EFFECT OF TEMPERATURE ON RECOVERY

AND ON PLASTICITY OF HARDENED STEEL

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Recovery of quench - hardened steel at room temperature consists in a simultaneous increase of its strength and plasticity with time prior to testing [1-7].

We have made a more detailed study of the temperature at which recovery takes place in hardened low-carbon steel and alloyed ferrite.

Procedure and Results.

An O.H. steel 12Kh2N4A (0.12% C, 2% Cr, 4% Ni) and a Fe-alloy with 0.04% C and 7.21% Cr made in a vacuum laboratory furnace were studied.   Tension specimens of 6 mm (0.24 in) diameter were prepared from the steel and bars of 1.5 mm (0.06 in) dia. from the chromium-containing alloy.

The steel specimens were heated to 1150°C (2100°F), quenched in 15% aqueous KOH and then immersed in liquid nitrogen for 30 minutes to prevent the possibility of retained austenite transforming into martensite during recovery.   The specimens of the chromium alloy were quenched from 1200°C (2190°F) in 10% aqueous NaCℓ at 3-4°C (37-39°F).
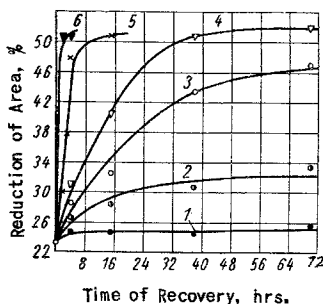

Fig. 1. Dependence of reduction of area of steel 12Kh2N4A specimens on the time of recovery at different temperatures   after quenching.
1 = -196°C (-321°F);   2 = -30°C (-22°F);   3 = 0°C (32°F);   4 = 20°C (68°F);   5 = 50°C (120°F) ; 6 = 100°C (212°F).

The quenched specimens were kept at various temperatures between -40 and 100°C (-40 and 212°F) for 1 to 72 hours.   The time elapsing between quenching and the start of holding at the temperature specified was 1.5 minutes for the chromium alloy specimens and 2 hours for the steel specimens, reckoned from the moment of removal from liquid nitrogen.   The specimens were held in Dewar vessels in gasoline, cooled with solid carbon dioxide or filled with preheated water; temperatures were determined with mercury thermometers and kept constant to within + 1°C.   One series of specimens of the steel was kept in liquid nitrogen at -196°C (-321°F).

Tension tests were made at room temperature.   The steel specimens were tested on an IM-4A machine, and those of the chromium alloy on a Chevenard microtester.   The reduction of area was determined since, according to a

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study by Moroz [2] it is extremely sensitive to the structural state of the lattice.

The technique adopted made it possible to establish the temperature-time dependence for recovery.

Figs. 1 and 2 show the temperature and time dependences of reduction of area. The initial ordinate is the result of tests performed following the initial quench and the time intervals quoted above.

These data show that the rate of recovery judged from the reduction of area figures is strongly temperature dependent. It increases with temperature and virtually ends at -196°C (-321°F).

Energies of activation were calculated in the usual way [2], it being assumed that the rate of change of the reduction of area, ψ, is exponential

$$v = d\psi/dt = A \exp(-\mathcal{E}/RT)$$

If $\ln t$ is plotted against $1/T$ for various fixed values of ψ, a family of straight lines is obtained, each for a definite ψ; from the slope of these lines, the energy of activation can be determined. These plots are in Figs. 3 and 4, and show that the energy of activation does not remain constant during recovery but gradually increases; the extent of recovery can be represented by $(\psi_i - \psi_s)/(\psi_{rec} - \psi_s) = X$, where the subscripts i, s and rec refer respectively to the instantaneous, initial and maximum reductions of area (Figs. 1 and 2).
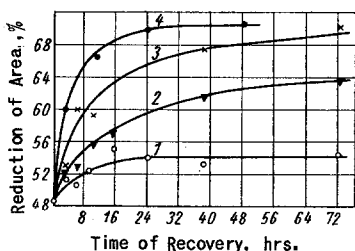

Fig. 2. Dependence of reduction of area of specimens of chromium alloy on time of recovery at different temperatures after quenching.
1 = -40°C (-40°F); 2 = -20°C (-4°F); 3 = 0°C (32°F); 4 = 20°C (68°F).
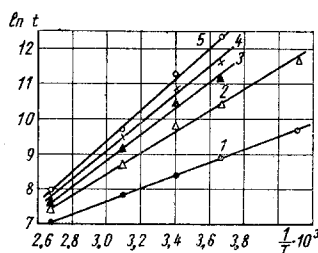

Fig. 3. Dependence of the time necessary for attaining a specified reduction of area (steel 12Kh2N4A) on the temperature. 1 = 26%; 2 = 33%; 3 = 36%; 4 = 41%; 5 = 46%.
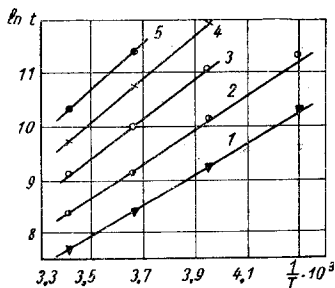

Fig. 4. Dependence of the time needed to attain a specified reduction of area (chromium alloy) on the temperature. 1 = 52%; 2 = 54%; 3 = 58%; 4 = 62%; 5 = 66%.
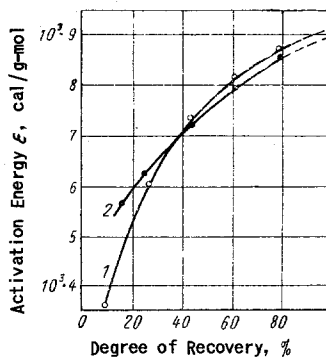

Fig. 5. Dependence of activation energy on the degree of recovery; 1 = steel; 2 = chromium alloy.

Fig. 5 shows the variation of energy of activation with X (in %) for the steel and the alloy; it will be seen that after full recovery the activation energies of both alloys are identical at 9 kg-cal/g-atom, despite the great difference in composition.

Tension tests were made after 25 minutes and after 4 days of recovery, one series of specimens being tested at room temperature, and the other at the temperature of liquid nitrogen (Table 1). The liquid nitrogen tests were made on Gagarin specimens of the steel (0.14% C) quenched in water from 1150°C (2100°F).

Table 1. Results of Tests at Room and Liquid Nitrogen Temperatures

Duration of Recovery at room temperature	25 minutes	4 days
Tests at + 20°C		
Tensile Strength:		
kg/mm²	133.8	131.2
psi	190,300	186,600
Elongation, %	7.1	11.6
Reduction of Area, %	24.7	55.1
Tests at -196°C		
Tensile Strength:		
kg/mm²	166.0	164.9
psi	236,100	234,500
Elongation, %	8.5	7.4
Reduction of Area, %	23.0	18.5
Note: each figure is the mean of four measurements.		

All specimens tested at room temperature failed with cup formation, the cup bottom having a fibrous structure. Failure in liquid nitrogen occurred across a section normal to the axis and its appearance was crystalline.

Table 1 shows that in room temperature tests, four days' recovery increases the elongation and specially the reduction of area (more than twofold). In liquid nitrogen the difference between freshly quenched and recovered steel vanishes.

The recovery of hardened steel cannot be explained by transformation of retained austenite into martensite and decomposition of the martensite [7]. This is confirmed by the present results; the energy of activation for martensite formation is only 1 kg-cal/g. atom [8,9] and 33 kg-cal/g-atom for its decomposition [10]; the energy of activation for the diffusion of carbon in α iron is 19.2 kg-cal/g-atom [11]. None of these figures comes anywhere near the energy of activation for recovery, 9 kg-cal/g-atom, and so these processes cannot be responsible for the effect studied here.

However, the value for the activation energy of recovery does agree with that for the diffusion of hydrogen in steel, which is 9.4-11 kg-cal/g-atom [12-14]. It is known that when hydrogen-charged specimens are aged at room temperature, hydrogen escapes from them by diffusion, and the reduction of area gradually increases [15]. Since a certain quantity of hydrogen is always present when steel is melted in the usual way, experiments were carried out to find what part it plays in recovery of hardened steel. We compared the recovery in steel with the usual hydrogen content and in one specially degassed, and also investigated whether the hydrogen content is changed by heat treatment and subsequent recovery.

Studies were made on steel 12Kh2N4A of the same heat, as was used in the experiments in Table 1. Cylinders of 6 mm (0.24 in) dia. and 15 mm (0.6 in) long were used for hydrogen content determinations, and 6 mm dia. specimens for tension tests.

The hydrogen content was determined by vacuum fusion in unquenched steel (initial state), in the same steel after annealing for 10 hours at 10^{-4}mm Hg at 650°C (1200°F), and after vacuum annealing and then quenching from 1150°C (2100°F) in water.

To eliminate the possibility of error due to the hydrogen content of scale, 0.2-0.3 mm (0.08-0.12 in) was machined away from all the surface of the specimen, which was copiously cooled during this operation, so that its temperature did not rise above 10°C. Forty minutes after quenching, the specimens were held for four days at room temperature in a container with hydrogen-saturated alcohol. Then hydrogen contents were determined.

The tension specimens made from degassed steel, were machined all over like the specimens for hydrogen determination. Table 2 shows the effect of duration of recovery on the reduction of area of degassed and undegassed steel, and Table 3 shows hydrogen contents.

Table 2. Results of Tension Tests on Degassed and Undegassed
Specimens of Steel 12Kh2N4A

Heat Treatment	Duration of Recovery	Reduction of Area, %
Quenching from 1150°C (2100°F) in water	25 minutes 4 days	24.7 55.1
Vacuum Annealing at 650°C (1200°F) and quenching from 1150°C (2100°F) in water	40 minutes 4 days	28.5 55.4

It will be seen that initially the steel contained 1.67 to 5.8 ml of hydrogen per 100 g. Vacuum annealing reduced the content to below 0.9 ml/100 g and quenching did not increase it. No hydrogen was liberated from the quenched cylinders kept in the containers for four days and the rates of recovery of the degassed and undegassed specimens of steel were practically the same (Table 2).

Table 3. Hydrogen Contents of Steel 12Kh2N4A

State	No.	ml /100 g of Hydrogen
Initial	1	1.67
	2	2.16
	3	3.60
	4	3.20
	5	5.80
Vacuum annealed at 650°C (1200°F)	1	0.546
	2	0.379
	3	0.689
	4	0.896
	5	0.563
Ditto, plus water quenched from 1150°C (2100°F)	1	0.900
	2	0.153
	3	0.145
	4	0.500
	5	0.153

It can therefore be concluded that recovery is not connected with the amount of hydrogen in the specimen. It has been established [5-7] that in quenched

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steel there is a close connection between recovery and delayed failure, the latter consisting in a fall of strength during the application of a static force, and this points to a common physical basis of the two phenomena. It has also been proved that delayed fracture is not connected with the presence of the 'ordinary' amount of hydrogen in the steel.

In [1-7] recovery is connected with viscous or 'quasi-viscous' behavior of the grain boundaries of quenched steel at room temperature, due to the presence of heavy localized distortions in the grain boundaries. Recovery in an unloaded specimen consists in relief of distortions or an increase in the degree of order of boundaries, thanks to which shear resistance is increased and the initiation of cracks is retarded.

The data on recovery found in [2,7] can be well explained from this viewpoint. A slowdown of recovery with a drop in temperature can be accounted for by a retardation of recovery processes in the grain boundaries. If with short durations of recovery and in room-temperature tests, the flow of material starts at grain boundaries and is responsible for premature failure at low reductions of area, recovery will strengthen the boundaries and increase the reduction of area. In testing in liquid nitrogen (Table 1) the viscous behavior of the boundaries is suppressed, and this is responsible for the similarity between the reductions of area of specimens tested immediately after quenching, and after prolonged recovery.

Relaxational processes in unstressed specimens can, in the final analysis, occur because of individual atom displacements or self-diffusion of iron. The average activation energy for iron self diffusion is 47.4-77.2 kg-cal/g-atom [16], which is considerably greater than the energy of activation of recovery in quenched steel (9 kg-cal/g-atom).

It is possible that such a low value for the energy of activation of recovery is connected firstly with the fact that self-diffusion occurs only in localized zones at grain boundaries, and secondly with the expecially severe distortions at the boundaries, due to specific features of martensite formation. The activation energy of boundary diffusion is usually lower than that of bulk diffusion, and diffusion usually occurs the more easily, the greater the degree of distortion.

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