Microstructural Design by Solidification Processing

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STRUCTURE FORMATION BEHAVIOUR OF ALLOYS DURING GAS-EUTECTIC TRANSFORMATION AND PROSPECTS OF THE USE OF HYDROGEN IN ALLOYING

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Abstract

This paper describes certain effects discovered by the author showing that hydrogen is a most valuable, perhaps unique alloying element affecting structure and properties of metals and alloys in a number of remarkable ways. In particular, data are given about new types of three-phase reactions, namely gas-eutectic and gas-eutectoid tranformations.

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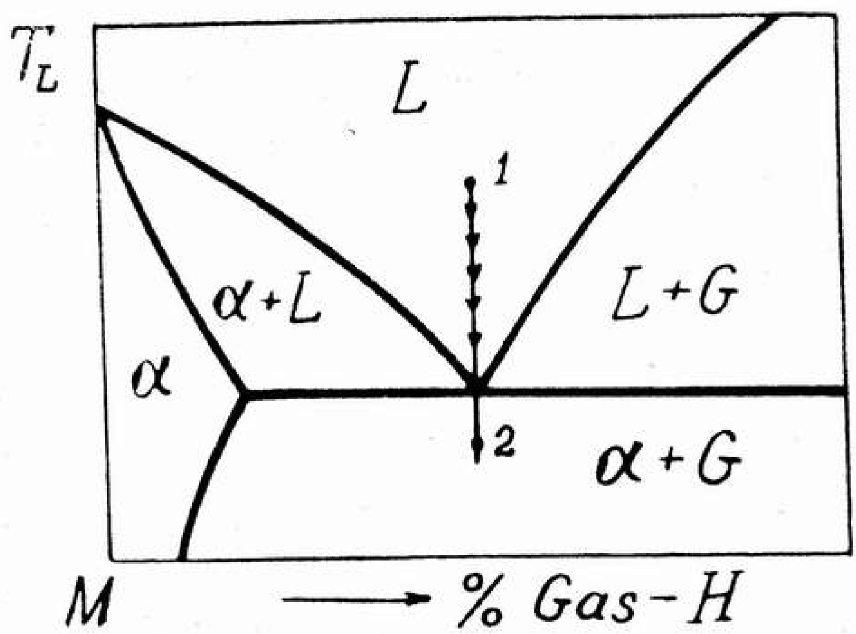

Figure 1 - Isobaric section of phase diagram for a metal-hydrogen system with gas-eutectic equilibrium.

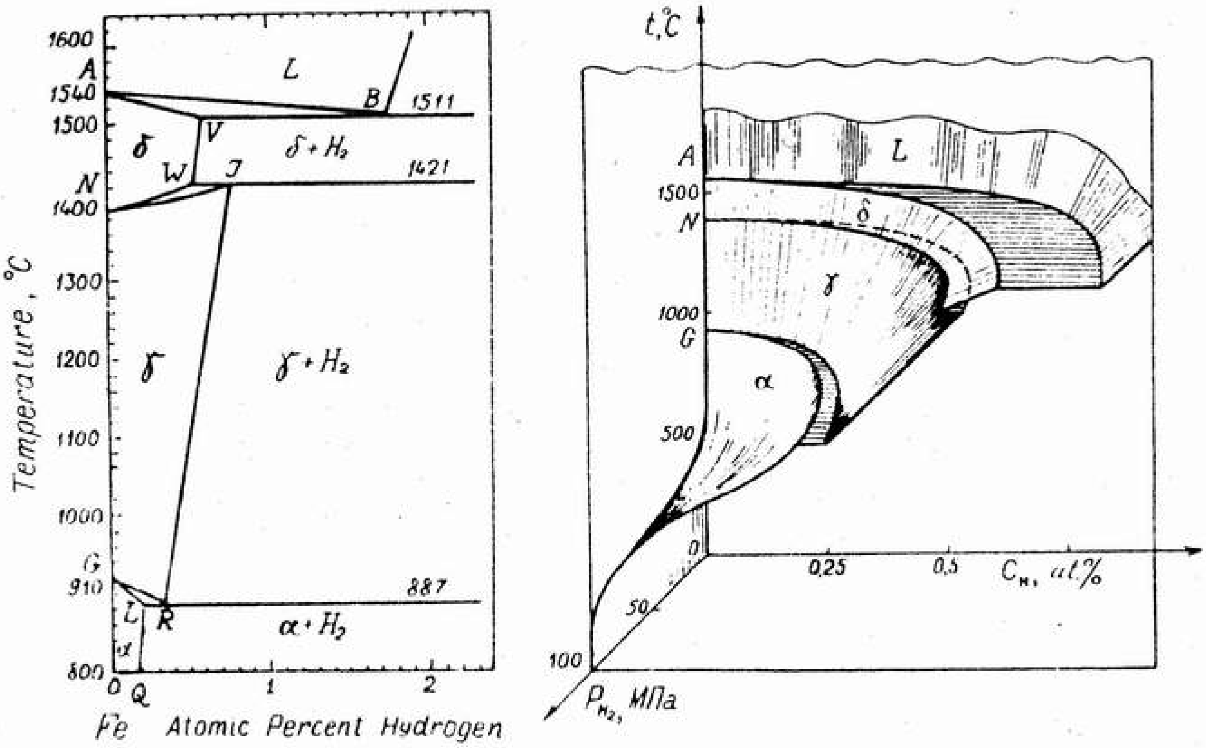

Figure 2 - Iron-hydrogen phase diagram:

(*a*) isobaric section at 40 MPa;

(*b*) three dimensional diagram on the pressure concentration-temperature coordinates.

Gas-eutectic transformations

Essentially none of the metals used widely in production of important structural and tool materials of today - Fe, Ni, Co, Mn, Cr, Cu, Al, Mo, W, Be, Mg - forms hydrides in normal conditions, i.e. at low hydrogen pressures and temperatures above 250 K. In the respective systems the main phase transitions capable of affecting metal structure and properties are precipitation of a proeutectic (proeutectoid) phase from a supersaturated solution and multiphase transformations that can, by analogy with those known earlier, be named gas-eutectic ($L \Rightarrow \alpha$ + gas) and gas-eutectoid ($\alpha \Rightarrow \beta$ + gas) transitions.

Based on the fundamentals of eutectic solidification theory, gas-eutectic transformation can be represented as coupled growth of two phases one of which, in contrast to the previous findings, is gaseous, Fig. 3. In order to test this assumption, experiments were carried out for Fe-H, Ni-H, Cu-H, Mg-H, Cu-Al-H systems. Samples were prepared in a special unit, Fig. 4, by melting the metal in an atmosphere of hydrogen at a preset pressure, holding the melt and finally carrying out directional solidification at specified values of pressure and solidification rate.

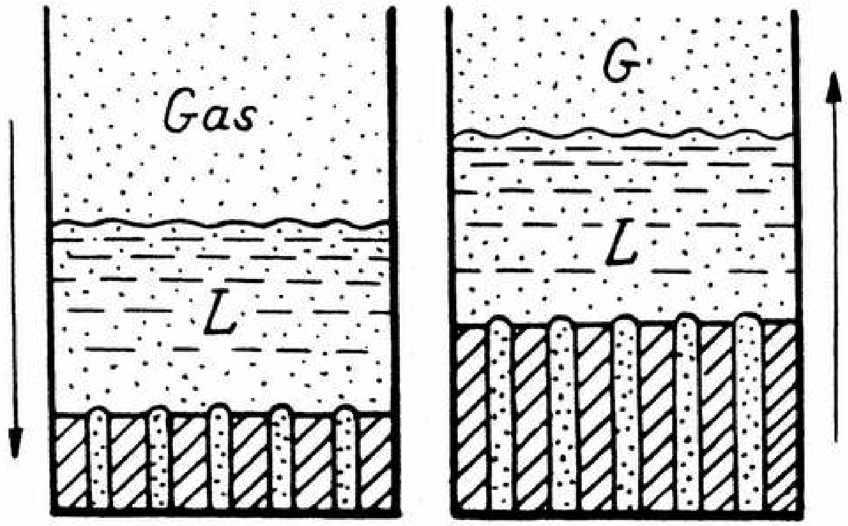

Figure 3 - Simultaneous growth of the solid and gaseous phase in gas-eutectic transformation in directional solidification. Downward and upward arrows show direction of heat removal and direction of gasar growth respectively.

It was found that, in gas-eutectic transformation, structures may form that are similar to eutectic ones: irregular, colony or finely spaced structures. Transition from the first to the last one is determined by an increase in solidification rate, gas-eutectic colonies always having honeycomb structure.

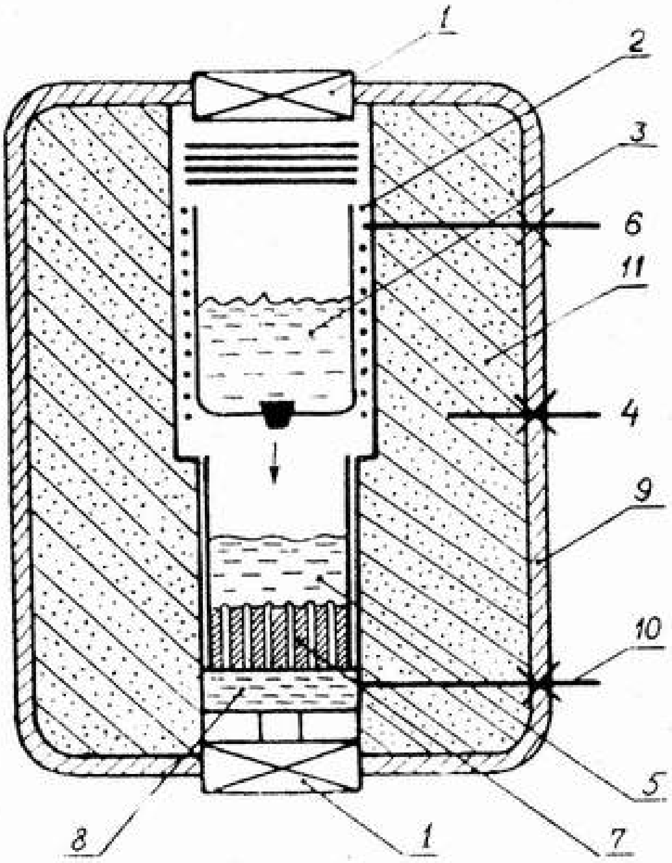

Figure 4 - Schematic of a laboratory apparatus for manufacture of gasars:

1	top and bottom covers
2	heater
3	melt to be saturated
4	gas supply and evacuation system
5	solidifying melt
6	heat supply system
7	gasar casting with axial structure
8	heat sink for directional solidification
9	strong hermetic casting
10	mold cooling system
11	heat shielding means.

The principal feature of the gas-eutectic transformation is that qualitative and quantitative changes in structure are easy to achieve by pressure control in solidification. For instance, colony, spherolite and disrupted colony structures can be readily obtained, Fig. 5. Concurrent control of gas/solid ratio is also possible without changing the alloy chemical composition.

At present, gas-eutectic reaction provides a scientific foundation for processes of manufacture of revolutionary gas-solid materials based on Fe, Ni, Cu, Mg, Al and their alloys. Since gaseous phase in them looks like reinforcer inside a metal matrix, such materials may be named gas-reinforced ones or, more shortly, gasars.

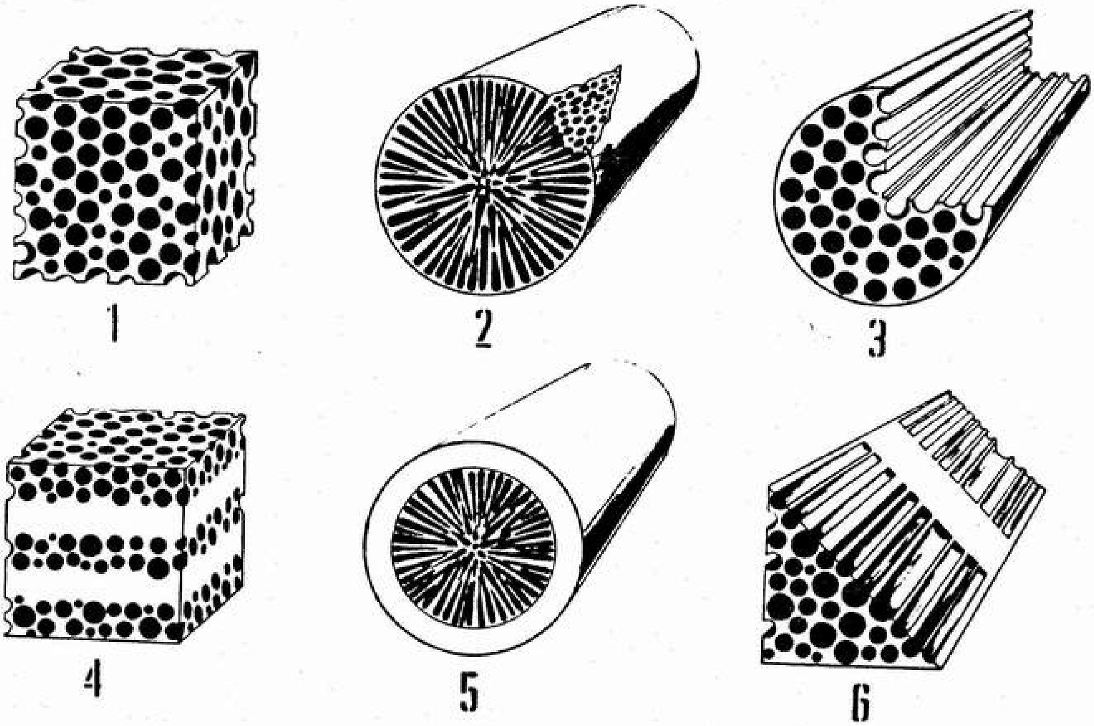

Figure 5 - Gas-solid structures formed in gasars in various conditions of gas-eutectic reaction.

Mechanical tests of gasars have shown that directional pores below 10 mm in diameter make them superior in strength to monolithic materials having the same composition, Fig. 6,7,8. This ensures feasibility of unique solutions to engineering problems and provides a saving in scarce materials. Gasars are well suited for machining and forming, allow hardening by conventional heat treatment, possess unique damping capacity, can be produced with a heat conductivity value lower or greater than the one for the monolithic material and have good capacity to absorb vibrations and sounds. In future these features may make gasars common structurals and a base for a number of composites.

Gas-eutectoid transformation

Also, research was carried out into gas-eutectoid transformations in Fe-H system (austenite ⇒ ferrite + hydrogen gas) (9,10). The experiments were conducted at hydrogen pressures below 100 MPa and involved thermal cycling in the vicinity of gas-eutectoid equilibrium point (1125-1225 K) with heating and cooling rates from 10 to 600 K/min. An automated control system was used to stabilize process parameters in each run. Samples were prepared from carbonyl iron containing less than 0.03% impurities. In the first series of runs the samples were rods 2.5 mm in diameter and 5-20 mm in length. Check runs were carried out in an atmosphere of high purity inert gas (He or Ar).

Tests showed that hydrogen present in the gas phase during thermal cycling brought about a remarkable reduction in iron yield stress. In the presence of hydrogen, At present it is difficult to give an exhaustive explanation for occurrence of ASD in gas-eutectoid transformation in Fe-H system. It is probable that the heavy accumulation of hydrogen at γ-α transformation front brings about major changes in the structure of the interface and the adjoining zones. It is also possible that some contribution to this effect is made by the quicker motion of dislocations and vacancies owing to the presence of hydrogen.

Conclusions

Materials scientists and physical metallurgists have been used to regarding hydrogen as an undesired impurity in metals and alloys, causing flakes, hydrogen embrittlement, porosity and hydrogen corrosion. The above gas-eutectic and gas-eutectoid transformations have provided a basis for revolutionary technologies of manufacture and processing of metals and alloys. This opens up new possibilities of diffusionally reversible alloying in which hydrogen, on having played its role in modifying the structure and properties, can be removed from an alloy by heating below the recrystallization temperature.

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