Investigation of phase composition of high temperature chromium steels and chromonitriding process in austenitic alloys

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The creep resistance of 9% chromium high temperature steels is determined by the alloy content and structure resulting from heat treatment. This paper describes the analysis of the phase composition using CALPHAD numerical modelling methods, of known modifications of 9% high temperature chromium steel: 9Cr–0·1C, 0·9Mo, 0·21V, 0·1Nb, 0·04N (P91) and 9Cr–0·1C, 2W, 0·5Mo, 0·21V, 005Nb, 0·05N, 0·005B (P92). The effect of alloying elements on the phase composition of the steel and the mutual effect of the composition on the nature and quantity of the phases Me23C6 and Me(CN) in the temperature range 570–620°C is described. On the basis of calculated data and experimental results, a composition for new high temperature steels with additional Co alloying (up to 3%) and varying carbon contents in the range 0·02–0·10% is proposed. Results are shown for investigations on high temperature chromium steels containing cobalt, including: effect of complex alloying with tungsten, molybdenum, and cobalt on the service properties and structural composition of steels; heat treatment processes for alloy variants and kinetics of structural change during creep and prolonged thermal aging. Data have been obtained comparing calculated and experimental data for the phase composition in chromium steel, also the effect of the phase composition on creep characteristics. On the basis of a complex laboratory investigation and industrial pilot heats, optimal composition variants for the alloy content of high temperature Cr–Mo–V–Co steels have been determined for practical applications. CNIITMASH has developed a chromonitriding technology for improving the corrosion, wear and scratch behaviour, as well as for protection against self-welding and other service characteristics of austenitic steel components and nickel alloys. Chromonitriding technology includes saturation of the component surface with chromium and nitrogen. The technology is intended for strengthening valves and bushings, water pump components, and components operating in liquid metal, burnt fuel residue, and other aggressive environments. The conditions governing the formation of the strengthening layers, consisting of an austenitic matrix (γ solid solution) and containing Cr_2N with a depth of up to 250 μm and a hardness of 750–950 HV have been determined. Thermodynamic analysis of phase formation conditions during the chromising and subsequent nitriding process over a wide range of temperatures and saturating media has been carried out. The technology has been optimised for process and media composition leading to a structure with maximum surface properties.

Keywords: Creep resistace, Phase composition, High chromium martensitic steels, Chromonitriding, Austenitic alloys

In recent years, the creation of coal powered generating units with a working temperature of steam exceeding 600°C has caused interest in 9–12% chromium high temperature martensitic steels to grow dramatically. Typical heat treatment of these steels consists of two stages: normalisation and high temperature tempering. Such heat treatment results in martensitic transformations that form the dislocation structure which remains intact after the high temperature tempering and in the course of creep flow. High temperature tempering makes the excess alloy elements precipitate from the solid solution in the form of secondary phases (e.g. $M_{23}C_6$, MX) largely scattered along the boundaries of former austenite grains as well as borders of blocks and martensite laths.[1–3] Lengthy isothermal exposure causes

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Table 1 Scope of research of phase composition of chromium steel (bal. Fe)

Weight range of elements/%

C	Cr	Co	Mo	W	V	Nb	B	N
0·00–0·15	7·0–11·0	0·0–5·0	0·0–2·0	0·0–4·0	0·0–0·3	0·0–0·3	0·00–0·01	0·0–0·1

additional precipitation and coagulation of secondary phases as well as precipitation of Laves phases depending on the chemical composition of the steel.

The growth of secondary phase particles in the course of creep flow also facilitates transformation of the martensitic structure into a subgranular structure thus lowering the creep resistance of the steel. Hence, the main condition for high creep resistance of martensitic steels is the resistance of the secondary phases to coarsening. Increasing the stability of the structure produced by heat treatment is a common way of improving the chemical and phase composition of martensitic steels, thereby increasing the creep resistance.

One of the methods to increase the creep resistance is to introduce cobalt into the steel, limit the precipitation of Laves phases and reduce the hydrocarbon content to the level at which the main contribution to the precipitation strengthening is from MX carbonitrides/nitrides that are more resistant to coarsening than carbides such as $M_{23}C_6$.

This paper studies the impact of the alloy element content on the phase composition of high temperature steels of the 9Cr–3Co–2W–MoVNb type.

Using the thermodynamic database TCFE 6·0 and the thermodynamic modelling methods in the Thermo–Calc program, we assessed the impact of alloying elements on the phase composition of steel 0·1C–9Cr–3Co–2W–0·5Mo–0·21V–0·6Nb–0·05N–0·005B, in which the content of alloy elements was changed successively within the range specified in Table 1.

Thermodynamic modelling showed the wisdom of introducing 3% cobalt in view of the substantial content of molybdenum and tungsten, which completely excludes the possibility of formation of δ-ferrite at high temperatures (up to 1250°C) and increases the stability of the carbide phase at operating temperatures (up to 650°C). The calculated assessment revealed that the introduction of cobalt into the steel reduces the diffusion of carbide forming elements. In particular, the modelling of $M_{23}C_6$ carbides growth kinetics showed that the introduction of 3% cobalt helps reduce the conglomeration speed of this type of carbide by ~1·5 times.

In order to restrict the Laves phase, which leads to the fusion of the solid solution with tungsten and molybdenum and thus diminishes the strengthening effect on the solid solution, it is necessary to reduce the combined upper limit of tungsten and molybdenum content in accordance with the formula $W+2Mo \leqslant 3\cdot6$. The lower combined limit of tungsten and molybdenum content is determined by the effectiveness of solid solution strengthening. The available data suggest that the most effective strengthening of a solid solution is achieved when the following condition is met: $W+2Mo \geqslant 2\%$.[4]

Vanadium and niobium, with their high affinity for carbon, contribute greatly to increased high temperature strength by forming ultrafine particles of (V,Nb)(C,N) type that are characterised by high coagulation resistance at high temperatures and are an effective barrier against structural changes. As far as the achievement of an optimal phase composition in 9Cr–2W–MoVNb+3Co steel is concerned, of particular interest is the area where the niobium content is about 0·06% and vanadium – from 0·17 to 0·28%. In this case, aside from the ferrite matrix, the phase composition at temperatures ranging from 600 to 650°C also contains the phases of (V,Nb)N, $M_{23}C_6$ and Laves types.

The lab studies of the 9Cr–3Co–2W–MoVNb family steels generally confirmed the estimated data.

The structure of 9Cr–3Co–2W–MoVNb steel after heat treatment (normalisation and high temperature tempering) is a tempered martensite with precipitation along the boundaries of the $M_{23}C_6$ carbide grains. High temperature tempering results in additional precipitation of ultrafine carbonitrides (V,Nb)(CN) in the crystal body.

The presence of 3% cobalt in the composition of 9Cr–3Co–2W–MoVNb helped obtain more ultrafine secondary phases than in X10CrWMoVNb9–2[5,6] steel, as well as increasing the structure stability during prolonged isothermal exposure. Table 2 contains data on the amount of secondary precipitation products.

The resulting structure of 9Cr–3Co–2W–MoVNb features a high level of hot strength. Thanks to optimisation of the alloy elements ratio we managed to reduce the creep speed ninefold and prolong the predisintegration period: if the creep rupture strength limit reaches 56 N mm^{-2} within 10^5 h at the temperature of 650°C in T/P92[7] basic composition steel, then in the case of 9Cr–3Co–2W–MoVNb steels it will amount to 96 N mm^{-2}, i.e. 1·7 times higher. Figure 1 shows the results of creep rupture strength limit tests.

In modern machine building the task of comprehensive improvement of the service properties of metals is to a considerable extent connected with the development of new technological processes for surface strengthening them.

The heat and power industry, for example, faces serious problems with using austenitic steels for wearing

Table 2 Size and amount of secondary phases

Steel brand	Theoretical calculation of the amount of secondary phases/%			Initial state size/nm	
	$M_{23}C_6$	MX	AB$_2$	$M_{23}C_6$	MX
X10CrWMoVNb9–2	2·061	0·269	0·615	70–250	40–100
9Cr–3Co–2W–MoVNb	2·217	0·337	1·002	30–170	5–40
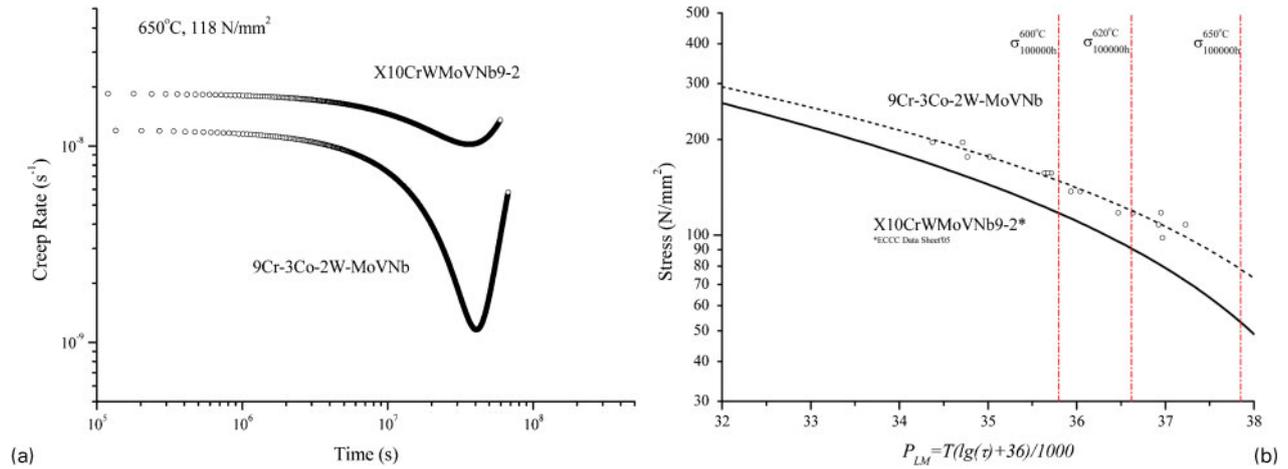
1 Creep data of tempered X10CrWMoVNb9–2 steel and 9Cr–3Co–2W–MoVNb steel

surfaces of components of steam distribution (rods, bushings, etc.) and steam supply (bushings, piston rings, etc.) units that operate under prolonged exposure to high temperatures (up to 650°C) and high contact pressures.

Traditional methods, nitriding and carbonitriding, cannot be applied due to insufficient structural stability and low scaling resistance of the strengthened layer when operated in the temperature range 600–650°C for a long period of time. Apart from that, nitriding and carbonitriding considerably, by more than 10 times, reduce the corrosion resistance of the material in various media.

In view of the above PJSC RPA CNIITMASH has developed a unique chromonitriding technology for strengthening austenitic steels which involves comprehensive saturation of the steel surface with chromium first and then with nitrogen. As a result, a strengthened layer is formed on the surface of austenitic steels. It consists of the austenitic matrix (γ-solid solution) with inclusions of the nitride Cr_2N. The hardness of the chromium nitride layer reaches 950 HV and the thickness – 0·15 mm.

Successful application of the carbonitriding technology in power engineering is restricted by the absence of data on service characteristics of the strengthened layer.

PJSC RPA CNIITMASH has conducted comprehensive studies of service properties of the strengthened layer.

Scoring resistance, particularly at high temperatures, is one of the key indicators of friction couples.

The scoring resistance tests conducted using the methods which involve one sample moving back-and-forth at a speed of 0·69 m s^{-1} between two motionless samples until seizure, showed that the scoring resistance for XH35BT steel in steam at a temperature of 650°C is more than 700 kg cm^{-2}, which exceeds by over 10 times the scoring resistance of non-strengthened steels.[8]

The study of wearing properties and friction coefficients was conducted on a friction test machine of the type 'motionless hemisphere – moving disc' in a medium of argon (in order to exclude surface oxidisation). The disc rotation speed was constant ($n=52$), which provided a sliding speed of 0·14 m s^{-1} at the contact point of the samples. During the tests we registered the changes in the friction speed and at the end of the test we also measured the wear and tear of the spherical (spot diameter) and disc (friction track width) samples.

It was established that the value of the friction coefficient in austenitic steels with no strengthening layers amounted to $f=0·8–1·0$ in the 20–400°C temperature range. With the increase in the testing temperature to 600°C the value of the above parameter increased
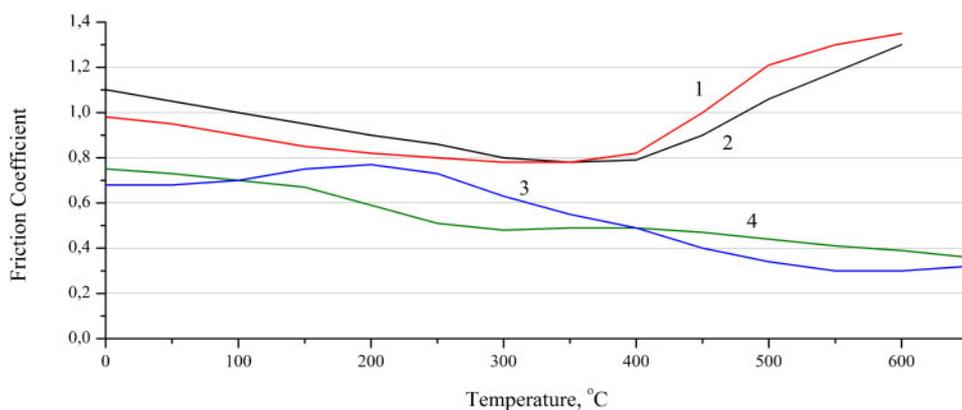
1: 1X18H9T steel; 2: XH35BT steel; 3: 1X18H9T steel after chromonitriding; 4: XH35BT steel after chromonitriding

2 Dependence of friction coefficient on temperature

sharply to 1·4–1·5 (Fig. 2). Chromonitriding of the steels lead to a gradual decline in the friction coefficient through the entire temperature range. At the testing temperature of 600°C, the value of the friction coefficient amounted to 0·3–0·4, which is 3–4 times lower than the untreated steels.

Lengthy wear tests at a temperature of 500°C of different friction pairs with and without a chromium nitride layer revealed the following:

- in the case of friction between a strengthened and non-strengthened surface, one can observe intensive wear of the non-strengthened surface accompanied by considerable plastic deformation and seizure
- in the case of friction between two strengthened surfaces the wear track is smooth, narrow, with no traces of seizure and with the lowest friction coefficient (f=0·58).

One of the main properties of austenitic steels is their heat resistance which is determined by the degree of alloying with such elements as Cr, Ni, Al and Si. These elements form protective 'spinel-type' oxide layers that serve as a barrier for oxygen diffusion inside the metal. The protective properties of steels with diffusion layers depend on the structural stability and diffusion mobility of alloying elements in the solid solution of this layer. Scaling resistance tests conducted in air at a temperature of 800°C show that chromonitriding leads to more than a fivefold increase of this parameter. High heat resistance of the chromium nitride layer on austenitic steels is determined by its stability under prolonged exposure to high temperatures. Chromium incorporated into the nitride Cr_2N, which has a very high dissociation temperature, constitutes a fairly stable phase. The thermal stability (continued hardness and thickness) of the chromium nitride layer at testing temperatures of up to 800°C remains high. No noticeable changes in the structure, thickness and hardness of the layer were observed.[8]

It should be emphasised that in contrast to other strengthening methods, such as, for instance, nitriding and carbonitriding, chromonitriding does not diminish the corrosion properties. For example, the corrosion resistance of austenitic steels with a chromium nitride layer remains unchanged or even exceeds the level of high chromium steels when tested in a 3% solution of NaCl and a 25% solution of nitric acid.[8]

In terms of erosion resistance the chromium nitride layer can be equated with the category of highly erosion resistant materials second only to titanium.

Conclusions

1. Based on estimated and experimental data obtained by studying the phase composition of 9% heat resistant chromium steels, we have shown that comprehensive alloying of the 2%W and 0·5%Mo solid solution enriched with up to 3%Co boosts the dispersion capacity of MX and $M_{23}C_6$ type secondary phases as well as their stability under lengthy isothermal exposure and creep.

2. Based on the results of conducted tests we came to the conclusion that optimisation of the weight ratio of alloying elements helped reduce ninefold the creep speed of 9Cr–3Co–2W–MoVNb type steel compared with 9Cr–2W–MoVNb steel and increase the creep rupture strength characteristics on the 100 000 basis by 1·5 times.

3. The chromonitriding technology, which has been successfully tested in power engineering, can be used in the chemical industry to, for example, strengthen the components employed in the production of fertilisers and acids as well as in the food industry. The chromonitriding technology can also be applied in fields where the use of austenitic steels is necessary but requires a considerable increase in such characteristics as scoring resistance, wear resistance and heat resistance whilst at the same time preserving all of the important properties intrinsic to these materials, namely corrosion and erosion resistance.

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