Relaxation of stress occurring in Cd-Ni diffusion zone with formation of intermetallic phase

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Relaxation of mechanical stress occurring in Cd-Ni diffusion zone was studied by metallographic methods. Brittle relaxation of tensile stress was revealed in $Cd_{21}Ni_5$ intermetallic phase growing in the diffusion zone. Evaluation of this stress made by the geometry of macroscopic cracks in the intermetallic phase showed values being by a factor 1.2 lower than stress values calculated by volume defect related with the intermetallic phase formation. As plastic deformation within the intermetallic phase is excluded, whereas brittle relaxation begins at the $Cd_{21}Ni_5$ -Ni boundary, it was concluded that induced in Ni compressive stress relaxed by plastic deformation mechanism to the level of Ni elastic limit.

Keywords: intermetallic phase, diffusion zone, brittle relaxation, plastic deformation.

Металлографическими методами исследован процесс релаксации механических напряжений, возникающих в диффузионной зоне системы Cd-Ni. Показано, что имеет место хрупкая релаксация растягивающих напряжений в растущем в диффузионной зоне интерметаллиде Cd₂₁Ni₅. По геометрии макроскопических трещин в интерметаллической фазе сделана оценка величины этих напряжений, которая оказалась в 1,2 раза ниже величины напряжений, вычисленных по дефекту объема, связанного с формированием интерметаллида. Поскольку пластическая релаксация внутри интерметаллида исключена, а хрупкая релаксация напряжений начинается на границе Cd₂₁Ni₅-Ni, сделан вывод о том, что имел место сброс сжимающих индуцированных напряжений в Ni механизмом пластической деформации до уровня предела упругости материала Ni.

Релаксація напружень, що виникають у дифузійній зоні при формуванні інтерметаліду у системі Cd-Ni. В.В.Богданов, В.Г.Кононенко, М.А.Волосюк, А.В.Волосюк.

Металографічними методами досліджено процес релаксації механічних напружень, що виникають в дифузійній зоні системи Cd-Ni. Показано, що має місце крихка релаксація розтягуючих напружень в інтерметаліді Cd₂₁Ni₅, що зростає в дифузійній зоні. За геометрією макроскопічних тріщин в інтерметалевій фазі зроблено оцінку величини цих напружень, яка виявилася в 1,2 рази нижчею за величину напружень, обчислених за дефектом об'єму, що пов'язаний з формуванням інтерметаліду. Оскільки пластична релаксація в середині інтерметаліду виключена, а крихка релаксація напружень починається на межі Cd₂₁Ni₅-Ni, зроблено висновок про те, що має місце скидання стискаючих індукованих напружень в Ni механізмом пластичної деформації до рівня границі пружності матеріалу Ni.

1. Introduction

It is known that at higher temperatures in macroscopically inhomogeneous crystalline media, various relaxation processes take place; these are often accompanied by plastic deformation [1], diffusion [2, 3], and other transport phenomena [4] resulting in redistribution of substance and internal stress, change of dislocation structure, generation

of pores and cracks, recrystallization, etc. To understand regularities of physical processes in complex systems, consistent analysis of rather simplified models is necessary which may be useful to construct the complex process under study.

One of the model conceptions is the problem on interdiffusion of two substances A and B with strongly different atomic sizes which are in diffusion contact by a flat boundary in the case where not solid solutions but ordered compounds of A_mB_n type (m and n are integers) are formed. Such compounds occurring between two metals in the diffusion contact are named intermetallic phases.

Because generally a $A_m B_n$ compound has a crystalline structure different from both A and B structures, their specific volumes in A and B lattices are different from these in the $A_m B_n$ lattice. It is the main reason for appearing stress both in the intermetallic phase bulk and in neighboring areas of initial A and B components.

The deformation caused by the volume jump can be free realized only in the OX direction (Fig. 1), whereas in YZ plane it is hampered by mechanical adhesion between the intermetallic phase and initial components at interfaces; thus near interphase boundaries, shearing stress σ_{YZ} would act which sign and distribution depend on the ratio of specific volumes of atoms in each of contacting phases.

In Fig. 2, stress distribution near a $A-A_mB_n$ interphase boundary is shown for the case where $V_A>V_I$ (V_A and V_I are specific volumes of an A atom in A lattice and in intermetallic phase lattice, respectively). Near the interphase boundary, stress attain maximum values, and their sign changes abruptly from positive (compressive) to negative (tensile) in going from A phase to A_mB_n intermetallic one.

Evaluation of the maximum stress occurring in the intermetallic phase near the $A-A_mB_n$ interface can be made using a simple relation:

$$\sigma_{\rm max} \approx G \, \frac{\Delta V_{\sf A|}}{V_{\sf A}},$$
 (1)

where G is elastic modulus of an intermetallic phase, and $\Delta V_{A_1} = V_{\rm I} - V_{\rm A}.$

If the stress level exceeds the elastic modulus of A or A_mB_n material, excess stress will relax by the mechanism of plastic deformation [4, 5]. Relaxation processes

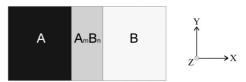


Fig. 1. Schematic representation of the sample where the reaction of $A_m B_n$ intermetallic phase formation takes place as a result of interdiffusion between A and B substances brought in the diffusion contact by a flat interface.

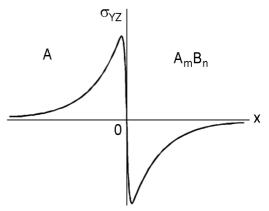


Fig. 2. Scheme of stress distribution near $A-A_mB_n$ interface.

result in decreasing the stress level near interfaces down to elastic limit σ_{el} (Fig. 3). As the stresses on both sides of the interface are opposite by sign, so, compensate each other, the steady state stress levels on the both sides are equal by absolute value and are determined by σ_{el} of the phase with lower elastic limit.

Plasticity of a crystal is specified mainly by mobility and density of present dislocations. Necessity to retain a regular configuration in atomic arrangement decreases significantly the dislocation mobility and, consequently, reduces the ability to plastic relaxation of elastic energy in them. Therefore, tensile stress in intermetallic phases is able to relax by crack formation [6, 7]. In this way of stress relaxation we can evaluate them by arrangement and width of formed cracks.

As it is known, stress relaxation due to crack formation is realized in the area with a characteristic linear size close to the crack size [8]. Therefore, relaxation of tensile stress occurring, for example, in a layer of $A_m B_n$ intermetallic phase (Fig. 1) near a flat interface $A-A_m B_n$ (Fig. 3) may take place due to formation of a row of cracks (parallel to each other and perpendicular to the plane of the interface) which are distanced by l being of the order of crack length (Fig. 4).

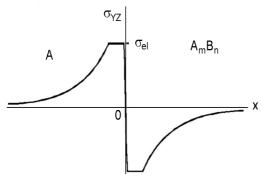


Fig. 3. Damping of excess stress by mechanism of plastic deformation.

In assumption that the brittle fracture of an intermetallic phase with formation of cracks with Δl width (Fig. 4) is the only mechanism of relaxing the stress (1) caused by the relative deformation $\Delta V/V_0$, the deformation in the direction of crack opening (in our case, along Y axis) will be $\Delta l/l{\approx}1/3\Delta V/V_0$. Then the value of stress occurring in the intermetallic phase can be expressed as

$$\sigma_{\max} \approx 3G \frac{\Delta l}{l}$$
. (2)

2. Relaxation processes in Cd-Ni diffusion zone

A rather convenient object for experimental studying the processes of brittle relaxation of tensile stress occurring in an intermetallic phase growing in the diffusion zone is Cd-Ni system which diffusion properties are well investigated [9, 10].

According to the equilibrium diagram [11], solubility in solid state is practically absent in Cd-Ni system. As a result interdiffusion between Cd and Ni plates contacting by a flat boundary, a layer of $\mathrm{Cd_{21}Ni_5}$ intermetallic phase appears and grows; it has a cubic structure with unit cell parameter $a_{\mathrm{I}}=9.753$ Å. The unit cell includes 52 atoms: 42 atoms of Cd and 10 atoms of Ni. The volume of the unit cell is $V_{\mathrm{I}}=a_{\mathrm{I}}^{3}$.

Cd has a hexagonal close-packed lattice with parameters $a=2.9851\,\text{Å}$ and $c=5.6206\,\text{Å}$. The unit cell is a body-centered right-angle prism with height c and rhomb base with side a. The volume of the unit cell is $V_{\text{Cd}}=ca^2\sqrt{3}/2$. The unit cell contains 2 atoms. Ni face centered cubic lattice has the parameter $a_{\text{Ni}}=3.524\,\text{Å}$. The volume of the unit cell consisting of 4 atoms is $V_{\text{Ni}}=a^3_{\text{Ni}}$.

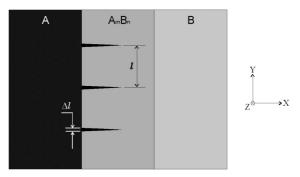


Fig. 4. Scheme of brittle relaxation of tensile stress in the $A_m B_n$ layer.

The reaction of formation of a single $Cd_{21}Ni_5$ unit cell can be written as:

$$42\text{Cd} + 10\text{Ni} \rightarrow 2\text{Cd}_{21}\text{Ni}_{5}$$

or as

21Cd unit cells + 2.5Ni unit cells
$$\rightarrow$$
 1 Cd₂₁Ni₅ unit cell.

Therefore the relative deformation accompanying the formation of the intermetallic phase is:

$$\Delta V/V_0 = \frac{V_{\rm I} - (21 \cdot V_{\rm Cd} + 2.5 \cdot V_{\rm Ni})}{21 V_{\rm Cd} + 2.5 \cdot V_{\rm Ni}} = -0.09.$$

Taking the elastic modulus of the intermetallic phase as $G = 5 \cdot 10^{10} \, \text{N} \cdot \text{m}^{-2}$, we obtain the evaluation of tensile stress corresponding to this deformation:

$$\sigma_{\rm max} \sim G \left| \frac{\Delta V}{V_0} \right| \approx 4.5 \cdot 10^9 {\rm N \cdot m^{-2}}.$$
 (3)

The process of stress brittle relaxation was studied by metallographic methods. Two-layer Cd-Ni samples were prepared: plane-parallel plates cut from cadmium and nickel bars were grinded and polished. Then the plates were brought in contact by their polished surfaces and annealed isothermally at T = 280°C during about 10 h in the atmosphere of flowing hydrogen. After annealing, the sample was treated by metallographic polishing in the direction perpendicular to Cd-Ni contact plane. Structure of the intermetallic phase layer formed between Cd and Ni plates was studied by a metallographic microscope. A typical micrograph of this layer is shown in Fig. 5. Using an ocular micrometer, an average width Δl of cracks formed in the intermetallic layer and a characteristic distance l between the cracks were measured.

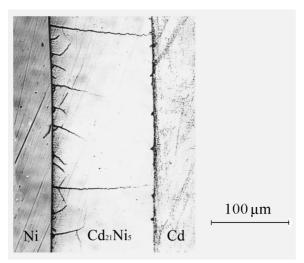


Fig. 5. Micrograph of a Cd-Ni sample after annealing at 280°C for 10~h.

3. Results and discussion

Experimental values σ_{exp} of stress (which relaxation resulting in crack formation) were evaluated by Eq. (2):

$$\sigma_{\rm exp} \approx 3G\frac{\Delta l}{l} \approx 3.75 \cdot 10^9 N \cdot m^{-2}$$
.

As it is seen, the level of experimentally measured stress acting in the intermetallic layer is by a factor 1.2 lower than the value obtained from Eq. (3) calculated by the relative deformation accompanying the formation of the compound. This fact, evidently, indicates their partial relaxation by the mechanism of plastic deformation. Because the action of this mechanism is excluded in the intermetallic layer, we have to assume that the stress rapid damping took place in the materials of initial components.

The shape and distribution of cracks in the intermetallic phase (Fig. 5) show that stress attains its maximum absolute value near the Ni–Cd $_{21}$ Ni $_{5}$ interface. Hence, the stress plastic relaxation occurred in Ni; and the stress level calculated by the crack geometry in the intermetallic layer corresponds to the Ni elastic limit.

In [12, 13] intended to studying the influence of stress in the diffusion zone on the interdiffusion kinetics, the possibility of compressive stress plastic relaxation in Cd material during $Cd_{21}Ni_5$ layer growth. It was shown that the plastic relaxation results in lowering the stress down to $10^7~\mathrm{N/m^2}$ (Cd elastic limit) at the $Cd_{21}Ni_5$ -Cd boundary and changes significantly the Cd structure. Because no cracks occur in $Cd_{21}Ni_5$ on the

Cd side, the Cd elastic limit, evidently, does not exceed the $\text{Cd}_{21}\text{Ni}_5$ ultimate strength.

4. Conclusions

Tensile stress occurring within the $Cd_{21}Ni_5$ layer formed in interdiffusion process in Cd-Ni system exceeds the compound ultimate strength and relaxes by the mechanism of crack opening. Comparative estimation of the stress value by the geometry of cracks and by the volume jump accompanying the compound formation shows that before opening the cracks in the intermetallic phase, partial relief stress takes place as a result of plastic deformation in initial materials.

As the plastic relaxation inside the intermetallic phase is excluded, whereas the stress brittle relaxation begins at the Cd₂₁Ni₅-Ni interface, the conclusion is made that the damping of induced compressive stress in Ni took place down to the Ni elastic limit by the mechanism of plastic deformation.

Evidently, the stress plastic relaxation occurred also in Cd material which elastic limit is lower than the intermetallic phase ultimate strength.

References

- A.Wasilkowska, M.Bartsch, F.Stein et al., Mater. Sci. Eng., A 381, 1 (2004).
- 2. Ya.E.Geguzin, Diffusive Area, Nauka, Moscow (1979) [in Russian].
- V.G.Kononenko, V.V.Bogdanov, M.A.Volosyuk, A.V.Volosyuk, Functional Materials, 23, 158 (2016).
- 4. B.D.Dun, Materials and Processes for Spacecraft and High Reliability Applications, Springer International Publishing, Switzerland (2016).
- Ye.Ye.Deryugin, N.Antipina, Mechanics. Mater. Sci. Eng., 1, 48 (2015).
- L.E.Kar'kina, O.A.Elkina, L.I.Yakovenkova, Bull. Russian Acad. Scie. Physics, 71, 618 (2007).
- Ming-Che Chen, Che-Wei Kuo, Chia-Ming Chang et al., Materials Trans., 48, 2595 (2007).
- 8. Y.P.Raizer, Usp. Fiz. Nauk, 100, 329 (1970).
- 9. L.N.Paritskaya, V.V.Bogdanov, Defect and Diffusion Forum, 143-147, 615 (1997).
- L.N.Paritskaya, Yu.S.Kaganovskii, V.V.Bogdanov et al., Functional Materials, 6, 235 (1999).
- M. Hansen, K. Anderko, Constitution of Binary Alloys, 2nd Ed., McGraw-Hill Book Company, New York (1958).
- 12. L.N.Paritskaya, V.V.Bogdanov, Defect and Diffusion Forum, 129–130, 79 (1996).
- Yu. Kaganovskii, L. N. Paritskaya, V. V. Bogdanov, W. Lojkowski, Defect and Diffusion Forum, 264, 123 (2007).