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HIGH TEMPERATURE BRITTLENESS OF CAST ALLOYS

KRUCHOŚĆ WYSOKOTEMPERATUROWA STOPÓW ODLEWNICZYCH

Over-all mechanical properties of alloys are extremely low at the last stage of solidification where alloy exists at brittle temperature range (BTR). When the solidification process is completed a sudden and marked change in strength and ductility of metal is observed. It means that as long as liquid phase is present, metal will fail in a brittle manner. There are known different theories of brittleness of alloys in existence of liquid phase. The idea involved by authors of the paper is as follows: three major factors caused by presence of liquid may be taken into account:

- decreasing the energy needed for crack nucleation,
- increasing atomic diffusional flux out of the crack tip,
- creating a path for abnormally quick diffusion of atoms from the crack tip.

Keywords: high temperature brittleness, hot tearing, shrinkage brittleness, mushy state

Własności mechaniczne stopów są bardzo niskie w ostatnim stadium krzepnięcia, w którym stop wykazuje kruchość wysokotemperaturową. Przy końcu procesu krzepnięcia obserwuje się nagłą zmianę wytrzymałości i plastyczności metalu. Dopóki występuje faza ciekła metal ulega zniszczeniu w sposób kruchy. Przyczyną tego mogą być trzy główne czynniki związane z obecnością fazy ciekłej: a) spadek energii potrzebnej do zarodkowania pęknięcia, b) wzrost strumienia dyfuzji atomów od wierzchołka pęknięcia, c) utworzenie ścieżki do anomalnie szybkiej dyfuzji atomów od wierzchołka pęknięcia.

1. Introduction – Mechanism of tear formation in solidifying alloy

The results of tensile tests of alloys at high temperatures [1-5] have shown the following relationship between temperature and mechanical properties of alloys: in general at high temperatures alloys are fully ductile until the point at which they fail in a brittle manner, the maximum stress decreases progressively with rising temperature until the sharp drop in stress occurs. Samples of cast carbon steel (0,22%C) after testing at different temperatures [5] are shown in Fig. 1.

The diagram of the influence of temperature on mechanical properties of different grades of carbon steel is shown in Fig. 2 and Fig. 3 [5].

There is a temperature at which the rapid change in reduction of area begins and a very distinct change in the tensile strength of cast steel occurs as well. Above the brittle-ductile transition temperature the tensile strength of cast steel does not exceed the value of a few MPa, the reduction of area is not more than a few tenths of percent. Let us notice that, irrespective of the chemical composition, the mechanical properties of cast steel within the range of crack formation temperatures are always very low.

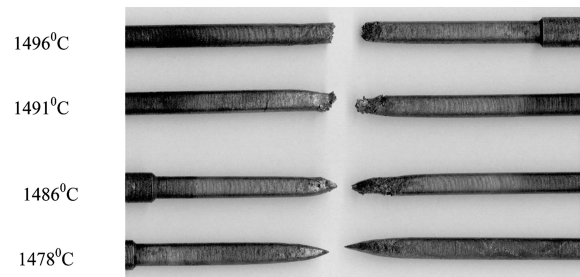


Fig. 1. Samples of cast carbon steel (0,22%C) after testing at different temperatures

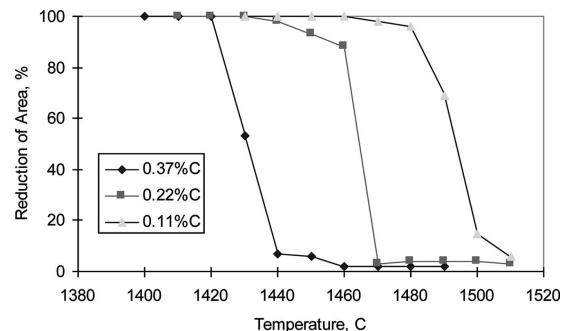


Fig. 2. Influence of temperature on the reduction of area of cast carbon steel

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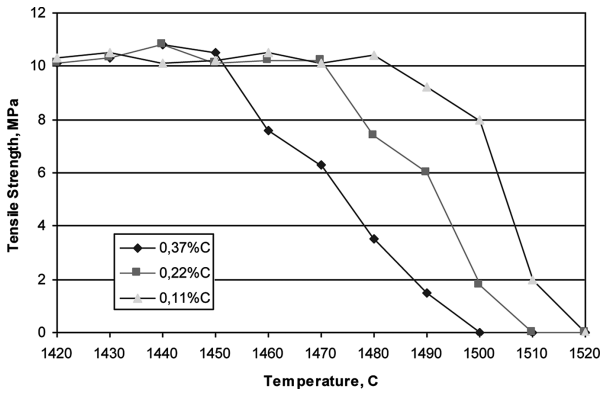


Fig. 3. Influence of temperature on tensile strength of cast carbon steel

The latest variation of the mechanism of extremely low mechanical properties of solidifying alloys is proposed by Campbell [6] (Fig. 4).

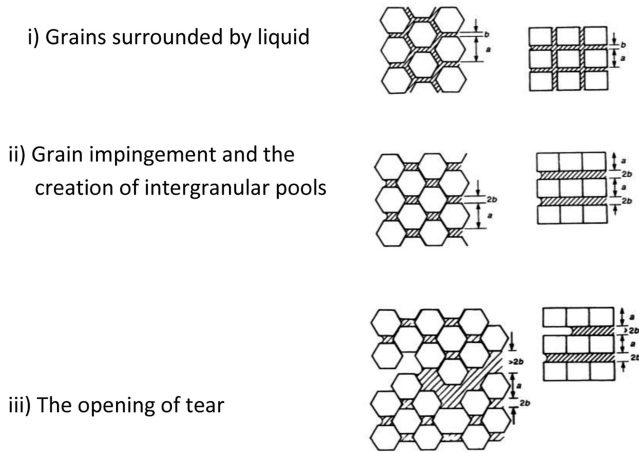


Fig. 4. Hexagonal and square models of grains, size a , surrounded by a liquid film of thickness b . The development of isolated regions of segregates is seen as tensile strain is applied. When this finally exceeds the ability of the liquid film to accommodate it, the action of the continued extension drains the liquid film, forming a tear [6]

During the first stages of solidification the quantity of solid phase is small and the dendrites are freely dispersed in liquid, i. e. they are not in contact with each other (Fig. 4i). The metal possesses very little coherence and the contraction (because of cooling process) can be accommodated without difficulty. As the temperature falls the quantity of solid phase increases. The development of coherent network of the dendrites with liquid films between their arms is observed as tensile strain is applied. (Fig. 4ii). For the condition of lower liquid content, less strain can be accommodated by slip along the lubricated boundaries. The metal approaches “liquid film” stage [7] at the temperature that is near to solidus. According to widely accepted Pellini “liquid –film” theory [7], at the “liquid film” stage of solidification over-all mechanical properties of alloys are extremely low because the very narrow liquid films that separates solid grains have no appreciable strength compared to the adjoining solid dendrites. If stresses arise, extension is highly concentrated in liquid film regions resulting in high unit strains. The liquid film is widened under the external stress until the critical width has been exceeded, at which point the liquid film recedes (Fig. 4iii). A crack

starts to develop. The tear propagates as the meniscus recedes further. Separation takes place between crystals. Fracture (hot tear) forms by disturbing of continuity of the liquid layer between crystals. Fig. 5 a shows a scheme of fracture of an alloy formed by the liquid film mechanism [7], Fig. 5b – an example of cracked surfaces of cast steel.

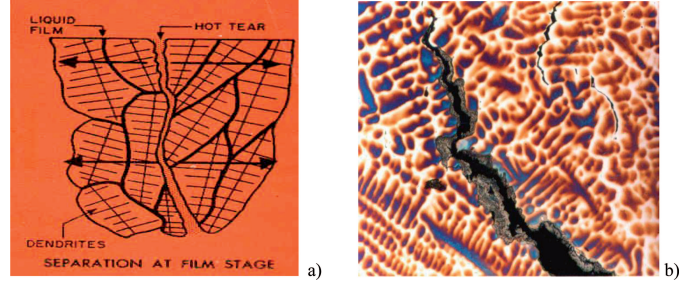


Fig. 5. Model of hot tear formation in cast alloys formed by the liquid film mechanism (a) [7] and example of hot tearing in cast steel (b) [5]

With a further fall in temperature the residual liquid freezes progressively. Dendrites form a coherent solid network with liquid between the arms of the dendrites. Even if the direct crystal-crystal contact is reached, the hundreds micrometers thick frontier zone of metal at the grain boundary has a freezing point considerably below that of the bulk crystalline material. The effect of liquid film at the grain boundaries, but perhaps only a few atoms thick, is still present. This can be explained by the presence of impurities which have segregated to the grain boundaries. The fracture process involves the rupture of solid/solid contact areas (Fig. 6) or “bridging points” (Fig. 7).

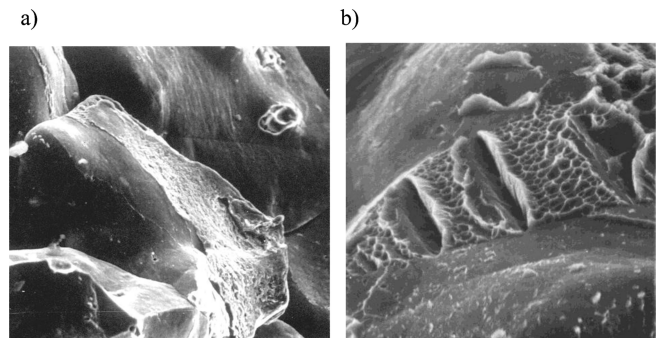


Fig. 6. Fracture of cast carbon steel (0.37% C) showing the ruptured solid/solid contact a) magn. 600 x, b) fragment of fracture from Fig. 6a, magn. 2400 x [5]

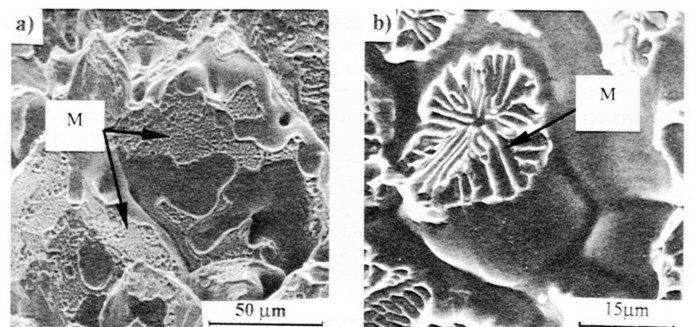


Fig. 7. Fracture surface of an weld of steel, showing the ruptured solid bridges M [8]

If contact zones have progressed to such an extent that the strength of the metal will be greater than required to prevent interdendritic separation the general flow of the bulk material can occur and the hot metal may fail in a ductile manner. Extension occurs by uniform creep flow of solid metal. The strains are distributed in a relatively uniform fashion through the coherent metal. No concentration of strains is possible. The effect is that the velocity of crack growth is reduced quite drastically [7].

Taking into consideration liquid film model of hot tearing, some workers have analysed the possibility to increase the tensile strength of an alloy at the liquid film stage. This results in the following conclusions: tensile stress required to cause a separation of crystals covered by liquid (strength of metal at liquid film state):

- is proportional to surface tension of liquid and inversely proportional to the thickness of liquid film; the effect of elements on the tensile strength of an alloy at the liquid film stage can be attributed to their influence on the surface tension [9,10],
- depends on distribution of liquid phase; low dihedral angle (ie low interfacial energy between liquid and crystals) results in “spreading” of liquid over grain boundary and increases grain boundary area covered by liquid [11-12],
- depends on grain size; for a fixed dihedral angle and volume fraction of liquid a small grain size gives an increased area of solid-solid contact [3, 13].

There are known models [5,7,14] that discuss an effect of various factors on the brittle temperature range (BTR) or on the time the alloy remains within this range. The broader is this range, the greater is the probability that the solidifying weld or casting will suffer a failure.

2. Model of hot tearing

The assumption of liquid film theory that the last-solidifying liquid is distributed in a film-like morphology is correct only for unrealistically low difference temperature between surface and core of solidifying ingot. This introduces some doubts on the generalization of the liquid film theory. When real solidification process takes place one can distinguish at least two zones in the cross section of an ingot: a solid layer and an internal mushy zone.

Let us isolate the fragment of solidifying metal (Fig. 8) that compounds of two crystals and inclusion of liquid on their boundary – nuclei of crack.

An analysis of the energy required per unit increase in area of crack [1,5,15,21,22] implies that:

1. the lowest energy requires developing of crack which goes along the crystal boundaries being in contact with the liquid phase,
2. the presence of liquid phase in an alloy causes a decrease of the amount of the energy needed for the formation of the crack.

Thus, the presence of the liquid phase makes the process of the crack formation easy to start.

As tensile stress is perpendicular to crystal boundary, vacancies create on crystal boundary. The tip of liquid phase inclusion is under compression stresses and lack of vacancies

appear. Diffusional flux out from the tip creates the nuclei of crack. The velocity of crack propagation by diffusion mass transfer is proportional to the diffusional flux out from the tip. At a given driving force for diffusion (governed by the acting stress) diffusional flux increases with the concentration of the atomic defects at the surface. The equilibrium concentration of these defects is expected to grow exponentially with the surface energy reduction.

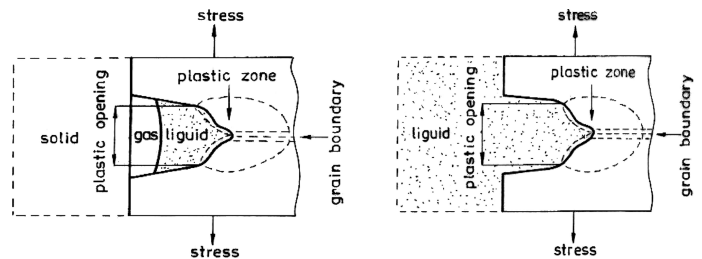


Fig. 8. Scheme of building of an alloy (end of solidification of casting): a) – not enough liquid to fill a nuclei of crack and b) enough liquid to fill nuclei of crack [16, 20]

In general, the surface energy at the solid metal-wetting liquid interface γ_{s-l} is typically from several to ten times smaller than γ_{s-g} at the solid – inert atmosphere interface [16]. The surface energy at the liquid metal – crystal formed from this liquid should be much lower. The first, chemical composition of crystal and liquid is almost the same, the second – there is almost ideal the fineness of crystal surface been in contact with liquid. Thus, surface energy reduction makes a wetted surface more efficient source of defects [16-19]. This suggests that a solid-liquid interface, in particular crystal – liquid metal formed from this crystal which is the most surface-active, should have much larger the equilibrium concentration of atomic defects than a free surface, that is to say should be more atomically rough [16]. At the given driving force for diffusion of vacancies from the wetted surface to climbing dislocations or growing vacancial voids in the near surface layer (governed by the acting stress) the diffusional flux should hence increase with the concentration of the active sites (“kinks”) at the surface. Thus, surface energy reduction because of presence of liquid makes the driving force for the crack extension greater [16].

The number of atoms have to be removed from the tip to increase crack length. Robertson [19], probably as the first, recognized that liquid can act as a very fast pathway. Glickman [16] submits the abnormally fast surface diffusion as the possible transport mechanism. The important is that the constituents which form with the base metal low melting point surface products make surface diffusivity D many orders of magnitude larger than its normal value in solid D_s and larger than in liquid D_L [16, 19]. At the late stages of solidification there is insufficient liquid metal available and the path of liquid from other areas is blocked by the network of dendrites to allow refilling and healing of the created tears. The volume of liquid phase decreases with time lapse. When the liquid is sucked into a crack, a void within the interdendritic space occurs on the back side of the crack as a consequence of crack developing. (Fig. 8a). The increasing liquid viscosity brings a simultaneous drop of diffusivity. Because of the small volume, liquid concentrates at the crack tip and within a narrow area

around the tip and finally there is lack of liquid at the crack tip and there is no longer the path for an easy diffusion.

In general, type of cracking (brittle or ductile) is controlled by velocity of crack growth. The mechanism of failure depends on whether during the deformation process the crack is able to attain its length before the ultimate deformation occurs. The idea is presented in Fig. 9 [16].

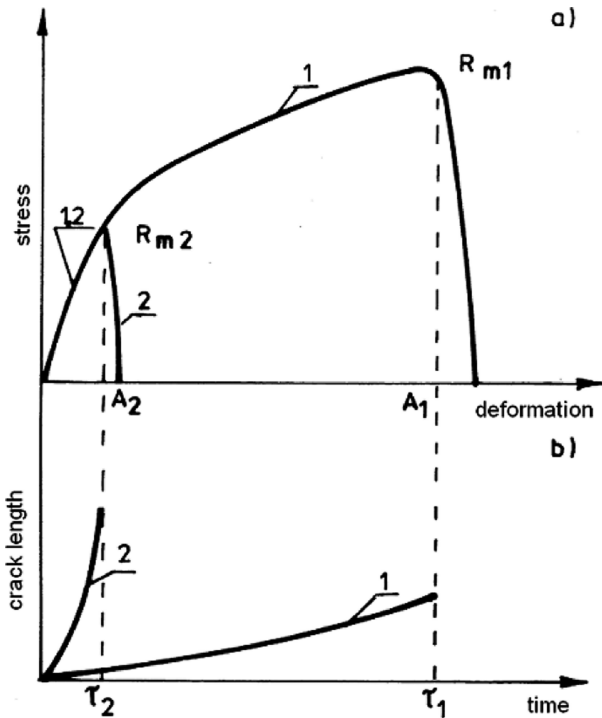


Fig. 9. Scheme of strain-stress diagram (a) and kinetics of development of crack nuclei (b) [16]

It is assumed that because of presence of liquid the grain boundary crack increases its dimensions with the velocity according to curve 2 (Fig. 9b) and reaches a characteristic dimension L_{ch} in a short time τ_2 . At a given strain rate, the short time of crack growth determines a small deformation to failure – elongation A_2 – as well as small stress to failure – ultimate tensile stress R_{m2} (Fig. 9a). If velocity of crack growth is small (Fig. 9b, curve 1, no liquid) before the length of slow growing crack attains dimension L_{ch} the sample fails ductile after long time τ_1 , and mechanical properties attain values: elongation A_1 , tensile stress R_{m1} (Fig. 9a). The lower is the crack growth the longer the time-to-failure. At a given strain rate, long time to failure determines directly high elongation to failure. The increase in elongation causes a proportional increase in the tensile strength.

3. Verification of model

Presented model suggests that alloys fail in the brittle manner because liquid accelerates crack extension while the fundamental properties of the solid are not affected. To verify this suggestion the results of tensile tests of steels at high temperatures were used. Fig. 10 shows the deformation curves of samples showing in Fig. 1.

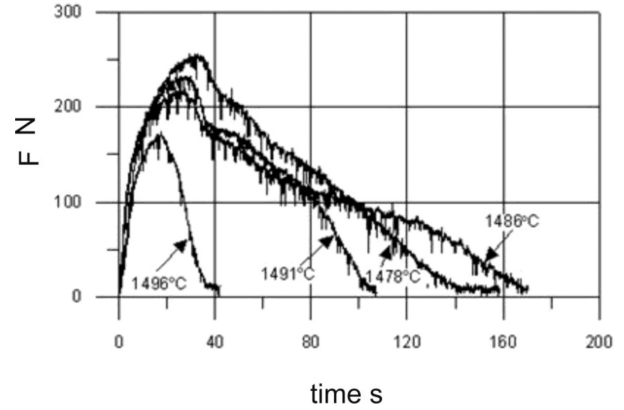


Fig. 10. Cast steel 0.22%C, force – time curves for different temperatures, rate of deformation 0.13 mm/s [5]

At the initial stage, these curves are similar to each other. In the case of curve for steel tested at temperature 1496°C the rapid drop of force after short time of test is observed. The crack size has been reached diameter of sample, finally resulting in brittle fracture. Remaining curves have a rounded maximum drop in a mild way due to the formation of a severe necking down, reaching 100%. Therefore it is to be expected that in spite of a reduced force, the stress in the specimen will continue to increase until the plastic failure occurs. Similar results were obtained for the other grades of steel. Examples of diagram for cast steel 0.42%C is shown in Fig. 11.

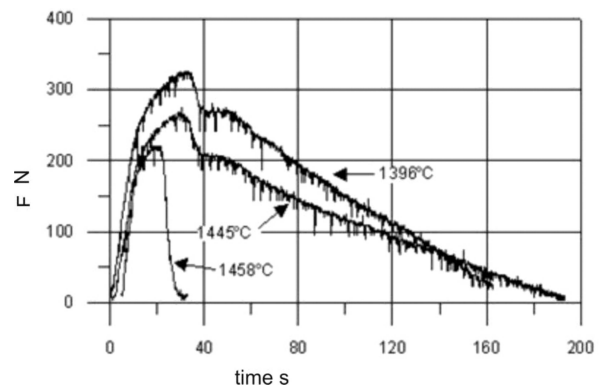


Fig. 11. Cast steel 0.42%C, force – time curves for different temperatures, rate of deformation 0.13 mm/s [5]

It suggests, that presence of liquid does not affect the fundamental properties of the solid metal. The solid phase fails in a macroscopically brittle manner because liquid accelerates dramatically the crack kinetics.

4. Discussion of results

Results of present investigations show that there are three main reasons of high temperature brittleness leading to a sudden increase of the rate of crack nucleation development. Presence of liquid phase in alloy has influence on:

1. the increase of flux diffusion atoms from the tip of fracture nucleus
2. development of easy path of rapid diffusion of atoms from the tip of fracture nucleus
3. rapid decrease of the energy of crack formation

Therefore at temperatures above the solidus, until the liquid phase in solidifying alloy is present, the alloy is in brittle cracking temperature range. At temperatures below solidus, when in alloy the only solid phase exists, the alloy is in ductile temperature range. The above statement does not mean that the temperature which separates the brittle and ductile range can be identified as solidus temperature estimated using the phase equilibrium diagram. Such diagrams present the solidus temperature at the thermodynamic equilibrium conditions. At such conditions the composition of liquid varies along the liquidus line, whilst the composition of solid phase varies along the solidus line. This state exists only in case of extremely low decrease of temperature of solidifying alloy, when diffusion process enable to compensate the chemical composition of previously and actually formed solid crystals. Usually the solidification process in real conditions is performed with a rate, which enable the only partial diffusion process. Therefore the composition of solid phase will be different from the equilibrium composition. Also it must be taken into account that alloys always contain some impurities. For example a steel except of iron and carbon always contains such elements as oxygen and sulphur. These elements may form eutectics with low solidifying temperature. The appropriate mode of deoxidation of liquid steel significantly reduce the effect of oxygen on the level of temperature of finishing the brittle state of steel (nonequilibrium solidus temperature). As far as sulphur is concerned, this element always concentrates on grain boundaries of solid phase and by diffusion and convection processes is carried away into liquid. In case of contact of grains, which is close the limited volume of liquid, the content of sulphur is increased because of the repulsion from the crystallization zone. In binary system of Fe-S, even at very low sulphur content always forms the Fe-S eutectic, solidifying at 988°C. However, in case of steel solidification the precipitation of excess of sulphur will occur as sulphides of iron and/or other elements showing higher chemical affinity to sulphur in comparison to iron. In effect the precipitation of eutectics containing sulphides will occur. Their solidifying temperature may be lower than the solidus temperature of matrix. These sulphides may act as liquid nucleus of hot brittle cracks. In final step of solidification steel can be considered as iron and sulphur alloy. The effect of other elements is related to their effect on the behaviour of sulphur. Finally the formation of residual phases with lower solidification temperature than iron matrix may occur. Usually the thermal effect of solidification of such thin low melting layers on the grain boundaries is not detectable by thermal analysis. In this case the limit between brittleness and ductility is lower than the measured solidus temperature of alloy.

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