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Fire resistance increase of structural steel through the modification of its chemical composition

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Abstract

In the article the possibility for increasing the fire resistance of structural steel used in building load-bearing structures is presented and discussed in detail. The recommended approach is based on a suitable modification of its chemical composition, in particular by adding the carefully selected alloying elements. With such a change, not only a high-temperature strength of this material may be significantly increased in relation to that which would be achieved for the typical structural steel with an unmodified composition but also its sufficient weldability should be ensured by the entire duration of its exposure to a fire. The steel modified in this way would be undoubtedly more expensive to manufacture but due to the fact that it will not require any special protection against fire it seems that it can provide an interesting alternative to the solutions currently used in engineering practice.

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Keywords: structural steel; fire resistance; weldability; chemical composition; alloying elements.

1. Introduction

The fire resistance of structural steel commonly used in building constructions is usually not high enough to ensure that all external and internal loads applied to such structures under fire conditions will be safely carried if the members made of such a steel will not be adequately protected from direct fire exposure. Therefore, both the

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active as well as the passive fire protection measures, which are relatively expensive and not always sufficiently effective, must be used in engineering practice in order not to exceed the acceptable risk level of the building damage in case of a fire. The aim of the presented paper is to discuss the application possibility of an alternative approach to provide the required fire resistance of steel structures. This resistance would be achieved by replacing the traditional types of structural steel on the special fire resistant steel grades with a carefully selected chemical composition. It is essential that the steel of this type should be characterized by the yield limit which under fire conditions becomes significantly higher than the analogous yield limit relating to the conventional structural steel. Defining more precisely, according to the requirements developed by the Japan Institute of Metals (Fushimi et al. [1]), its yield point relating to the steel temperature equal to $600\text{ }^{\circ}\text{C}$ must be guaranteed to be in the range of two-thirds of that specified at room temperature. Let us note that this restriction is much stronger than the analogous one, specified in the United States [2], according to which only at least one-half of a room temperature yield strength is required as the remaining in such circumstances. In addition to this basic requirement, the weldability of such a fire resistant steel during the whole time of a fire exposure has to remain similar to that relating to the conventional steel not exposed to a fire. It is common knowledge that there are at least several approaches to effectively obtain a structural steel having such properties. They usually deal with the identification of the recommended method of the steel production, such that its preferred microstructure could be obtained. In general, it is reasonable to claim that a mixed steel structure, of bainite and ferrite, is effective in achieving a low yield limit reduction, especially with a high-strength steel (Mizutani et al. [3]). However, in this article the special attention is paid to the relation between the applied chemical composition of the considered steel and the material characteristics obtained as a result of its use. In particular, the effectiveness as well as the desirability of the use of various type of alloying elements and other admixtures are considered in detail in terms of their suitability to achieve the intentional properties of steel.

2. Structural mechanisms affecting the steel resistance under fire temperature

The strength of a steel is in general determined by the strength of its metallic matrix. It is a well-known fact that such strength decreases with the material temperature growth. This happens due to the increasing dislocation mobility, which becomes activated by the thermal energy supplied to the matrix. The stress necessary to move a free dislocation in a metallic matrix is called the Peierls - Nabarro stress. It is obvious that its value is strongly temperature-dependent because the thermal agitation is helpful in moving dislocations around the short-range obstacles. Let us underline that at room temperature these dislocations are usually constrained to move only in certain glide planes; however, at high temperature diffusion of the point defects can change the outline of a dislocation, enabling an edge dislocation to move around an obstacle. Such a process is usually called “the dislocation climb”. The second process, named “the dislocation cross-slip”, occurs when a screw dislocation moves to a parallel slip plane using an intersecting slip plane of the same system. Recently Cottrell [4] has reported that the dislocation cross-slip can occur at lower temperature value in relation to that which is needed to initiate the dislocation climb.

The precipitation may be another process affecting the stability of a metallic matrix. In alloy systems it occurs heterogeneously because the precipitate coarsening is accelerated on dislocations and grain boundaries due to the faster diffusion of solute elements along these channels. Nevertheless, if a precipitate is coarsening at high temperature then the process referred as “the Ostwald ripening” can be initiated. In such conditions the interface energy of the precipitate/matrix interface is lowered and a more stable configuration is achieved in a considered metallic matrix. Dispersion of precipitates may result in the strengthening of metallic matrix provided that their size is not too big; however, this effect strongly depends on such a size and on the inter-particle spacing in a matrix. Therefore, if a critical size of the precipitates is surpassed and, furthermore, if the inter-particle spacing in metallic matrix is sufficiently increased as a consequence of the impact of high temperature, the contribution of this process to the strengthening of the considered structural steel will start to decrease and finally will become disadvantageous.

Weakening of a steel strength may also be caused by creation of the vacancies in metallic matrix when some atoms are missing from one of the lattice sites. These vacancies are the unfavourable point defects which are frequently interpreted as the so called Schottky defects. Such creation is significantly intensified at fire temperature because the thermal agitation moves all atoms from their atomic sites; however, it is obvious that few vacancies may occur even at much lower temperature. As it has been shown in the experiments, about one site in 10^4 becomes vacant near the steel melting point. Moreover, the creation of the vacancies on dislocations in metallic matrix decreases the effect of precipitates at high temperature by enhancing the process of dislocation climb.

The detrimental effect on the strength of structural steel have also the impurity inclusions. Such effect is noticeable even at room temperature when these particles detach from the matrix soon after the plastic yield begins; however, at high temperature it is much more damaging because of a different coefficient of thermal expansion characterizing the particles of the impurity in relation to that assigned to iron. This difference is the source of the thermal stresses induced in a metallic matrix as a consequence of the impact of fire temperature, leading to the premature de-cohesion. It is a well-known fact that at room temperature de-cohesion occurs first at MnS inclusions, then at smaller oxides and finally at small carbides. Furthermore, Honeycombe and Bhadeshia [5] stated that calcium aluminates and alumina are the most detrimental in this field due to their substantially smaller coefficient of thermal expansion than that relating to the parent steel.

The next process affecting the strength of the considered steel at high temperature is the grain boundary sliding. As recently has been reported by Dieter [6] such sliding becomes significant when the steel temperature reach the value 630°C . This temperature is known as the equicohesive value because at this level the grain boundary strength and the matrix strength are equal. If the temperature exceeds this level the grain boundary will be weaker than the grain interior. The grain boundary sliding occurs by a shear process along the direction of the boundary. It is normally associated with creep deformation; however, its contribution to the overall matrix deformation during the relatively short-lasting fire is estimated as almost non-existent. In fact, creep defined as the progressive deformation of a material matrix at constant stress, which are frequently less than the material yield stress, is generally considered to be irrelevant in fire because the relatively short duration of such a fire. However, some processes being thermally activated, included those listed above, may become much more intensified when they occur in the interaction with creep. In particular, this refers to dislocation glide, diffusion creep and grain boundary sliding.

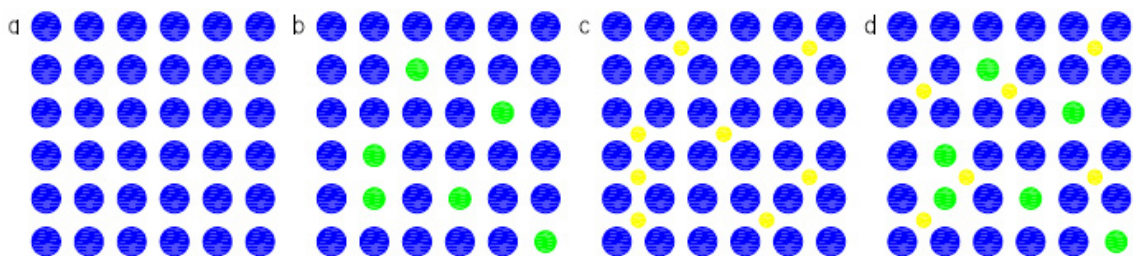


Fig. 1. (a) pure metal; (b) substitutional alloy; (c) interstitial alloy; (d) substitutional/ interstitial alloy.

When a metal is alloyed with another metal, either substitutional or interstitial solid solutions are usually formed (see Fig. 1). Substitutional solid solutions are those in which the solute and solvent atoms are nearly the same size, and the solute atoms simply substitute for solvent atoms on the crystalline lattice. On the other hand, interstitial solid solutions are those in which the solute atoms are much smaller and they fit within the spaces between the existing solvent atoms on the crystalline structure. However, the only solute atoms small enough to fit into the interstices of metal crystals are hydrogen, nitrogen, carbon and boron. The other small-diameter atoms, such as oxygen, tend to form compounds with metals rather than dissolve in them. When both small and large solute atoms are present, the solid solution can be both interstitial and substitutional. The insertion of substitutional and/or interstitial alloying elements strains the crystalline lattice of the host solvent structure. This increase in distortion,

or strain, creates barriers to dislocation movement. The distortion energy causes some hardening and strengthening of the alloy and is called solid solution hardening. Let us underline that interstitial atoms generally strengthen a metal matrix more than substitutional atoms do, since the interstitials cause more distortion (Campbell [7]). Both interstitial and substitutional solute atoms can associate with dislocations in order to lower their strain energy. This means the strong interaction between such atoms and the strain fields generated around these dislocations. However, the association of elements to dislocations becomes unstable at high temperature. For example, at a certain critical temperature, the carbon atoms can diffuse away from the dislocations, causing the disappearance of the yield point above this temperature. It is essential that the steel yield point can return to the value previously specified at lower temperature due to the segregation of carbon and nitrogen atoms to the dislocation cores. This process is known as strain ageing. As it has been reported by Sha et al. [8], the kinetics of strain ageing are highly dependent upon the interstitial content. The return of the steel yield point is accelerated if the interstitial content increases, ranging from months at low interstitial contents down to a few hours at high interstitial contents.

3. Influence of alloying elements on the resulting high-temperature resistance of structural steel

To effectively choose the type and the content of alloying elements which, when added to the chemical composition of conventional structural steel, result in an increased resistance to its exposure to a fire temperature it is necessary to recognize the mechanisms of actions of these elements on the resulting behaviour of the heated steel. In further analysis each of these mechanisms, relating to the particular elements, is discussed in detail.

3.1. Carbon and nitrogen

It is widely recognized that carbon and nitrogen are two of the most influential elements determining the high-temperature strength of structural steel. Both have an essential effect on the steel yield point as well as on the steel ultimate stress when they are in solid solution, even if these values are related to the room temperature. Such behaviour results from the occupation of the tetragonal interstitial site in α -iron body-centered cubic lattice structure. It is reported that the resultant large strains of metallic matrix give a strengthening increment of 5500 MPa computed per 1% by mass (Llewellyn [9]). However, the size of such an increment is limited by their low solubility in ferrite. This solubility is estimated to be equal to 0.02% mass for carbon when it is at the temperature 723°C and to 0.1% for nitrogen when it is at the temperature 590°C. According to Baird and Jamieson [10] the increase in the strength was observed also at the temperature up to 450°C for 0.12% mass carbon content but the mechanism of this strengthening was not thoroughly investigated. Furthermore, it has been reported that interstitials have little effect on creep resistance at the temperature above 450°C. The second mechanism identified with the increase of the steel yield stress is that relating to the segregation of carbon and nitrogen atoms to grain boundaries, where they pin grain boundary dislocations.

According to Houdremont [11] the conventional way to improve moderately the strength of the steel at high temperature (i.e. up to 350°C) is by increasing the carbon content. Let us note; however, that greater carbon content in hot-rolled steel usually worsens both its notch toughness and its weldability. For this reason, carbon content is normally limited in structural steels to a maximum of 0.2%. Therefore, for fire resistant steels which could be safely used under direct fire exposure a practical carbon range 0.05-0.2% is designed.

3.2. Manganese

As it is commonly known deoxidation is the primary function of manganese in structural steels. Another function is to prevent hot shortness by removing sulphur through the formation of MnS inclusions. Furthermore, it is used to reduce the formation of grain boundary cementite. It also can produce temper embrittlement. Manganese increases the strength of the steel by solid solution hardening in hot-rolled steels. The strain-hardening interaction between manganese and nitrogen and carbon is well-documented at temperature range 250-500°C, which produces

a moderate strengthening effect. Moreover, manganese tends to lower the eutectoid carbon content in the steel and promotes segregation of carbon and nitrogen atoms.

3.3. Silicon

Silicon is a solid solution strengthener and also a deoxidizer. In structural steels it is a mild ferrite former and solution hardener of ferrite. Appropriate addition of silicon to the steel chemical composition results in a higher high-temperature strength of such a steel by retarding the coarsening of cementite. As silicon increases the activity of carbon and nitrogen atoms the levels of grain boundary segregation of these elements are reduced. Furthermore, silicon retards softening of the steel at high temperature and thus increases its hardenability. If the silicon content in the steel exceeds the level 0.3% then it can adversely affect the weldability of this steel.

3.4. Molybdenum

Molybdenum is considered as the element essential for high-temperature applications of all types of structural steel but it is especially advantageous in relation to the low-alloy steels. In fact, it is used in most of the fire resistant steels currently manufactured all over the world. It significantly increases both the tensile and the creep strengths of such a steel at fire temperature. Furthermore, molybdenum increases the solubility of niobium in austenite, thereby the precipitation effects of carbides, i.e. Nb(C, N), in ferrite are also increased. However, it seems that the basic mechanism associated with the molybdenum activity and strengthening the steel under fire temperature is that relating to the annihilation of dislocations creating in the metallic matrix. Such dislocation locking occurs in association with carbon and nitrogen atoms. Furthermore, the formation of a layer of molybdenum atoms around NbC precipitates reduces the rate of coarsening by slowing the diffusion of niobium atoms to the precipitate. Molybdenum tends to hinder self-diffusion of iron thus increasing the recrystallization temperature of a steel. The another mechanism relating to molybdenum activity and increasing the high-temperature strength of a steel under fire exposure deals with the formation of molybdenum carbonitride. The molybdenum atoms can also form clusters, which have a similar effect to precipitates.

3.5. Vanadium

It is a well-known fact that vanadium is one of the main alloying elements identified in the chemical composition of conventional grade S355 structural steel. It is also frequently added to some of the higher-carbon constructional steels. Such an addition is very favourable if the steel would be used as the fire resistant because it increases the steel resistance to temperature, provides the tempering of such a steel as well as retards the growth of carbides at service temperature. This strengthening effect is achieved due to the precipitation of vanadium carbonitride.

3.6. Niobium

As it has been mentioned above (see p. 3.4), niobium is another element, used in combination with molybdenum, which is essential to increase the high-temperature strength for low-alloy steels. This effect is a consequence of the fact that niobium is a very strong carbide-former. Furthermore, such carbides are more stable than those formed by molybdenum. Consequently, the main role of niobium is to be a grain refiner in austenite. Through the interaction between niobium and molybdenum the NbC precipitation may be delayed so as to overlap after the transformation from austenite to ferrite during cooling (see p. 3.4). Niobium also has a considerable solid solution strengthening effect, especially at high temperature. For example, it is reported that the strength of a ferritic stainless steel at the temperature 950°C is directly proportional to the amount of niobium in solution, up to the level of around 0.8% , where a peak of such strength is reached.

3.7. Chromium

The effect of chromium to the steel strength obtained at fire temperature is complex, especially when it is alloyed together with molybdenum or vanadium. Chromium is also a carbide-former. Furthermore, it has a faster diffusion rate in ferrite than most metallic elements. Owing to this, the precipitation of chromium carbides may occur already when the temperature is not very high. For example, for Cr_7C_3 it is possible if only the temperature is as low as 500°C . The rapid coarsening is unfavourable in this case; however, molybdenum is generally being added to reduce the rate of such coarsening. The solubility of chromium in ferrite is up to 100%. Furthermore, chromium may dissolve in Mo_2C and make it less stable, by decreasing the crystalline lattice parameter, moving the secondary-hardening peak to lower temperature values. To sum up, the principal functions of chromium are those relating to increase of a steel hardenability as well as to give some contribution both to the high-temperature strength and to the oxidation resistance of such a steel.

3.8. Cobalt

The basic function of cobalt is to resist softening of a steel at high temperature when dissolved in either ferrite or austenite. Due to this, it has a little effect on hardenability of such a steel. It is also a ferrite stabilizer. Cobalt has 80% solubility in ferrite; however, its carbide-forming tendency is only slightly greater than that of pure iron.

4. Experimental evaluation of the benefits arising from the use of alloying elements on the obtained fire resistance of structural steel

According to a review given by Sha et al. [8] the following strengthening mechanisms are usually identified as those which determine the properties of the considered fire resistant steel when exposed to a fire:

- pure solid solution strengthening,
- interaction solid solution strengthening,
- strain ageing,
- strain induced ordering of interstitial solute atoms,
- precipitation,
- ferritic grain size.

Taking into account the results of many experimental studies, reported in the professional literature, it appears that the interaction solid solution strengthening, between substitutional and interstitial elements, as well as the precipitation may be considered as two major high-temperature strengthening mechanisms because the magnitude of those two mechanisms is significantly higher than the other contributions among the list presented above.

In general, it is reported that the mechanism relating to the pure solid solution strengthening by molybdenum or chromium is almost insensitive to temperature, provided that in the range of $20\text{-}750^\circ\text{C}$. Particularly, an addition of 0.01% carbon or nitrogen to pure iron produce no significant strengthening in this temperature range. However, in case when the temperature exceeds the level of 450°C the addition of only 0.01% carbon or nitrogen, to binary Fe-1%Mo and Fe-1%Cr alloys, produce considerable strengthening, especially in the molybdenum-containing alloys. In view of the fact that these ternary alloys are effectively pure solid solutions, i.e. no precipitation occurs during testing at temperature up to at least 600°C , this strengthening effect is usually attributed to an interaction solid solution strengthening mechanism. Furthermore, the effect of strain age-hardening is observed in iron-carbon alloys with a little nitrogen present, at temperature higher than 200°C , being a result of the addition of manganese, chromium, molybdenum, tungsten or copper. On the other hand, this effect is not obtained if vanadium or titanium is added to the chemical composition of a considered structural steel.

It is found experimentally by Panigrahi [12] that it is possible to obtain two-thirds of room temperature yield stress at 600°C with 0.20-0.25% molybdenum and 0.30-0.55% chromium in low-carbon hot-rolled structural steel. Furthermore, enrich the chemical composition of Cr-Mo steel by admixtures of niobium or vanadium, singly

or in combination, results in its higher yield stress guaranteed at fire temperature. According to the report from the experiments carried out by Zhen Zhi-Wang and Liu Qing-Chung [13 and 14] the addition of 0.10% V to the 0.60% Mo weathering steels has only a limited effect on the transformation of a steel whereas the addition of 0.20% V promotes the formation of polygonal ferrite. The precipitates of vanadium become finer and denser as the vanadium content increases.

As far as the precipitation of carbonitrides is concerned as one of the major strengthening mechanism at fire temperature its favourable effect depends on the several factors such as the composition, morphology, coherence and stability. However the first of these factors, i.e. the composition, seems to be the most important among them because all the other factors are largely dependent on it. Moreover, the effect of the precipitation may be difficult to precisely estimate, especially in relation to the early studies, mainly due to the limitations at that time in the development and availability of high resolution electron microscopy (HREM) techniques.

5. Influence of alloying elements on the weldability of fire resistant structural steels

The carbon equivalent value (CEV) is accepted as an objective measure allowing for prediction the weldability of the newly designed fire-resistant structural steels. In the application of this type the value of such a CEV-coefficient may be evaluated for the assumed chemical composition of the considered steel (in weight percent) using the Ito-Besseyo equation formulated as follows (Honeycombe and Bhadeshia [5]):

$$CEV = C + \frac{Si}{30} + \frac{Mn}{20} + \frac{Mo + Nb}{15} \quad (1)$$

If the calculated value of this factor is less than 0,4 than the predicted weldability of the examined fire-resistant steel will be good. Moreover, values of the CEV-coefficient being under 0.35 indicate not only a good weldability but also no need for the steel preheating. As it has been confirmed experimentally by Chijiwa et al [15] all fire resistant steels currently produced all over the world are characterized by the excellent weldability properties.

6. Concluding remarks

The main forms of a passive protection against the potential fire exposure relating to the steel members constituting the load-bearing structure are usually rigid boards, sprays, intumescent coatings or even simply masonry or concrete encasements. It is obvious that the practical use of these measures is not only a very expensive venture but also a labour-intensive activity with much of the cost being derived rather from the manual application of them than from the purchase of the material itself. This means that the mere reduction of the thickness of such the protection, even in case when it would be characterized by significantly improved thermal properties, will not necessarily significantly reduce the costs required to pay. For this reason, such the method of obtaining the sufficient level of structural fire resistance is intensively sought which will allow to eliminate the need for use any special thermal insulations for steel members the structure is made of. In fact, they could be eliminated provided that either a higher grade structural steels would be used or a larger section size of the structural elements would be designed. However, a very promising solution seems to be in this field the approach based on the development of the fire resistant structural steels with enhanced high-temperature strength that can delay the time at which the loads applied to the structure when exposed to a fire exceed the load capacity of structural members.

The earliest research associated with the designing of the fire-resistant structural steels was that carried out by the French steel company Creusot-Loire, in the 1970s. This was a very unsuccessful venture, because of the lack of understanding of the effect of thermomechanical treatment of the steel on its high-temperature properties. The next experiments in this area were conducted by the Australian steel company Broken Hill Proprietary (BHP). In these steels the high-temperature strength was correlated with microstructure of acicular type, combined with a secondary precipitation-hardening component (vanadium and/or niobium). Because the early studies on high-

temperature strengthening mechanisms were concentrated mainly on pure ferritic structures, so the investigation on the effect of acicular microstructure was very innovative at that time. The end of the twentieth century with respect to the study how to design the effective fire-resistant structural steels was connected to the strong dominance of some Japanese companies, such as Nippon Steel and to a lesser extent Kawasaki Steel and Sumitomo Metals. In these experiments the Nb(C,N) precipitation as well as the solid solution of molybdenum were analysed as the basic strengthening mechanism. The Nippon fire-resistant steels were further improved at the Queen's University of Belfast in Northern Ireland. It was confirmed that in these steels both precipitation and solutes with a large atomic misfit provide the necessary strength retention. This is the effect of the ultra-fine precipitates, which are slow to coarsen.

In the presented article the authors tried to discuss the basic structural mechanisms by which it is possible to achieve the sufficient resistance of structural steel on its direct exposure to a fire. As one can see, the obtained benefits depend on an appropriate adjustment of the chemical composition of the considered steel, especially by rational selection of alloying elements used in practice, although the effect obtained as a result of such activity is usually complex and frequently multi-faceted.

Presently fire-resistant steels are not the merely experimental curiosities. They are widely used for many types of the building structures, most frequently for drive-in-multi-level car parking lots as well as for roof frames designed for atria and sports facilities like gymnastic halls. An interesting example of a multi-storey building with the skeletal load-bearing structure made entirely of the fire-resistant steel is Tobihata Building completed in Japanese Kitakyushu as early as at the beginning of the nineties of the last century. This structure is presented in many publications, for instance by Sakumoto et al. [16] or by Chijiwa et al. [17]. Another example worth noting in this area may be the fire-resistant steel structure of the Hokke Club Ikenohata Hotel building (at present known as the Sofitel Hotel), located in Tokyo and described in detail in the report prepared by Fushimi et al. [1].

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