph (fig. 5e) illustrates precipitates at very high magnification. The size of precipitates is of about 30-50nm, although the strain contrast is rather weak and the reason is probably not exact fulfillment of Bragg's conditions [7].

4. Summary and conclusions

In this part we to concentrate on most essential and interesting results only. First of all it should be stated that the difference in temperature of long-term aging equal 100K leads to observable difference in mechanical properties of studied alloy (see part I). Moreover, the degradation of mechanical properties depends on the position (distance) of the material with respect to the hydrogen source which is the inner surface of the chamber. The most influenced properties of the Ni-based alloy are elongation and impact resistance. As can be seen from graph the (fig. 1c, d - see part I) the influence of hydrogen of elongation and impact resistance is function of the distance from hydrogen source and the higher the closer is the specimen being studied located with respect to the inner surface of the chamber. It is not surprising because the hydrogen atoms when adsorbed will diffuse from the surface into the wall of chamber and the highest its concentration will be observed close to the inner surface. It is interesting, that despite substantial decrease of elongation (fig. 1c) the fracture surface exhibit ductile mode characterized by dimples with small contribution of cleavage (figs. 2 and 3). No brittle intergranular fracture was practically identified.

Discussing the results we have to take into consideration at least three parameters which are: hydrogen rich atmosphere, elevated temperature and stress. From point of view processes proceeding in the structure of alloy the most important is the temperature. As it is seen from TEM observations the aging at temperature 850K causes nucleation and growth of large needle-, rod-like or/and lath precipitates located mainly at the grain boundaries. It follows from analysis of selected area diffraction pattern and dark field microscopy that most of these precipitates are δ phase but other phases like e.g. η or carbides cannot be excluded. The appearance of other phases should be taken into account because of different size and morphology of the particles observed in thin foils (fig. 6). Absence large rod- or plate-like precipitates in alloy aged at temperature 750K suggest that temperature of about 850K is above the critical for decomposition of Ni-based alloy strengthened with ultra-fine γ" and γ' particles. As follows from our studies, partial transformation of nano-size γ" and γ' precipitates into δ phase lead to small increase of tensile properties of alloy (fig. 2a and b).

a.

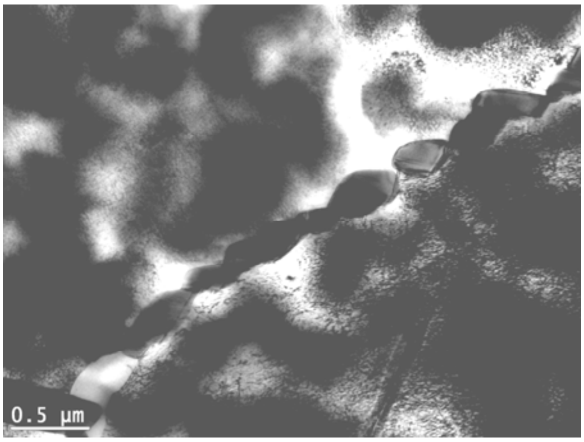


Fig. 6. The example of precipitates with morphology different from the most typical needle-like showed in fig. 5a (x50.000)

The next very interesting difference is dislocation structure of studied alloy. As was showed above the dislocations were seldom met in specimens cut from alloy aged at 750K while in case of alloy aged at temperature 850K appeared in high density forming dislocation cell structure (compare fig. 4a and 5b and c). Such observation can be explained by creep taking place at high aging temperature and high stress [9].

Since the elongation is the property exhibiting the most pronounced dependence on the distance from inner surface of the chamber we decided to evaluate roughly how deep could diffuse the hydrogen into the thick wall of the chamber. We used the simple well known formula:

$$g \approx (2D \cdot t)^{1/2} \quad (1)$$

where:
g - depth of diffusion [m]
t - time [s]
D - diffusion coefficient hydrogen in Ni alloy [m^2/s]
and diffusion coefficient D is described with equation:

$$D = D_0 \cdot \exp(-Q/RT) \quad (2)$$

where;
D_0 - frequency factor [m^2/s]
Q - activation energy [J]
R - universal gas constant [J/K·mol]
T - temperature [K]

Using data and procedure proposed by Liu and coworkers [10] we have calculate the values of diffusion coefficients for temperature 750 and 850K as equal $1{,}65 \cdot 10^{-10}$ and $4{,}17 \cdot 10^{-10}$ m^2/s respectively. On the basis of these calculation it was possible evaluate the depth of hydrogen diffusion as: $t_{750K} \approx 0{,}04$m and 0,067m respectively. This means that the depth of hydrogen diffusion exceeded the wall thickness of the chamber.

On basis of results presented in this elaboration the follow statements can be proposed:

1. The critical temperature from point of view decomposition of starting structure of the alloy lies between 750 and 850K.
2. The long-term aging at temperature 850K under high pressure of hydrogen causes creep which is accompanied with dislocation movement forming dislocation cell structure.
3. The degree of ductility and impact strength decrease depends on the distance from the hydrogen source.
4. No substantial degradation of proof stress, tensile strength and hardness as a function of distance from inner surface of the chamber was discovered.

Acknowledgments

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