

Letter to the Editors

**Hardening of Alloy N10276 by diluted flowing butane gas**

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Nickel-based alloys such as Alloy N10276 (Hastelloy C-276), Alloy N06600 (Inconel 600) and Alloy N06617 (Inconel 617) are commonly used in high temperature gas cooled reactors (HTGCRs) in Japan. These alloys are subjected to carburization due to the flow of hydrocarbon gases, such as butane or propane in the reactor primary loop [1]. Thermodynamic calculations [2] showed that a forward reaction occurs during butane cracking leading to carbon and hydrogen gas release. The deposited carbon and the liberated hydrogen diffuse into the alloy during normal operation of HTGCRs.

The aim of this letter is to present and discuss the results of carburization of Alloy N10276 by commercial butane gas as affected by the carburization temperature, carburization time, and the purity of the carburizing environment.

Alloy N10276 was supplied in the present work in the form of a plate. The chemical composition of the plate is given in Table 1. The plate was machined into coupons (10 × 20 × 10 mm). The specimens were solution annealed at 1150°C for 2 h, followed by water quenching. The specimens' surfaces were polished by emery papers, finished by  $\gamma$ -alumina powder (0.05  $\mu$ m) and cleaned by distilled water prior to the carburization process. The details of the carburization system used in this study are given elsewhere [3]. Pyrogallol powder placed in a container connected to the mixing chamber in that system was used to minimize oxygen content in the following gases. Calcium chloride powder was placed in another container connected to the pyrogallol powder container to reduce the moisture content of the flowing gases.

Argon and commercial butane gas flow rates were adjusted at 6 and 0.6 l/h (1.66 and 0.16 cm<sup>3</sup>/s), respectively, prior to the insertion of the reactor in the furnace preheated to the desired temperatures (850, 900 and 950°C).

The carburization times were 24, 48, 72 and 96 h. After the carburization, the specimens were water quenched and their surfaces were cleaned by a tooth brush to remove the surface products. The depth of carburized zones in the specimen were determined by optical microscope. The microhardness tests were carried out on the mirror-like surfaces of the specimens using the microhardness tester Shimatzu-V Type with a 200 g load applied for 10 s.

In this letter, the results of carburization of Alloy N10276 are presented. The carburized zone of the specimens at 850 or 900°C was finer than at 950°C for the same carburization time. Intra- and intergranular carbides precipitated in the specimens due to carbon diffusion. The values of the carburized zone depths at the different testing temperatures and times are given in Table 2. The carburization zone depth, as expected, increased by increasing the carburization time and temperature. These results are in agreement with the results of Shindo and Nakajima [1] and Abd El-Azim [4] on the carburized Hastelloy X and Alloy 800 H, respectively, by Ar containing 10% CH<sub>4</sub> gas. The Cr contents in the Hastelloy X, Alloy 800 H and Alloy N10276 (in the present works) are 22, 20.5 and 15.5%, respectively. According to Yukitoshi et al. [5], the carburization depth increases by increasing the Cr content. However, the case depth in the present investigated alloy (15.5% Cr) is approximately equal to that reported [5] for Hastelloy X (22% Cr) tested at the same temperature and time.

In the present investigation, great care was taken to minimize the oxidation of the specimens and the formation

Table 1  
The chemical composition of the investigated Alloy N10276 (wt%)

C	Cr	Fe	Mo	Si	W	Ni
0.01	15.5	5.5	16.0	0.08	4.0	bal.

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Table 2

The carburized zone depths ( $\mu\text{m}$ ) at the different temperatures and times

Time (h)	Temperature ( $^{\circ}\text{C}$ )		
	850	900	950
24	100	190	270
48	140	220	350
72	180	270	420
96	220	320	500

of Cr and Ni oxides which increase the carburization resistance of the alloys. However, three specimens of Alloy N10276 were carburized without the use of the vacuum system, argon flushing, pyrogallol and calcium chloride powders, in order to allow for a slight oxidation of the specimens. The carburizing time in these tests was 96 h, and the carburization temperatures were 850, 900

and  $950^{\circ}\text{C}$ . The determined carburized depths were 100, 210 and  $300\ \mu\text{m}$  in that 'oxygenated' condition for tests at 850, 900 and  $950^{\circ}\text{C}$ , respectively. These values of the carburized depths are less than those measured in the 'de-oxygenated' system as given in Table 2 at the same carburizing temperatures and time (96 h). This is attributed to the formation of Cr-oxide on the specimens' surfaces which acted as a barrier for carbon diffusion and increased the carburization resistance of the alloy. It was reported that the alloys, which formed a protective oxide layer, are highly resistant to carburization [1]. Carburization of this alloy is thermodynamically unlikely except at very low oxygen partial pressures because the protective oxides are more likely to form than carbides. Therefore, it seems that the presence of oxygen and moisture in the coolant of HTGCRs is beneficial to overcome, or mitigate, the carburization problem. However, the possible oxidation problems in the coolant loops, which might arise due to oxygen

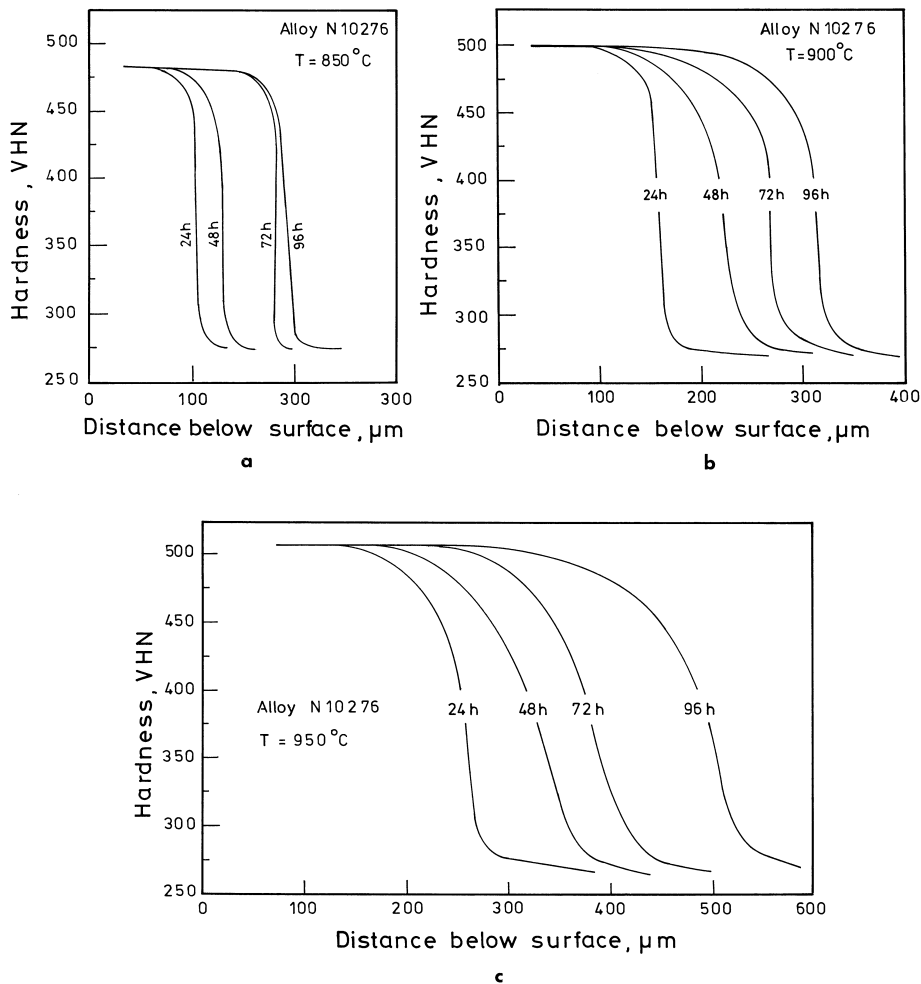


Fig. 1. The hardness–depth profiles for Alloy N10276 carburized at: (a)  $850^{\circ}\text{C}$ , (b)  $900^{\circ}\text{C}$  and (c)  $950^{\circ}\text{C}$ .

and moisture, should be taken into consideration. More investigations are needed to optimize the oxygen content in HTGCRs with respect to the carburization and oxidation problems.

The hardness–depth profiles for the specimens carburized at temperatures up to 950°C and for times up to 96 h is given in Fig. 1. It is clear from these profiles that increasing testing temperature and time markedly increase the depth of the hardened zone. This is attributed to the diffusion of carbon into the specimens and the formation of Cr-carbides, which are both temperature and time dependent [6].

The square of the carburized zone depth ( $\mu\text{m}^2$ ) increased linearly with the carburization time, as shown in Fig. 2. Therefore, the carburization kinetics follow a parabolic rate relation. This is in agreement with the results of Ennis and Lupton [7] on alloys with no oxides formed on their surfaces. In the present work, the evacuation process, followed by argon flushing and the use of pyrogallol and calcium chloride powders, reduced water and oxygen contents in the system. Thus, the carburization process was controlled by diffusion as well as precipitation process in the alloy.

The determined values of the parabolic rate constants ( $K_p$ ) for the carburization of Alloy N10276 at 850, 900 and 950°C were 0.5, 1.1 and  $2.6 \times 10^3 \mu\text{m}^2/\text{h}$ . These values are close to those values reported [1] for Hastelloy X despite the difference in the Cr-content in the Hastelloy X compared to that of Alloy N10276.

The plot of the logarithm of the carburization depth measurements versus the reciprocal of their corresponding

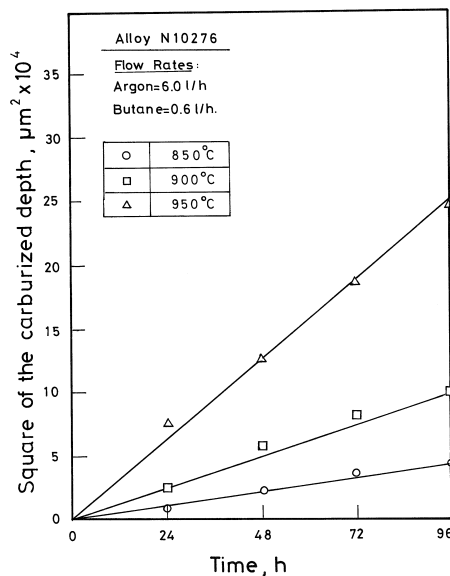


Fig. 2. The square of the carburized zone depth vs. carburization time at the temperatures 850–950°C.

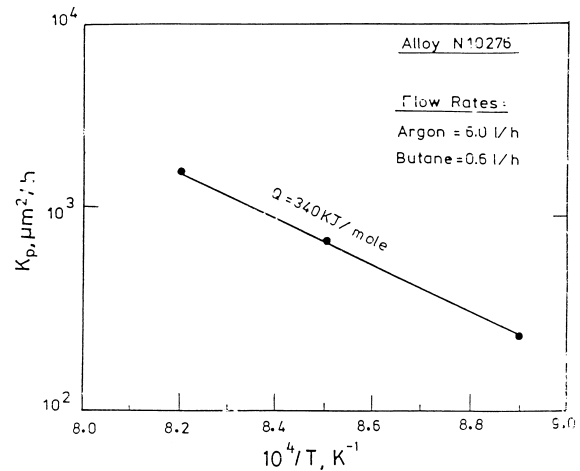


Fig. 3. Temperature dependence of the parabolic rate constants determined by the depth of the carburized zone.

absolute carburization temperatures, as shown in Fig. 3, gives an activation energy of about 340 kJ/mol. The reported values for the activation energies for carburization of Hastelloy X and Inconel 617 (22% Cr) are 209 and 290 kJ/mol, respectively [1,7], and are both less than that found in the present work for Alloy N10276 with a lower Cr content.

Therefore, it is emphasized from the present work that the carburization kinetics of Alloy N10276 by flowing butane gas follows a parabolic rate law. The activation energy for the carburization of Alloy N10276 under the de-oxygenated condition equals 340 kJ/mol. Also, the carburization problem of Alloy N10276 can be mitigated by allowing for some oxygen and moisture to exist in the flowing butane gas.

## References

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