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Behaviour Of Urea-Soda Baths for Liquid Nitriding Of Steels

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Abstract :

Variation in the compositions of the liquid nitriding baths based on Urea and Soda, with treatment temperature and time, has been studied by chemical analysis. Optimum bath compositions for satisfactory nitriding in the temperature range of 500-570°C has been established by optical metallographic studies and microhardness measurements on En40B steel specimens nitrided in such a bath. It has been found that the composition of the bath greatly affects the results obtained by nitriding in these baths. The useful life of such a bath has also been determined.

Introduction :

Earlier experiments[1-4] on liquid nitriding in a new bath based on urea and soda yielded very encouraging results. These studies, however, also showed that it was not possible to obtain satisfactory nitriding in this bath after a certain time and the salts had to be discarded It was therefore considered necessary to study the characteristics of this bath so as to determine the useful life and to ascertain the optimum composition of the bath capable of giving satisfactory results.

Experimental :

The experimental set up used for this study was essentially the same as described earlier[3] and the detailed description of preparation, operation, chemistry and maintenance of this bath can be found elsewhere[2]. Equal volumes of urea and soda were thoroughly mixed and the mixture was melted in the bath. Isothermal variation in bath composition was determined by withdrawing the salt-samples at a prespecified interval of time. Standard procedure[5] was followed to determine the amounts of the various components present in the salt samples. Specimens of En40B steel were also nitrided for 1 hr each at these time intervals, the timing being adjusted so as to be able to withdraw a sample after 1 hr of nitriding along with a sample from the salt bath. This, it was believed, would give the bath composition capable of giving the best results. The process was continued till the salt became viscous and unsuitable for further use.

Specimens cut from rolled stock of En40B steels were quenched from 930°C in water and tempered at 600°C for 0.5 hr. These were then cleaned mechanically, degreased in trichloroethy-

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lene and stored in a desiccator prior to nitriding. After nitriding the samples were washed thoroughly in water, neutralised in alkaline calcium hypochlorite solution and dried.

The effects of nitriding were studied by optical metallography and microhardness measurements. Sections orthogonal to the nitrided surface, cut off using a silicon carbide disc, were mounted in thermo-setting resin. These were prepared by using standard techniques and etched in nital for observation.

Microhardness measurements were made on the specimens prepared for optical metallography to determine the extent of penetration of nitrogen. The resultant variation in hardness from surface to core were then determined from the hardness versus penetration distance profiles. Microhardness on the surface of nitrided specimens were also determined. A Shimadzu microhardness tester has been used to carry out the hardness measurements and a load of 50 gm was applied for 5 seconds to cause the indentations.

Results and Discussion :

The bath on isothermal aging became viscous after about 60 hours at 500°C and 40 hours at 540°C. No nitriding could then be performed, and the salts in the bath had to be discarded Analysis of salt-samples collected from the bath at regular intervals are shown in Fig. 1 and Fig. 2. It can be seen from these figures that the amounts of the components in the bath change with time at constant temperature. This is expected because the cyanide formed in the bath due to reaction between urea and soda is heated in contact with air and hence gets oxidised to cyanate. This cyanate, on decomposition, forms atomic nitrogen, carbon and also sodium carbonate and sodium cyanide. The cyanide formed on decomposition of cyanate again gets oxidised to cyanate and the process continues.

Fig. 1 shows that the carbonate content in the bath is high even after only 1 hr of aging and increases continuously. It can also be noted that after a certain time, a higher amount of carbonate forms at higher temperature, i.e., the rate of reaction is higher at higher temperature. This gradual increase in the amount of carbonate is not unexpected because the sodium cyanide formed in the bath gets oxidised to cyanate and then on decomposition to cyanide and carbonate.

The cyanate content, on the other hand, can be found to decrease with time. The rate of decrease is also faster at higher temperature. It can be noted (Fjg. 2) that the cyanate content is rather high during the initial stages of aging at 500°C. In these experiments cyanate content was estimated by fixing nitrogen as ammonium sulphate. It is therefore possible that the ammonia gas which formed and was present in the bath at the initial stages interfered with the estimation. The expulsion of ammonia from the bath resulted in the change of slope. At higher temperature ammonia is expelled at a much faster rate and in the absence of ammonia the change is gradual. Since the amount of cyanate decreases with time, it is to be expected that the amounts of active carbon and nitrogen formed in the bath also decrease with treatment time. This would mean a decrease in the nitriding potential. The results obtained by nitriding (Figs. 5, 6 and 7) in the bath confirmed this observation. The bath was found to have a limited useful life and the salt became viscous due possibly to the increase in the quantity of high melting carbonate. It may be noted from Fig. 1 that the carbonate content increased to as high as 98 percent. This useful life was found to be inversely proportional to the temperature of nitriding. The results obtained suggest that addition of more urea and lesser amount of carbonate could be made to replenish the spent salt and also to maintain the bath composition within suitable limits. Detailed experimentation is however required to determine the exact amounts of the components to be added. The possibility of using a higher amount of urea together with a smaller amount of carbonate as starting bath composition, so as to obtain a longer useful bath life may also be investigated.

Fig. 3 and Fig. 4 show the microstructures of the nitrided samples. It can be seen that a thick compound layer forms during the early hours of

treatment whereas a thin layer is formed by nitriding towards the end of useful life of these baths. It is to be noted that all these test pieces were nitrided for the same duration of 1 hour.

The surface hardness was found to remain unaltered during most of the useful life of the bath (Fig. 5). However, the hardness decreased rather drastically towards the end of useful life of the bath.

The hardness versus penetration distance profiles (Figs. 6 & 7) show that the depth of nitrogen penetration at first increases and then decreases with bath life. The deeper penetration of nitrogen at the earlier stages of aging is perhaps due to the higher rate of dissociation (Fig. 2) of cyanate liberating more active nitrogen and carbon ; and thus creating a higher nitriding potential. The formation and the presence of ammonia gas in the bath during this period might also have contributed to this greater thickness. The ammonia gas is gradually expelled from the bath. The expulsion of ammonia and a decrease in the cyanate content in the bath cause a decrease in the nitriding potential of the bath and so the case depth (Fig. 8) falls off rather rapidly towards the end of the bath life.

These studies indicate that this bath is satisfactory for nitriding even at 500°C. It is to be noted that conventional cyanide-based baths give satisfactory results in the temperature range of 550 570°C. Moreover, only about 3 hours of aging of this bath is sufficient for satisfactory nitriding, while 12 hour aging treatment is recommended for conventional cyanide based baths.

It is well-known that hardening in nitriding is caused by finely dispersed nitride particles. These particles, at lower temperatures, take longer time to grow and thus cause greater hardness as can be seen in Fig. 5. The depth of penetration at lower temperatures, however, is low because of a slower rate of diffusion of the saturating elements. A higher case-depth together with a somewhat lower surface as well as core hardness is obtained at higher temperatures (Fig. 7). This is because the saturating elements diffuse faster at higher temperature leading to a greater depth of penetration. The lower surface hardness is due to the faster growth of nitride particles at higher temperatures while the decrease in core hardness is caused by the simultaneous tempering action occuring during nitriding of the quenched samples.

It is thus seen that satisfactory nitriding in this bath could be obtained in the temperature range of 500-550°C. Lower temperatures would give a higher surface hardness with a shallow case whereas higher nitriding temperatures would give a greater depth of penetration together with a lower surface hardness.

Attempts to study the behaviour of this bath at 570°C failed because of a much higher rate of evaporation of the salt. Only two samples of salt could be collected and the same trend in the variation of bath composition was observed.

Conclusions :

The following conclusions may be drawn from this study :

1. The bath requires aging, but the aging time is less than that required for cyanide based baths.
2. At higher temperatures evaporation loss is too great to permit economical use of this bath. The bath is satisfactory for nitriding at temperatures 500-550°C.
3. The bath life is shortened by the excessive formation of carbonate in the bath.

References :

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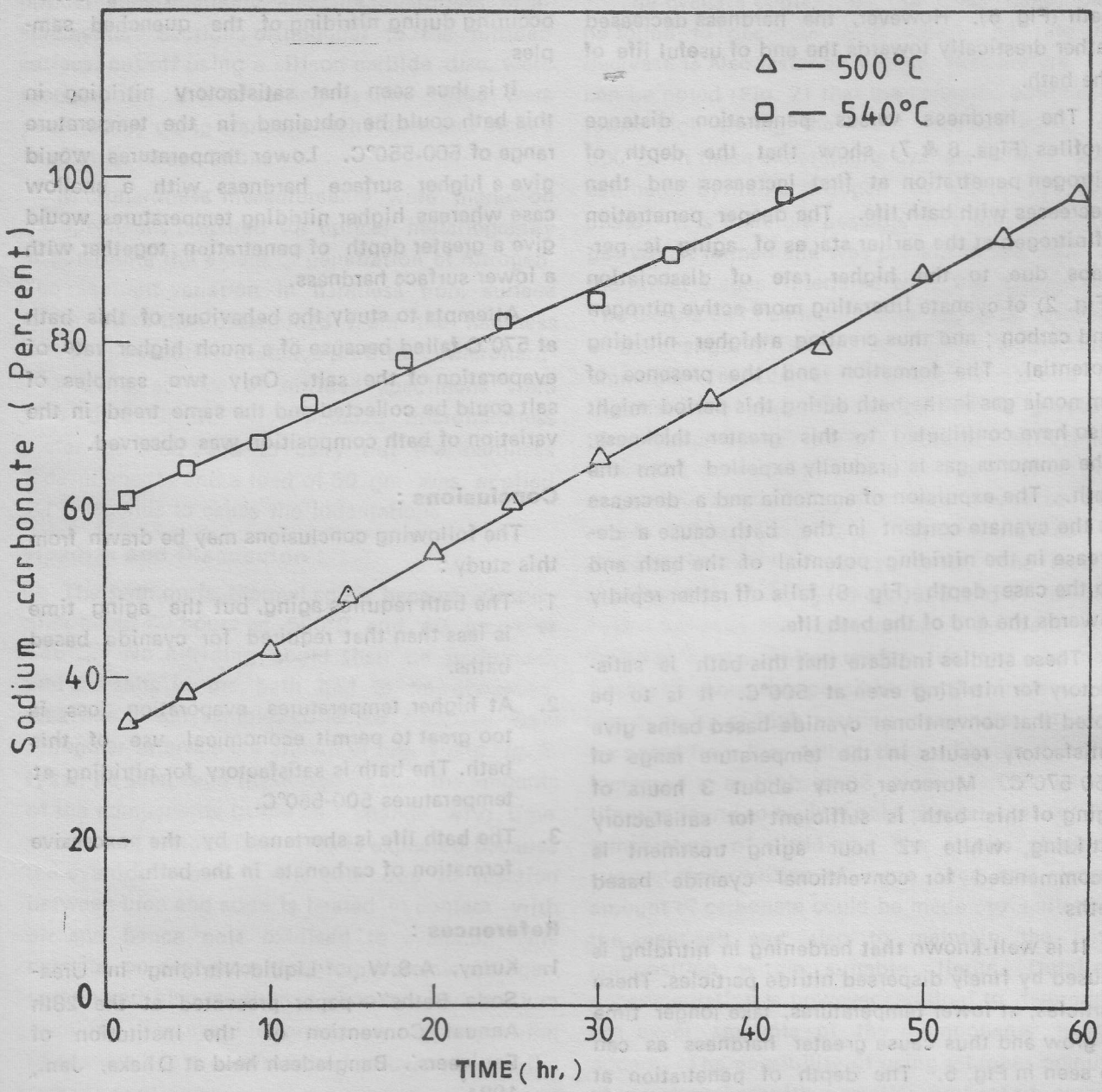

Fig. 1. Variation in the amount of Sodium carbonate with aging time at different temperatures.

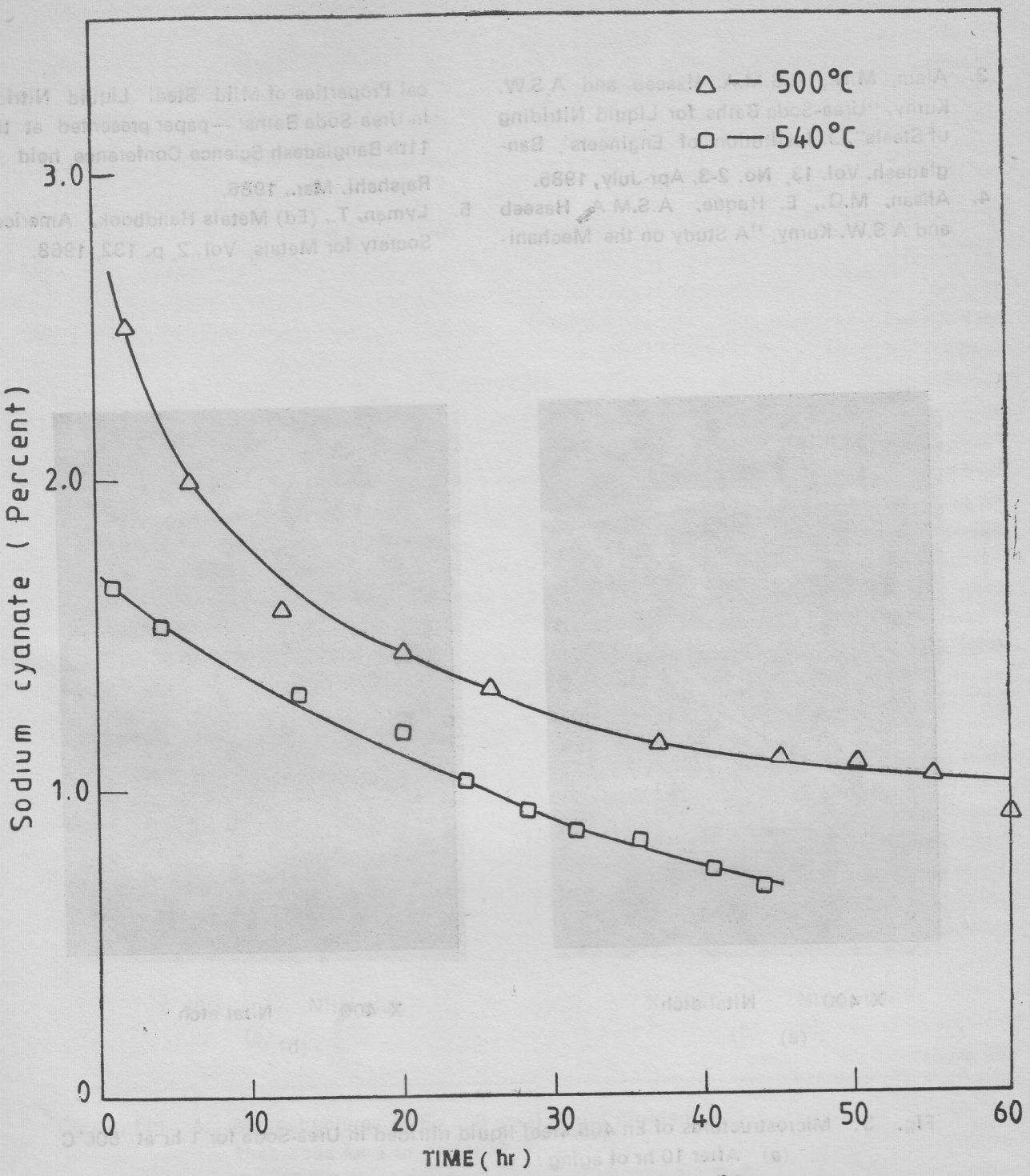

Fig. 2. Variation in the amount of Sodium cyanate with aging time at different temperatures.

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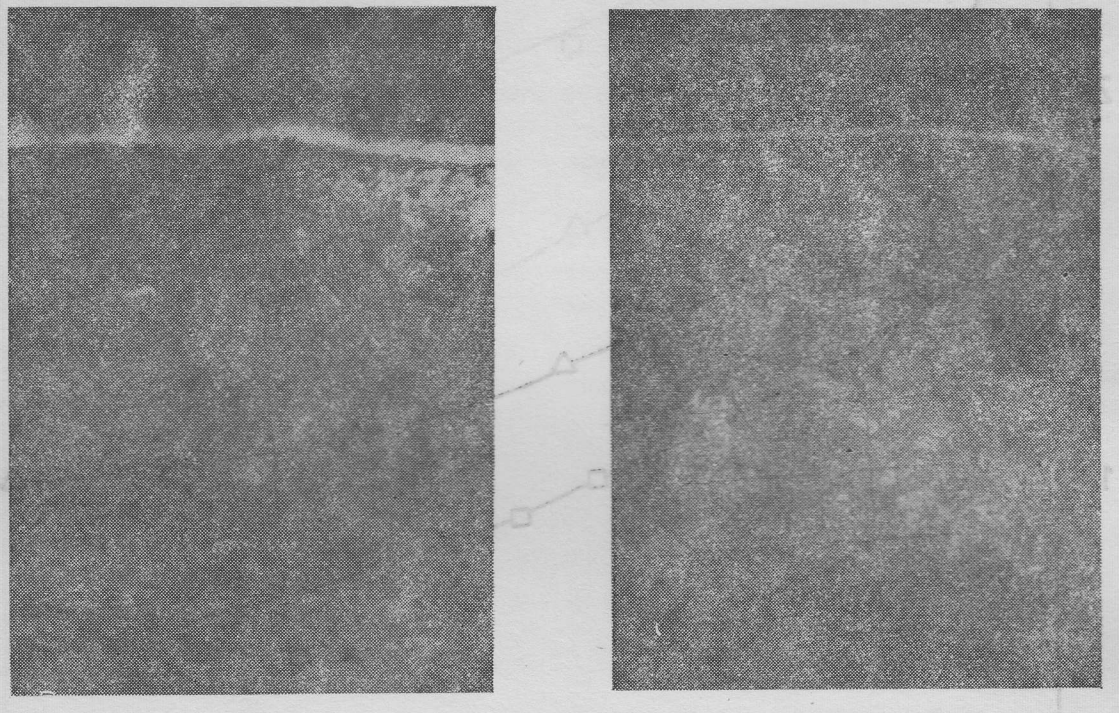


X 400 Nital etch (a)

X 400 Nital etch (b)

Fig. 3. Microstructures of En 40B steel liquid nitrided in Urea-Soda for 1 hr at 500°C
(a) After 10 hr of aging
(b) After 44 hr of aging.

X 400 Nital etch (a)

X 400 Nital etch (b)

Fig. 4. Microstructures of En 40B steel liquid nitrided in Urea-Soda for 1 hr at 540°C
(a) After 4 hr of aging
(b) After 34 hr of aging.

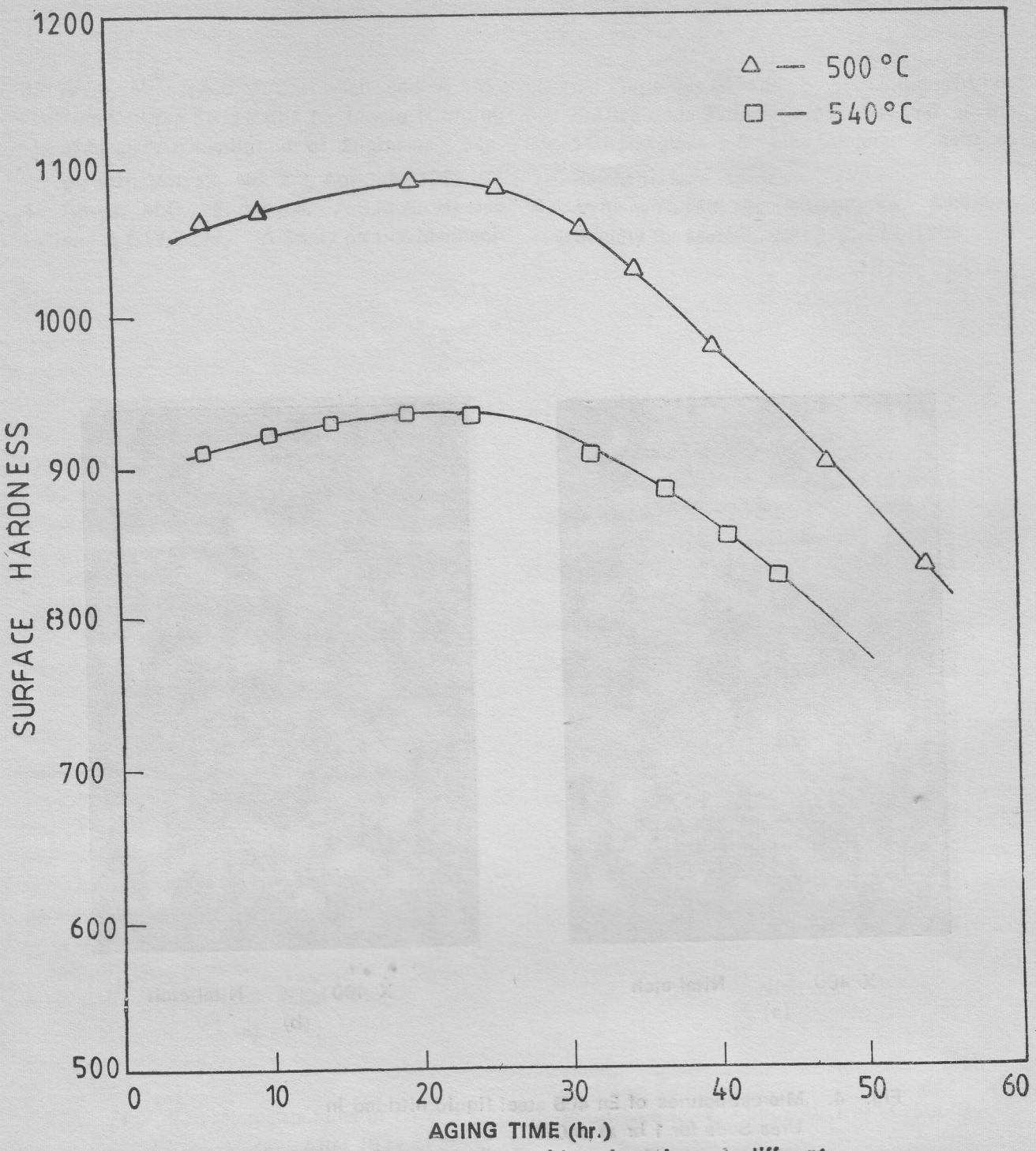


Fig. 5. Variation in surface hardness with aging time at different temperatures [Each specimen nitrided for 1 hr.].

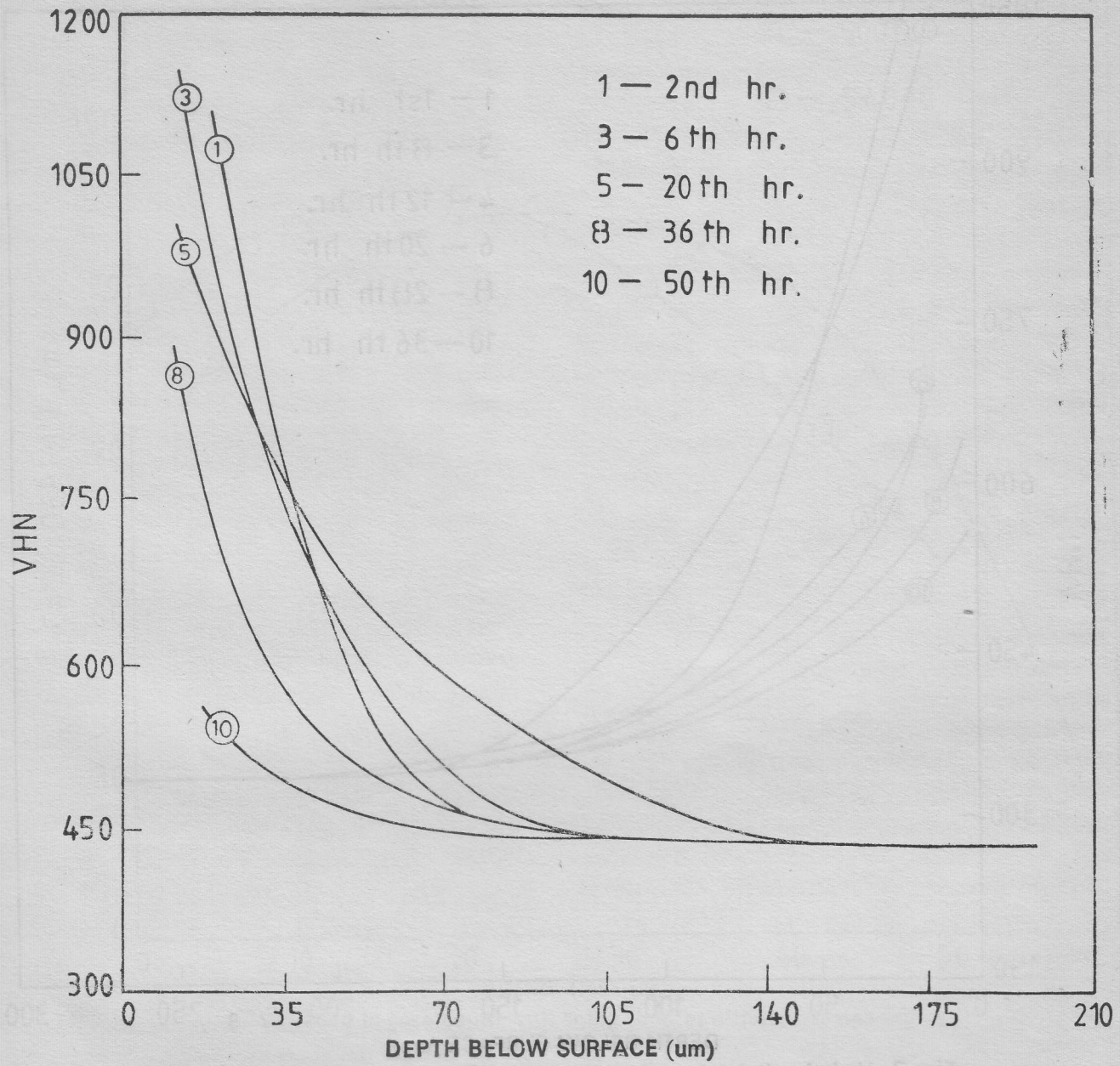


Fig. 6. Variation in hardness Vs. distance profiles with aging time at 500°C [Each specimen nitrided for 1 hr.]

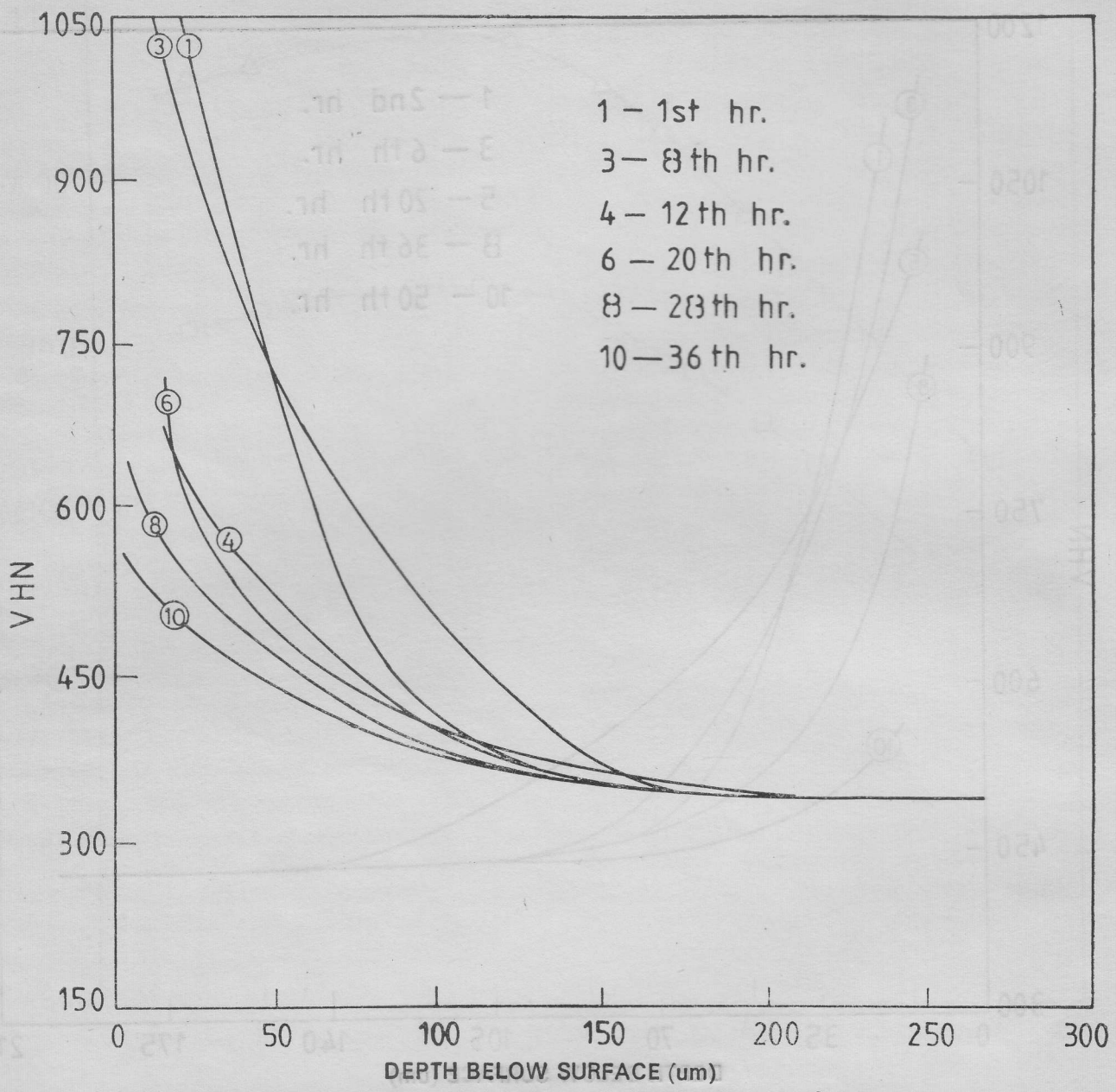
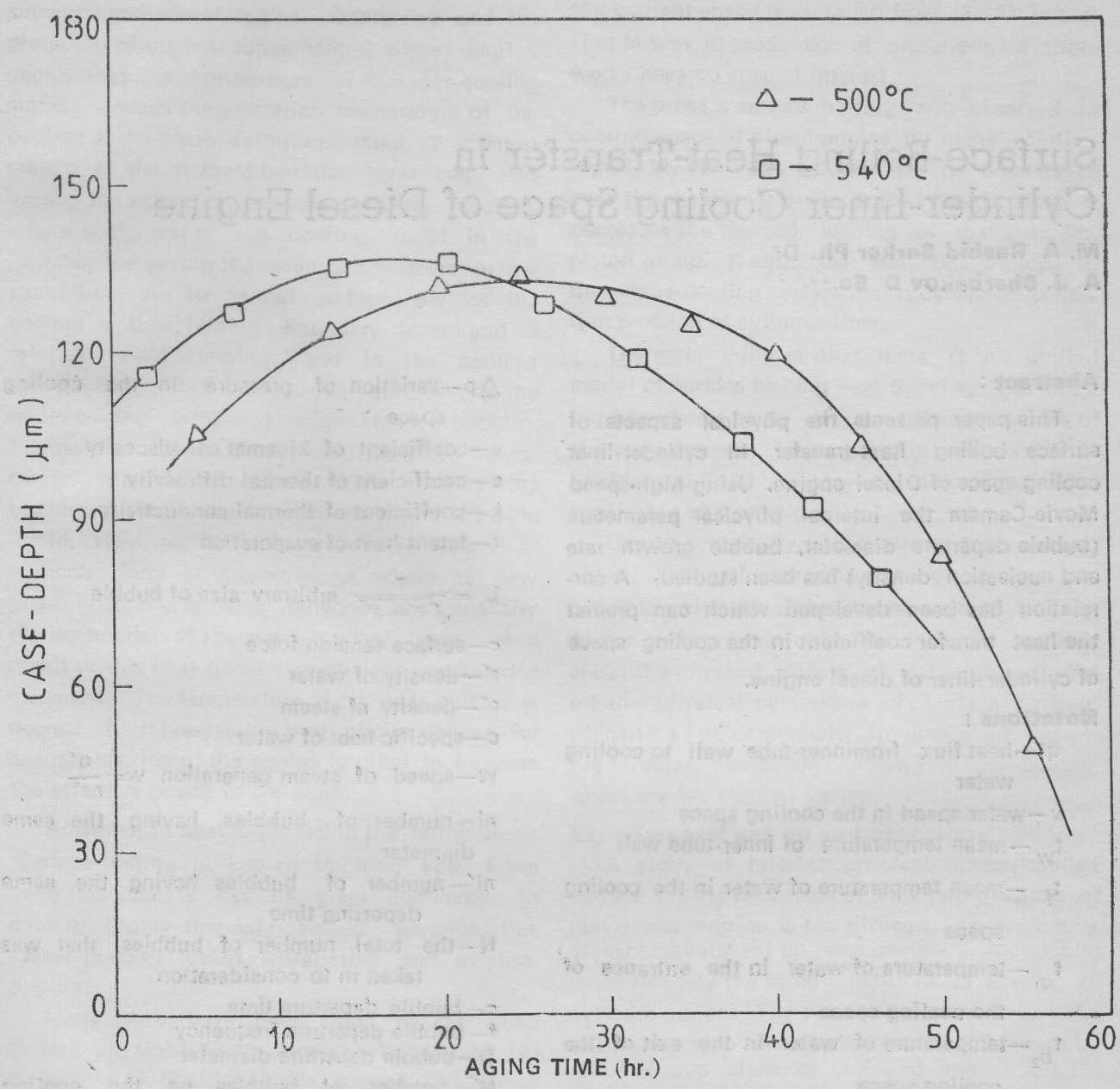


Fig. 7. Variation in hardness Vs. distance profiles with aging time at 540°C. [Each specimen nitrided for 1 hr.]



Fig, 8. Variation in case-depth with aging time at different temperatures.