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DEVELOPMENT OF HELIUM POROSITY NEAR BY GRAIN BOUNDARIES IN NICKEL—CARBON ALLOYS

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Introduction

The problems of studying helium porosity development in metals and alloys have been lately paid of special attention in relation to the problems of thermonuclear materials study. The problems of study of helium porosity development on grain boundaries and near them present the greatest interest among the existing problems of helium behaviour in materials as far as, namely, the boundary and nearby boundary bubbles determine the tendency of structural materials towards high-temperature radiation embrittlement. It has been stated in copper [1] for the first time and then in nickel [2] that the most intensive development of helium bubbles takes place near free surface and grain boundaries. In some papers [3,4,5] the peculiarities of the development of helium bubbles in near-boundary regions and near free surface of nickel samples have been investigated. It has been stated that the development of helium bubbles in the mentioned regions is nonuniform. Thus, the paper [3] shows that the greatest rate of bubble growth takes place in close vicinity to the grain boundary and free surface. On the other hand, the paper [5] notes the fact indicative of the moment that the most intensive growth of bubbles is on the contrary not near the free surface but at some distance from it in the region of the sample bordering with its unirradiated volume. Realization of these contradictory experimental facts needs new data about the role of such factors as material purity, for example, as far as the presence of impurities can exert a significant influence on

energy of formation and migration of vacancies and, consequently, on concentration profile of vacancies near grain boundary.

The present paper investigates the peculiarities of helium porosity near grain boundaries in nickel depending on carbon concentration in the process of post-irradiation isothermal annealing.

Experimental

As the object for investigations the samples of nickel with 0.002, 0.007, 0.010, 0.039 and 0.065 wt.% carbon content have been taken.

The samples after annealing at 900°C for 2 hours have been uniformly doped with helium up to $2\cdot10^{-2}$ at.% concentration for 20 μm depth on the cyclotron according to the methods [6]. After irradiation the samples have been annealed at 800°C for 1, 5, 10 and 50 hours. Nearby boundary zones with intensively developing helium bubbles have been detected metallographically and investigated by means of transmission electron microscopy (TEM).

To obtain sufficient statistics in the conditions of coarse-grained structure of nickel-carbon alloys one needed high-quality TEM objects which were prepared by means of "Micron" installation [7].

Results

Metallography. Fig.1 displays special peculiarities of development of nearby boundary porosity in nickel samples depending on carbon concentration and annealing time at 800°C. As it is seen, nearby boundary region with intensively developing helium bubbles is exposed in metallographic pictures in the shape of zones of intensive electrochemical etching. The width of these zones depends both on annealing time and carbon content in nickel (Fig.2 a,b). Intensive growth of the near-boundary zone width takes place after annealing for more than 5 hours. In this case nonmonotonous character of changing near-boundary zone width due to carbon concentration in nickel which is defined by the peculiarities of development of nearby boundary porosity in nickel samples with 0.007% carbon should be noted. In this sample, in relation to the others, after one hour annealing more intensive growth of near-boundary zone size takes place and vice versa after annealing in 10-50 hours interval the change of near-boundary zone size is retarted.

Electron microscopy. Characteristic image illustrating the peculiarities of helium bubbles development in near-boundary zones of the investigated samples are shown in Fig.3 a. It is seen that intensive development of helium bubbles occurs nearby boundary while in grain matrix the size of bubbles does not exceed 10 nm with density not less than 10^{21} m^{-3} (Fig.3 b). An important circumstance in the character of bubble distribution in near-boundary zone is the absence of coarse bubbles at grain boundaries and increase of their size as the distance from grain boundary increases. Quantitative calculations of changing helium porosity parameters (density, average size and relative volume) along the width of near-boundary zone in nickel samples with various carbon content are given in Fig.4. As it is seen from Fig.4, in the samples annealed at time interval from 1 to 10 hours the character of changing of helium bubble parameters along the width of near-boundary zone has a common tendency: the size of bubbles increases and their density decreases as the distance from grain boundary increases; relative volume of bubbles increases as the distance from grain boundary is about 2 μm, then it does not practically change. After fifty hour annealing the bubble size distribution in near-boundary zone improves, though in some samples the tendency towards the increase of their density is observed as the distance from grain boundaries increases.

Measured by means of the TEM images the near-boundary zone size in the samples annealed for 10 and more hours is several times less than that measured by means of metallographic pictures. This evidences about the fact that the effect of chemical etching nearby boundary zone is controlled not only by the presence of coarse helium bubbles in it but also by special stressed state of near-boundary zone material.

Discussion

The above mentioned results of the development of helium porosity in near-boundary zones of nickel-carbon binary alloy samples give possibility to distinguish two important circumstances. The first, intensive growth of helium bubbles is observed nearby boundary as compared to the bubbles in grain matrix. The second, the near-boundary zone itself non-homogeneous character of bubble growth take place consisting in the fact that the greatest rate of their growth is observed not near the boundary itself but in the part of near-boundary zone adjacent with grain matrix.

In all papers concerning investigations of the processes gas-filled bubbles growth near grain boundaries and free surface of the sample, the latter is considered as the major sources of vacancies monitoring the growth rate of helium bubbles, in particular.

To our mind such an approach is limited as far as it does not include consideration both of the evolution processes of dislocation-loop structure always accompanying helium porosity and possibility of the appearance of high compressing hydrostatic stresses in near-boundary zone. The latter is conditioned by the circumtance that the value of gaseous swelling of near-boundary zone material is by an order of magnitude higher than that of grain matrix material. In this case, naturally, significant gradients of hydrostatic stress arise in the volume of material adjacent between them.

In terms of the available results on the development of

dislocation-loop structure and matrix porosity in the samples under post-irradiation annealing at 500-900^{o}C interval and also mentioned above data on development of helium bubbles nearby boundary, in our opinion, new hypothetic explanation to the observed effect of nonhomogeneous development of helium porosity in near-boundary zones is in order to suggest. In this case the suggested scheme of physical explanation of this effect is based on the experimental data and requires, naturally, corresponding theoretical analysis that will apparently favour not only the realization of the reasons of different processes of helium bubble growth in grain matrix and near boundaries but, possibly, explanation of other phenomena, redistribution of impurity elements in polycrystalline materials in the presence of helium impurity, for example.

The suggested hypothesis is illustrated in Fig.5 by the corresponding structural peculiarities and consists of the following stages:

1. At the initial stages of evolution of the defect structure in the process of post-irradiation annealing at 500^{o}-600^{o}C temperatures grain boundary is the major source of vacancies. And they participate in two processes. The first process conditioned by interaction of vacancies with interstitial dislocation loops causes annihilation of the latter, as a result of this the loop depleted zone is formed near grain boundary (Fig.5 a, b). The second process conditioned by interaction of vacancies with helium atoms (helium-vacancy complexes) causes nucleation and growth of helium bubbles, at grain boundary and in immediate vicinity to it at first (Fig.5 c).

2. With annealing temperature increase the growth of dislocation loops in grain matrix is related to emission of vacancies by them which are captured by helium-vacancy complexes that causes nucleation and growth of bubbles in it. At the same time helium bubbles nearby boundary continue to grow due to their migration and coalescence mechanism mainly, as far as obstacles for bubble migration are absent in this zone. Consequently two systems of growing bubbles are formed in the grain: the first nearby boundary (primary), the second in grain matrix (secondary). As the results evidence, the growth of primary porosity occurs much more intensively, than that of the secondary one. The existing of two regions with different value of swelling in the grain conditions causes the appearance of different levels of hydrostatic stress in them. Thus, the near-boundary zone subjected to the greater volume change a greater compressive stress is formed. It is natural to suppose that at the boundary of these two regions the corresponding stress gradients originate. Namely the presence of stress gradient in the intermediate region between near-boundary zone and grain matrix is the force changing of the parameters of diffusion vacancies, helium-vacancy complexes, helium bubbles and, apparently, impurities. Thus, vacancies formed in grain matrix as a result of growth of interstitial dislocation loops and also helium-vacancy complexes will migrate from grain matrix volume to near-boundary region as the region is in the most stressed state. In this case they are captured by helium

bubbles that are in so-called intermediate region causing their accelerated growth. Moreover, helium bubbles from near-boundary zone will, on the contrary, migrate to the region with less stress level [8], i.e. to grain matrix causing the increase both of their size due to coalescence with matrix bubbles and the width of near-boundary zone (Fig.5 d,e).

3. For sufficiently high annealing temperatures (900°C and more) when fluxes to near-boundary zone from grain matrix of vacancies disappear (due to the absence of dislocation loops as their sources) and also helium-vacancy complexes (as far as all of them will operate in helium bubbles) growth of bubbles in the adjacent region will be retarted. Their migration in the direction of grain body (due to the presence of gradient of stress in the adjacent region) and coalescence with matrix bubbles will stay the only mechanism of their primary growth. However, the operation of this mechanism will gradually come to minimum as well, as far as at these temperatures the growth of matrix bubbles also becomes sufficiently intensive due to their ability to migration and coalescence (Fig.5 f). In consequence of this the conditions of forming two zones with various value of swelling in a grain vanish and, consequently, the presence of gradient of stress in their adjacent region. Thus, taking into account the above-mentioned once more grain boundary will become the main source of vacancies that will cause the primary growth of bubbles both on the boundary itself and near it (Fig.5 g).

Thus, formation of near-boundary zone depleted from dislocation loops and preferential formation and growth of helium bubbles in it determine the conditions of formation of two zones (nearby boundary and matrix) in a grain with different level of swelling and, consequently, hydrostatic stress as well. The formation of stress gradient in intermediate region between these two zones facilitates migration of helium-vacancy complexes and vacancies emitted by increasing dislocation loops from grain matrix, to our mind, is just the reason of the preferential growth of helium bubbles on it.

As far as carbon concentration is concerned, unfortunately, we failed to determine its role in helium porosity development in near-boundary zone. Apparently, it is necessary to have greatest statistics or the carbon concentration nearby boundary causes change. It should be noted, however, that starting with 5 and more hours annealing duration there is an explicit tendency (the samples with 0.007% carbon are excluded) towards the increase near-boundary zone width with increasing carbon concentration. The analysis of these results from the point of view of the carbon concentration effect on formation and migration of vacancies, change of surface energy and the energy of formation of ledge on the bubble surface will be listed in subsequent papers.

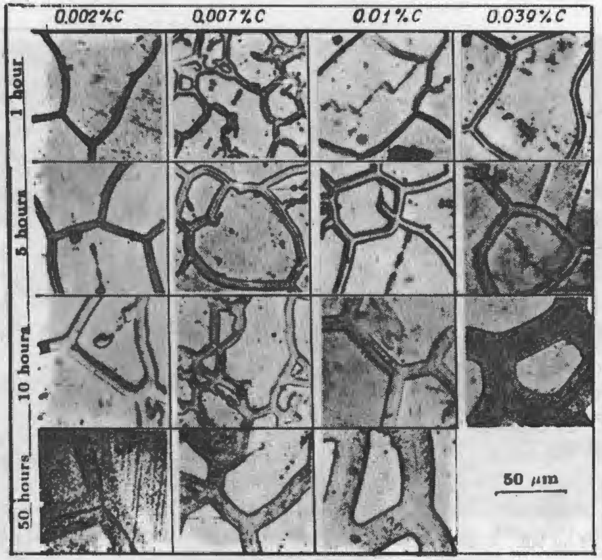

Fig.1. Development of helium porosity nearby grain boundaries of nickel depending on carbon content and annealing time at 800°C.

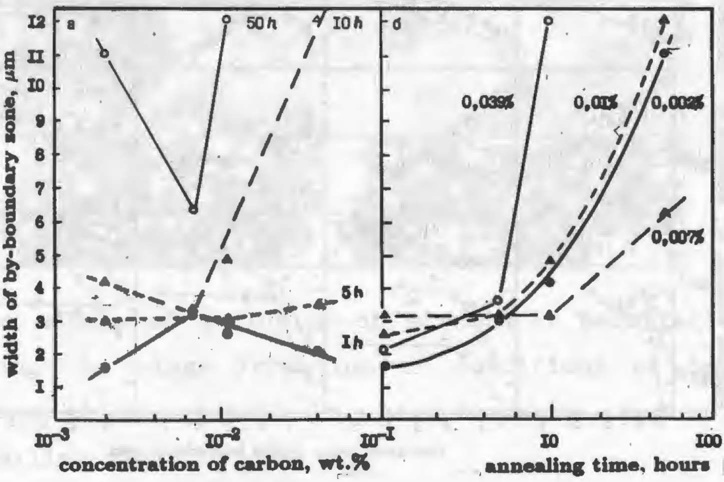

Fig.2. Change of near-boundary zone width with helium bubbles depending on carbon concentration (a) and time of annealing at 800°C (b).

Fig.3. Helium bubbles in near-boundary region (a) and in a grain matrix (b) after annealing at 800°C.

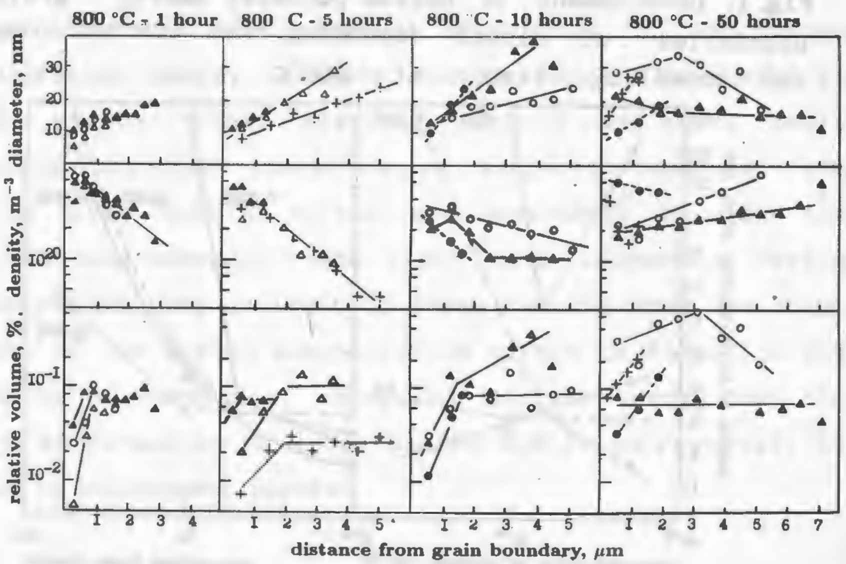

Fig.4. Change of average size, density and relative volume of helium bubbles in nickel with different carbon content along the width of near-boudary zone due to annealing time at 800°C (● - 0.002%C, o - 0.007%C, ▲ - 0.010%C, Δ - 0.039%C, + - 0.065%C).

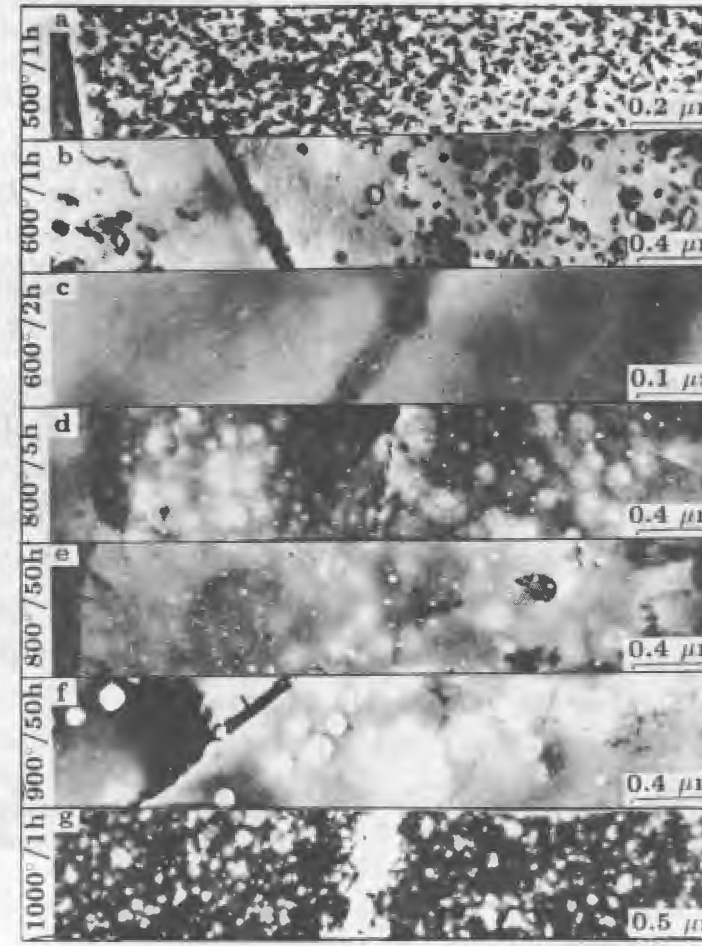

Fig.5. The scheme of evolution of strustural peculiarities illustrating the stage formation of conditions of helium bubble population growth in near-boundary region of polycrystalline nickel.

REFERENCES

1. R.S.Barnes, G.B.Redding, A.H.Cottrell. Phil. Mag. 3, 97 (1958).

2. V.F.Reutov, N.A.Konjahin, V.A.Tuev. Phys.-Chemic. Mechanic of Materials. 1, 80 (1972) (in Russian).

3. V.N.Chernikov, P.R.Kazansky. J.Nucl.Mat. 172, 152 (1990).

4. W.Kesternich, D.Sohwahn, H.Ullmaier. Ser.Met, 18, 1011 (1984).

5. L.J.Perryman, P.J.Goodhew. Acta Met. 36, 2685 (1988).

6. V.F.Reutov, G.T.Zhdan. The Method of Ion Doping of Materials. A.C. 591087. BOIPOTZ. 8,227 (1980) (in Russian).

7. V.F.Reutov, N.V.Bagaeva, A.N.Podilko. "Micron" Device and Procedure of Preparing Objects for Transmission Electron Microscopy from Highly-Radioactive Materials. Preprint 5-87. PTI of KAS, Alma-Ata. (1987) (in Russian).

8. D.B.Martin. J.Nucl.Mat. 33, 23 (1969).

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Развитие гелиевой пористости вблизи границ зерен в сплавах никель-углерод

Изучены особенности развития гелиевой пористости вблизи границ зерен в никеле с 0,002—0,065% С, легированном гелием до концентрации $2\cdot10^{-2}$ ат.%, в процессе послерадиационного отжига при 800° С в течение 1—50 час. Установлено, что интенсивное зарождение и рост пор наблюдаются в приграничной области, ширина которой возрастает как с увеличением времени отжига, так и с содержанием углерода. ПЭМ-исследования показали, что в самой приграничной зоне процесс роста пор идет неравномерно: размер пор увеличивается, а их плотность уменьшается по мере удаления от границы зерна. Наблюдаемый эффект обсуждается с позиции образования в зерне двух зон с различным уровнем распухания, а следовательно, и гидростатическим напряжением, обуславливающим поток вакансий и гелий-вакансионных комплексов из матрицы в направлении границы зерна.

Работа выполнена в Лаборатории ядерных реакций им. Г.Н.Флерова ОИЯИ.

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Development of Helium Porosity Near by Grain Boundaries in Nickel — Carbon Alloys

The peculiarities of development of helium porosity near grain boundaries in nickel with 0.002—0.065 at.% carbon uniformly doped with helium up to $2\cdot10^{-2}$ at.% in the process of post-irradiation isothermal annealing at 800° C for 1—50 hours are studied in the present paper. It is stated that at this annealing temperature intensive nucleation and growth of bubbles are observed in near-boundary region whose width grows both with increase of annealing time and carbon content. The TEM studies have shown that in near-boundary zone itself the process of bubble growth is non-uniform: bubble size increases and their density decreases as the distance from grain boundary is increased. The effect observed is discussed from the point of view of formation of two zones with different level of swelling in a grain (nearby boundary and matrix) and, consequently, hydrostatic stress as well conditioning the flux of vacancies and helium-vacancy complexes from matrix to grain boundary.

The investigation has been performed at the Flerov Laboratory of Nuclear Reactions, JINR.

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