The Diffusion of Sulfur-35 in NiO

D. R. CHANG, R. NEMOTO, AND J. B. WAGNER, Jr.

The diffusion of radiotracer sulfur in single crystals and in pressed powder compacts of NiO has been studied. The diffusivities for the undoped single crystals were:

$$D = 1.89 \times 10^{-5} \exp(-185.3 \text{ kJ}/RT), \text{ cm}^2/\text{s}$$

between 820°C and 1200°C and under virtually constant [0.77 to 1.0 atm] oxygen pressure. The diffusivities in pressed powders were greater than in the corresponding single crystalline specimens. The diffusivity of sulfur in NiO increased as the oxygen partial pressure over the crystal decreased. This result indicates that sulfur might migrate via oxygen vacancies. The diffusivity of sulfur in Cr-doped crystals was found to be about an order of magnitude lower than the undoped crystal. The results obtained on the doped crystals were consistent with the oxygen vacancy mechanism.

THE diffusion of host cations and foreign impurity cations in oxides has been relatively well studied compared to the diffusion of anions, especially anion impurities. In many practical applications the transport of anion impurities across an oxide layer is of primary importance. A well known example is the case of turbine engines operating in aircraft or ships. The combination of sulfur in the fuel and sodium chloride in the air over sea water reacts to form sodium sulfate which settles on the turbine blades and related engine parts. This situation leads to a degrading of the coatings on the blades and a subsequent failure of the blade. In some instances, a layer of sulfur or sulfide appears below the oxide coating on the affected engine part.[1,2] It is not known how sulfur is transported through the oxide coating layer. Since nickel-base superalloys are the most widely used alloys in the turbine industries, the present paper reports the results of the studies on the rate and mechanism of sulfur transport through a model system, nickel oxide.

EXPERIMENTAL

A) Sulfur Diffusivities in Doped and Undoped NiO

Table I. Impurity Concentrations in NiO (in ppma)

Element*	Detection Limit†	NiO(Cr)	NiO
Li	0.1	N.D	N.D.
F	0.1	0.1	3.4
Na	0.1	N.D.	14
Al	0.7	14	N.D
Si	3	2.5	N.D.
S	7	50	38
Cl	0.7	N.D	0.92
K	0.1	0.12	2.1
Ca	0.7	2.1	10
Mn	1	2.6	N.D
Fe	1	32	12
Co	3	N.D	46
Cu	1	1.5	N.D.
Zn	3	2.5	7.6
Cr	0.3	3,900	N.D

*No analysis was made for hydrogen. Analyses for carbon, nitrogen, tantalum, and gold are not given since tantalum slits are used in the mass spectrometer and the samples were mounted on styrene and sparked against gold counterelectrodes. Other elements not listed were not detected and have concentrations less than 10 ppma.

†Determined for 3 × 10^{-8} coulomb exposure

N.D.—Not detected

Single crystals were supplied by SIN CRYS, Inc., Oak Ridge, Tennessee. The crystals were grown by the flame fusion technique. Spark source mass spectrometric analyses of doped and undoped single crystalline NiO are listed in Table I. The crystals were first cleaved into rectangular parallelopipeds having faces parallel to the (100) planes. Typical dimensions were 0.3 cm × 0.3 cm × 0.1 cm. The nickel oxide crystals were preannealed under virtually constant (0.77 to 1.0 atm) oxygen pressure in a sealed quartz tube for at least 7 days.[3] This time was sufficient to homogenize the crystals according to the data of Price and Wagner.[4] After the preanneal, the crystals were withdrawn rapidly from the furnace and cooled to room temperature. Radiotracer sulfur-35 (≃0.01 mg) was applied to one face of each crystal by applying a solution of S-35 in benzene. The benzene was evaporated, leaving a thin layer of tracer. The crystals were then encapsulated in a quartz tube under the same conditions as the prediffusion anneal. The sealed tube containing the crystal was given a diffusion anneal for 5 to 15 days. The tube was then withdrawn rapidly from the furnace and the specimen was removed from the tube. Approximately 150 microns were ground from the faces of the crystal which were not originally coated with radiotracer. The crystal was mounted in a room-temperature setting plastic within a stainless steel ring. The radioactivity of the original surface was counted by using a model 1152 Nuclear Chicago low-background, gas flow counting system. Successive layers were ground off parallel to the original surface and the residual activity counted on each remaining surface. A total depth of about 100 μ was removed. A typical plot of erfc^{-1} (I/I_1) *vs* x for sulfur diffusing into NiO is shown in Fig. 1. The absorption effects of sul-

---

D. R. CHANG is with General Electric Co., Cincinnati, OH. R. NEMOTO is with Nippon Yakin Co., Ltd., Kawasaki, Japan. J. B. WAGNER Jr. is Director of Materials Research Center and Professor of Materials Science and Engineering, Northwestern University, Evanston, IL 60201. D. R. Chang and R. Nemoto were formerly Graduate Student and Visiting Scholar, respectively, in the Department of Materials Science and Engineering at Northwestern University.

Manuscript submitted June 22, 1973.

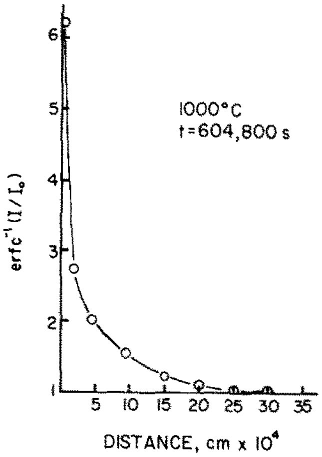

Fig. 1—Typical penetration profile for sulfur-35 in single crystalline NiO at 900°C.

fur-35 were corrected[5] by using a linear absorption coefficient of 1660 cm^{-1}.

The partial pressures of O_2 and SO_2 (assuming sulfur evaporated completely) inside the tube at elevated temperature were about 0.7 to 1.0 atm and 10^{-3} atm respectively. Attempts of varying sulfur activity under virtually constant oxygen partial pressure were made by adjusting the amount of S-35 deposited. However, no difference in the result was detected with different levels of sulfur activity. The amount of sulfur consumed by the specimen during each experiment was calculated to be about 10^{-6} mg (less than 0.1 pct of the initial amount deposited). This corresponded to a 0.2 ppma increase of sulfur in the specimen. The stoichiometry of the specimen was therefore not appreciably changed during the test. The data were then analyzed by using the constant source solution of Fick's Second Law. The constant source solution was used because the radioactive sulfur evaporated and yielded a constant gaseous source within the closed quartz tube. This solution is,

$$I = I_0\left[1 - \mathrm{erf}\left(\frac{x}{2\sqrt{Dt}}\right)\right] \qquad [1]$$

where I is the activity at any penetration distance x, I_0 is the activity of the diffusant at the surface, D is the appropriate diffusion coefficient in cm^2/s and t is the diffusion time in seconds. The data for both the undoped and Cr-doped single crystals are shown in Table II. The Arrhenius plot of the sulfur diffusion coefficient in the undoped crystals is shown in Fig. 2. For crystals equilibrated with virtually constant (0.77 to 1.0 atm) oxygen partial pressure, the data can be represented by:

$$D(\mathrm{S\ in\ NiO}) = 1.89 \times 10^{-5} \exp(-185.3\ \mathrm{kJ}/RT),\ \mathrm{cm}^2/\mathrm{s}.$$

The diffusivity of sulfur in the Cr-doped crystal was found to be about an order of magnitude lower than the undoped crystal. The results are shown in Table II and Fig. 3 and will be discussed later.

In a practical situation, a protective coating of an oxide is usually polycrystalline. Accordingly, powders of NiO (99.999 at. pct pure) obtained from Apache Chemicals were pressed in a cylindrical die of 0.78 cm diam under a load of approximately 5,000 psi. The pellets were sintered in air at 1500°C for 24 h. The density of the polycrystal following sintering was 93.1 pct of the theoretical. The grain size was about 10 to 12 μ. The samples were preannealed in the same way as for the single crystals in order to adjust the stoichiometry. The pellets were then quenched, radiotracer sulfur was applied to one face of the pellets, and the diffusion anneal and counting procedure were carried out in the same manner as described above for the single crystals. In order to compare these results with those on the single crystals, equations for calculating the bulk diffusion coefficient were applied to compute the diffusion coefficient in the compact

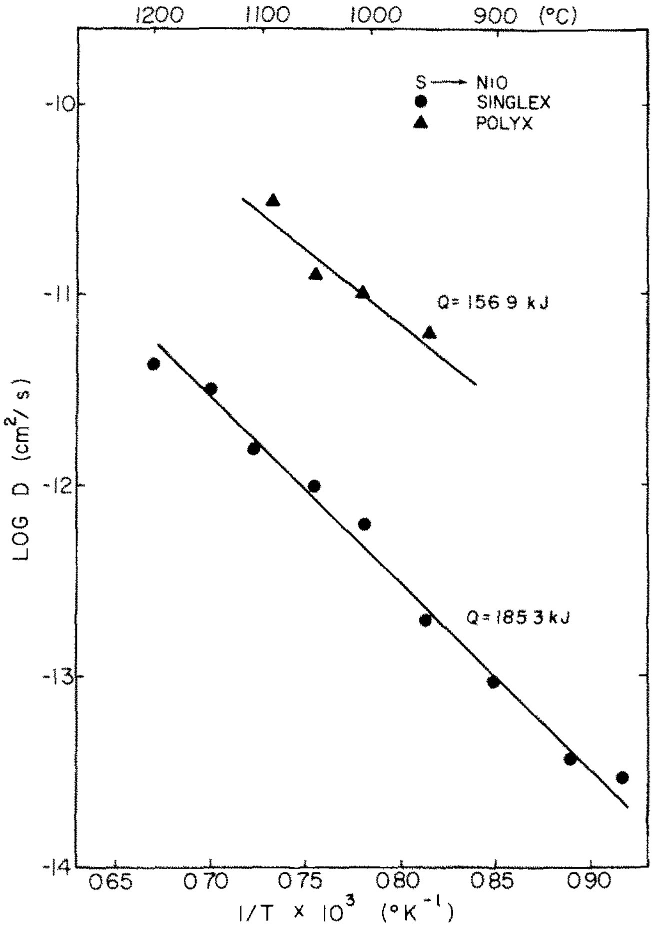

Fig. 2—Arrhenius plot of the sulfur diffusion coefficient in the undoped single and polycrystalline NiO heated under virtually constant [0.77 to 1.0 atm] oxygen pressure.

Table II. The Sulfur-35 Diffusion Coefficients of NiO Heated Under Virtually Constant [0.77 to 1.0 atm] Oxygen Partial Pressure

D(cm^2/s), C°	NiO Single Crystal	Cr-Doped NiO Single Crystal	NiO Polycrystal
820	3.4×10^{-14}	–	–
850	4.3×10^{-14}	–	–
900	8.8×10^{-14}	8.0×10^{-15}	–
950	1.9×10^{-13}	1.1×10^{-14}	6.3×10^{-12}
1000	5.4×10^{-13}	2.1×10^{-14}	1.0×10^{-11}
1050	8.9×10^{-13}	3.5×10^{-14}	1.2×10^{-11}
1090	–	–	3.3×10^{-11}
1100	1.9×10^{-12}	6.1×10^{-14}	–
1150	3.2×10^{-12}	8.5×10^{-14}	–
1200	4.8×10^{-12}	2.3×10^{-13}	–

specimens. The results are shown in Table II and Fig. 2. The diffusion coefficient for the specimens studied can be represented as:

$$D(\text{S in polyx NiO}) = 2.85 \times 10^{-5} \exp(-156.9 \text{ kJ}/RT) \text{ cm}^2/\text{s}$$

for oxygen pressures of 0.86 to 0.96 atm.

B) Diffusion of Sulfur Tracer Under Different Oxygen Partial Pressures

Experiments of sulfur tracers diffused into single crystalline NiO under different oxygen partial pressures were performed in order to study the mechanism of sulfur migration. The oxygen partial pressures were established as described in Section A and also by utilizing the oxygen pressure equilibrated over two phase mixtures of Cu/Cu_2O or Fe_3O_4/Fe_2O_3. The single crystalline NiO was placed inside a smaller quartz tube (one end open) to prevent direct contact with the Cu/Cu_2O (or Fe_3O_4/Fe_2O_3). The smaller tube was then placed inside a larger quartz tube containing the Cu or Fe oxide mixture. The larger tube was sealed off and the crystal was preannealed for two weeks to ensure equilibration to the desired stoichiometry. The radiotracer sulfur was then applied to the crystal and the diffusion anneal under the fixed oxygen partial pressure was carried out. The surface activities after the diffusion anneals were found to be similar to those annealed under 0.77 to 1.0 atm oxygen partial pressure. The diffusion coefficients were found to increase with decreasing oxygen partial pressure (Table III). The log D *vs* log p_{O_2} plot (Fig. 4) yielded negative slopes ($-1/7.5$ to $-1/6.2$). The possible diffusion mechanism will be discussed below.

DISCUSSION

The diffusivities of nickel[6] and oxygen[7] in NiO have been studied. For example, at 1000°C the diffusivity of nickel in NiO under 0.21 atm oxygen is 10^{-11} cm^2/s and the diffusivity of oxygen under 50 Torr is 8×10^{-14} cm^2/s. Thus, the diffusivity of sulfur lies between that of the host cation and host anion for the single crystalline oxides. In the present work, the oxides were heated almost isobarically [0.77 to 1.0 atm] so the activation energy, Q, is made up of several terms,[8]

Table III. The Sulfur-35 Diffusion Coefficient as a Function of Oxygen Partial Pressure Over NiO

Temperature, C°	Oxygen Partial Pressure, atm	D (cm^2/s)
850	0.79	4.3×10^{-14}
850	4.5×10^{-6}	$1\ 3 \times 10^{-13}$
850	$8\ 1 \times 10^{-9}$	$5\ 8 \times 10^{-13}$
850	$8\ 5 \times 10^{-10}$	5.9×10^{-13}
900	0 83	8.8×10^{-14}
900	$6\ 9 \times 10^{-8}$	$5\ 3 \times 10^{-13}$
900	$5\ 2 \times 10^{-9}$	1.4×10^{-12}
1000	0.89	$5\ 4 \times 10^{-13}$
1000	$4\ 5 \times 10^{-6}$	$3\ 8 \times 10^{-12}$
1100	0 96	$1\ 9 \times 10^{-12}$
1100	1.8×10^{-4}	$6\ 5 \times 10^{-12}$

$$Q = \left[\frac{-\Delta \overline{H}^M_{1/2 O_2}}{(m+1)} + \Delta H^{\ddagger} + \Delta H_S \right] \qquad [2]$$

where $\Delta \overline{H}^M_{1/2 O_2}$ represents the partial molar enthalpy of dissolution of oxygen, $\Delta H^{\ddagger}$ represents the activated enthalpy of migration, ΔH_S is the enthalpy of forming Schottky defects, and m denotes the ionization state of

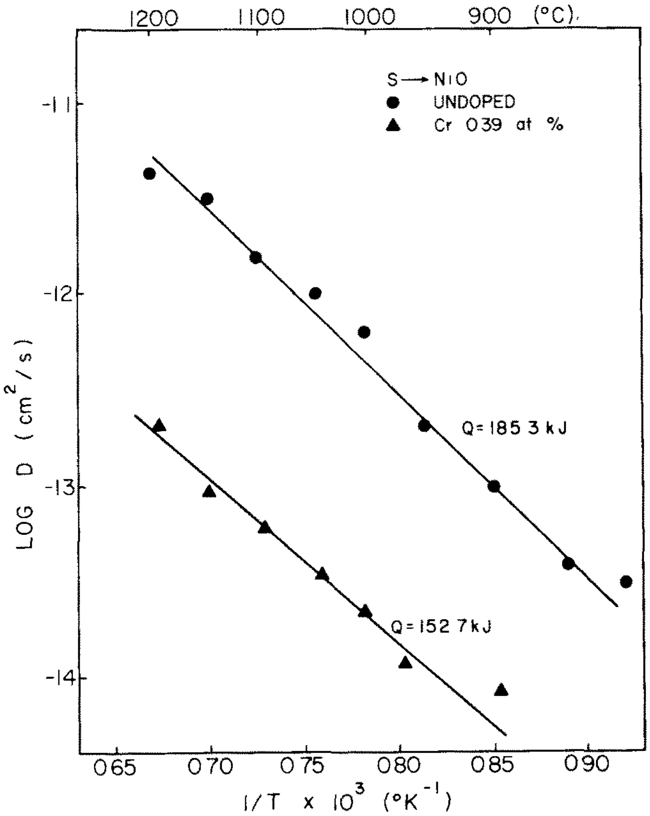

Fig. 3—Arrhenius plot of the sulfur diffusion coefficient in the Cr-doped and undoped single crystalline NiO heated under virtually constant [0.77 to 1 0 atm] oxygen pressure.

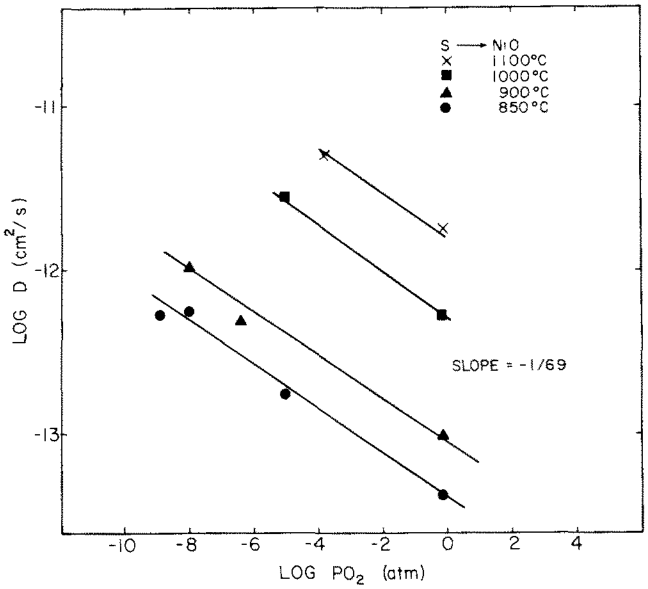

Fig. 4—The sulfur diffusion coefficient as a function of the oxygen partial pressure over NiO single crystals.

the majority lattice defects. Eror and Wagner[9] have estimated the partial molar enthalpy of dissolution of oxygen ($\Delta\bar{H}^{M}_{1/2\,O_2}$) into NiO in air to be about 131.8 kJ/mole. The value of ΔH_s is needed in order to determine the activation energy for the motion of sulfur. Unfortunately, this value has not been reported for NiO. The sulfur transport in polycrystalline specimens was more rapid than in single crystals as had been expected. Thus, short circuit diffusion is very important in practical applications.

The increased diffusion rate with decreasing oxygen partial pressure and the possible migrating mechanism may be interpreted as follows. Nickel oxide always exists with an O/Ni ratio greater than one. The dissolution of excess oxygen may be represented by

$$\tfrac{1}{2}O_2 = O_O + V''_{Ni} + 2h. \qquad [3]$$

Application of the law of mass action yields

$$K = [V''_{Ni}] \cdot [h]^2/p_{O_2}^{1/2} \qquad [4]$$

and the electroneutrality condition requires that

$$[V''_{Ni}] = \tfrac{1}{2}[h]. \qquad [5]$$

Hence,

$$K = 4\,[V''_{Ni}]^2 \cdot [V''_{Ni}]/p_{O_2}^{1/2} \qquad [6]$$

so that

$$[V''_{Ni}] \propto p_{O_2}^{+1/6} \qquad [7]$$

where $[V''_{Ni}]$ and $[h]$ are the concentrations of nickel vacancies and electron holes, respectively. Furthermore, the concentrations of anion and cation vacancies are coupled through the Schottky product as

$$K_s = [V''_{Ni}] \cdot [V^{\cdot\cdot}_O]. \qquad [8]$$

From Eqs. [7] and [8] it is seen that

$$[V^{\cdot\cdot}_O] \propto p_{O_2}^{-1/6}. \qquad [9]$$

If the sulfur tracer diffuses via oxygen vacancies, then

$$D \propto \Gamma \cdot g \cdot [V^{\cdot\cdot}_O] \qquad [10]$$

where Γ is the jumping frequency and g is the geometric factor. If these two factors are constant with respect to the oxygen partial pressure change, at constant temperatures

$$D \propto [V^{\cdot\cdot}_O] \propto p_{O_2}^{-1/6}. \qquad [11]$$

A plot of log D *vs* log p_{O_2} theoretically should yield a slope of $-1/6$. The experimental data (varied from $-1/7.5$ to $-1/6.2$) were in fairly good agreement with the theoretical value.* The difference could be due to impurities in the crystal, to the experimental errors and to interactions between the defects (nonideal solution). The migration of sulfur in NiO is therefore suggested to be via oxygen vacancies. On the other hand, if sulfur migrates via interstitial positions, the diffusivity should not be changed relative to the oxygen pressure change. The large sulfur species would also be very difficult to move via interstitial positions.

The proposed mechanism was further checked by studying the diffusivity in a Cr-doped crystal. The doping effect of chromium on a NiO single crystal has been well studied.[10,11] Chromium will substitute for nickel and generate an electron according to the following mass balance equation:

$$Cr_2O_3 = 2\,Cr^{\cdot}_{Ni} + 3\,O_O + 2e. \qquad [12]$$

Since NiO is a p-type conductor with nickel vacancies as its majority point defects,[9,10] the electroneutrality condition requires that

$$[Cr^{\cdot}_{Ni}] + [h] = 2\,[V''_{Ni}] \qquad [13]$$

where $[Cr^{\cdot}_{Ni}]$ is the concentration of the chromium substituted for nickel. The nickel vacancies will be increased and electron holes will be depressed in comparison to the undoped crystal.[10,11] Since oxygen vacancies are coupled with nickel vacancies through the Schottky product (Eq. [8]), the oxygen vacancies will therefore be depressed due to the increase of nickel vacancies. If sulfur migrates via oxygen vacancies, the diffusivity of sulfur in the doped crystal should decrease as compared to that in the undoped crystal. The experimental results indicated a decrease in diffusivity of about an order of magnitude for the Cr-doped crystal (Table II). The oxygen vacancy mechanism was therefore inferred to be the most probable.

From a practical point of view, sulfur diffusion is sufficiently rapid in an oxide to account for the transport to the underlying metal. The diffusivity of sulfur in nickel[12] is orders of magnitude more rapid than in the oxide. Furthermore, the solubility of sulfur in nickel shows retrograde solubility.[13] These facts, coupled with the possibility of forming low melting sulfides in a metal, make the coating on an engine part necessary.

SUMMARY

The diffusion of sulfur in single and polycrystalline NiO has been studied between 820°C to 1200°C. Sulfur diffuses more rapidly than the host anion and less rapidly than the host cation. Decreasing oxygen partial pressure over NiO increased the diffusion rate. This result indicates that sulfur migrates via oxygen vacancies. The lower diffusivity of sulfur in Cr-doped crystals is consistent with the proposed mechanism.

ACKNOWLEDGMENT

This work was supported by the U. S. Army Research Office-Durham under Contract Number DAHCO 4 70 C 0062.

REFERENCES

1 M. J. Donachie, Jr., R A Sprague, R N Russell, K G. Boll, and E P. Bradley *ASTM STP,* 1967, vol. 421, pp 85-104
2 P R. Belcher, R. J Bird, and R W Wilson *ASTM STP,* 1967, vol 421, pp 123-45
3 D R Chang, W. Stewart, and J B Wagner, Jr *Proc Seventh Int'l Symposium on the Reactivity of Solids,* p 231, Chapman and Hall, Ltd., Bristol, England, July 1972
4 J B Price and J B Wagner, Jr *Z Physik Chem (N F),* 1966, vol 49, pp 257-70
5 D. R Chang Ph D. Thesis, Northwestern University, 1973
6 J. S. Choi and W. J. Moore *J. Phys Chem* , 1962, vol 66, pp. 1308-11
7 M O'Keefe and W. J. Moore. *J Phys Chem.,* 1961 vol 65, pp 1438-39
8 J B Price and J. B. Wagner, Jr *J Electrochem Soc.,* 1970, vol. 117, pp. 242-47
9 N G. Eror and J. B Wagner, Jr *Phys. Status Solidi,* 1969, vol 35, pp. 641-51
10. K Hauffe *Ann Phys* , 1950, vol 8, pp 201-10
11 G M Schwab and H Schund *J Appl Phys* , 1962, vol 33, pp 426-28.
12. I F Kononyuk and M. M Pavlyuchenko *Geterogennye Khim Reakt* , 1961, p 231, known through *Chem. Abstr* , 1962, vol 57, p 3162h.
13 R J Brigham, H. Neumayer, and J S. Kirkaldy *Can. Met Quart* , 1970, vol 9, pp 525-29

---

*If singly ionized nickel vacancies predominate, the dependence on oxygen pressure would be one quarter. In any case the general argument remains unchanged. Increasing oxygen pressure decreases D.