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#### DISPERSION HARDENING OF HIGH-STRENGTH Ni-Co-Mo STEELS

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UDC 620.193.918:669.15'24'28'25

It is known [1] that the process of secondary hardening caused by precipitation of particles of special carbides in the tempering of alloyed martensite is accompanied by sharp embrittlement and therefore is little used in the heat treatment of existing and in the development of new constructional steels. At the same time, embrittlement may be prevented and neutralized to a significant degree in rational selection of the type and alloy content of steels, which makes it possible to use the phenomenon of secondary hardening with high effectiveness in the development of high-strength steel, including in combination with other hardening factors.

For these purposes the Fe-Ni-Mo system is of interest. In secondary hardening the iron-nickel martensitic matrix is subjected to embrittlement to a lesser degree [2] since as the result of the capability of nickel to reduce the energy of interaction of interstitial atoms with dislocations and to reduce the resistance of the lattice to the movement of dislocations in it the processes of stress relaxation are eased and consequently the probability of brittle crack origin and propagation is less [3]. It is known that the resource of toughness and plasticity of martensite (including of iron-nickel) depends not only upon its composition but also upon the morphology, and therefore the carbon content in an Fe-Ni-Mo system steel must be limited so that in hardening lath (packet) martensite is formed.

To create the secondary hardening effect in iron-nickel martensite it is desirable to use as the carbide-forming element molybdenum, which in this case possesses a number of unquestionable advantages. The precipitation of molybdenum carbide in tempering leads to intense dispersion hardening. In addition this carbide, in contrast to many others, dissolves in austenite starting with 1000°C and consequently it is not necessary to use high-temperature austenitization accompanied by grain growth. It should be noted that if the molybdenum content in the steel exceeds its content necessary for the formation of Mo<sub>2</sub>C-type carbide, then the conditions are created not only for the most complete binding of interstitial atoms but also for prevention of temper brittleness, which appears in tempering in the temperature range of secondary hardening [1]. Finally, with a molybdenum content significantly exceeding that necessary for formation of the carbide, the iron-nickel martensite matrix may be additionally hardened by particles of a molybdenum-containing intermetallide such as Fe<sub>2</sub>Mo type.

The purpose of this work is to determine the possibility of use of the secondary hardening effect for obtaining in steels of the Fe-Ni-Mo system a structural condition providing a sufficient reserve of plasticity and toughness together with high hardening.

In addition to nickel, the investigated steels contained 0.3% C, that quantity which is most characteristic of known high-strength constructional steels [4]. In accordance with the

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N. E. Bauman Moscow Higher Technical Institute. I. P. Bardin Central Scientific-Research Institute for Ferrous Metallurgy. Translated from *Metallovedenie i Termicheskaya Obrabotka Metallov*, No. 5, pp. 33-37, May, 1985.

TABLE 1

% cobalt in the steel	M <sub>s</sub>	M <sub>f</sub>	A <sub>res</sub> %	D, μm	a <sub>α</sub> , nm	ρ, μΩ·m
	°C					
0	200	30	25/7	19	0,28804	0,635
5	210	50	20/5	21	0,28790	0,660
10	225	60	15/tr	23	0,28778	0,685
15	235	80	10/-	27	0,28764	0,705

Notes: 1. All of the specimens were hardened from 1150°C.

2. The first figure is the residual austenite content before cold treatment and the second after it.

TABLE 2

% cobalt in the steel	σ <sub>t</sub>	σ <sub>0,2</sub>	δ	ψ	HRC <sub>e</sub>	a, kJ/m <sup>2</sup>
	MPa		%			
0	1760	1550	7,5	39	52	580
5	1850	1590	10	41	53	640
10	1950	1770	10	41	54	700
15	2000	1800	7,5	38	54,5	600

above all of the investigated steels were alloyed with 6% molybdenum. To intensify the dispersion hardening and also to create possible additional hardening as the result of formation in the matrix phase of Fe-Co type close-range ordering (similar to that observed in maraging steels of close composition [5]), the base steel (0.3% C, 12% Ni, 6% Mo) was alloyed with 5, 10, and 15% Co. All of the steels were melted of pure charge materials in an open induction furnace.

It was established that austenitization of the investigated steels at 1100-1150°C provides sufficiently complete solution of the excess phases with maintenance of a fine granular structure. According to the data of dilatometric analysis, transformation of austenite in such steels occurs according to the martensite mechanism even under conditions of slow cooling (at a rate of up to 10 deg/min). As the result of hardening, a structure of typical packet (lath) martensite with inclusions of particles of carbides undissolved in austenitization is formed in the steels.

The temperature of the finish of the martensite transformation in the base steel is close to room and therefore after hardening from 1150°C its structure still contains up to 25% residual austenite (Table 1). With an increase in cobalt content the quantity of residual austenite in the hardened steels decreases, which is related to shifting of the martensite range in the direction of higher temperature under the influence of cobalt. Cold treatment in liquid nitrogen, while not changing this rule, leads to a significant decrease (with 15% Co, to zero) in the residual austenite content in the steels.

The possibility of occurrence and practical use of the secondary hardening effect in the steels depends to a great degree upon the level of hardening and the reserve of plasticity of their martensite matrix. Therefore, there is definite interest in investigation of the influence of cobalt on the properties of the steel in the hardened condition in static tension and impact bending. The properties of the steels after hardening from 1150°C, cold treatment, and tempering at 150°C (for stress relief) are given in Table 2.

It should be noted that alloying with cobalt leads to a significant increase in the strength characteristics of the hardened steels. Since the contribution of cobalt to solid solution hardening of substitutional martensite may not be so significant, it is obvious that the observed increase in strength of the steels is only to a certain degree related to the decrease in them in the quantity of residual austenite but is primarily caused by changes in the martensite matrix itself under the influence of cobalt. An indirect manifestation of such changes is the significant increase in the specific electrical resistance of the hardened steels and the decrease in the lattice parameter of the martensite with an increase in cobalt content in the steels (Table 1). Such a combination of changes in these parameters is a characteristic sign of an increase in the interstitial atom content in the

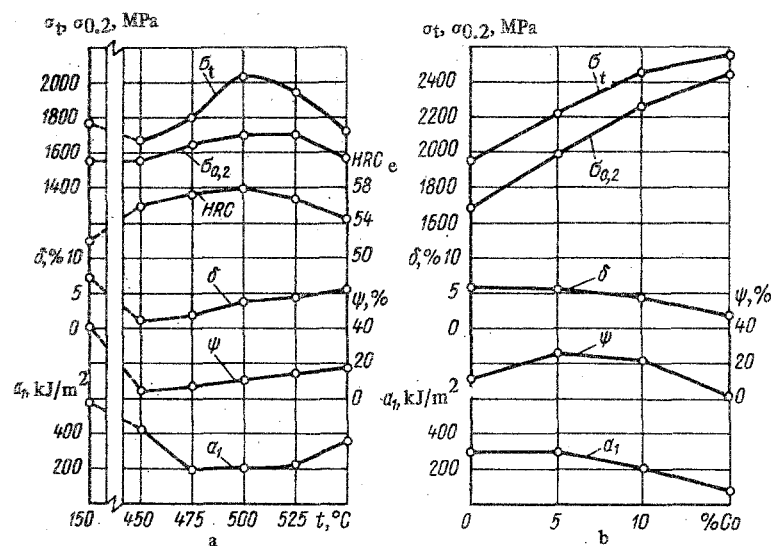


Fig. 1. Relationship of the properties of the base Fe-Ni-Mo steel to secondary hardening temperature (a) and cobalt content (b): a) water hardened from  $1150^\circ\text{C}$ , cold treated at  $-196^\circ\text{C}$ ; b) hardened from  $1100^\circ\text{C}$ , cold treated at  $-196^\circ\text{C}$ , tempered at  $500^\circ\text{C}$ .

martensite. In this case it is an indication of an increase in solubility of the carbide phase in the cobalt-containing austenite in heating for hardening. This conclusion is confirmed by data of microstructural investigations, as the result of which a higher tendency of cobalt-containing Fe-Ni-Mo steels toward grain growth was established (Table 1).

The mechanical tests showed that with a significant interstitial atom content iron-nickel martensite, which possesses increased strength, has a quite high plasticity. Despite the increase in the quantity of residual austenite, grain growth, and an increase in carbon content in the martensite as the result of alloying with cobalt, an increase in its content to 10% leads even to some increase in the reserve of plasticity and toughness of the steels. With a higher cobalt content the plasticity of the steels again drops.

Therefore, in investigations of the properties of the hardened steels it was established that their martensitic structure is characterized by significant strength, a sufficient reserve of plasticity, and a high degree of supersaturation of the  $\alpha$ -solid solution. This determines the possibility of its use as the matrix phase for additional strengthening as the result of secondary hardening. In connection with this it is necessary to establish the rules of the process of decomposition of martensite in tempering in the area of secondary hardening temperatures, which makes it possible to evaluate the effectiveness of such a tempering for improving the properties of steels of the selected system of alloying and to reveal the role of cobalt in the formation of the high-strength structural condition.

In tempering of all of the investigated steels intense secondary hardening was observed and the temperature range of this process in iron-nickel martensite is displaced in the direction of lower temperatures so that the peak of secondary hardening corresponds not to the  $580\text{--}600^\circ\text{C}$  range, which is characteristic of unalloyed martensite [1], but is observed at temperatures of about  $500^\circ\text{C}$ . Figure 1a shows the relationship of the properties of the base steel not containing cobalt to the temperature of secondary hardening. It may be seen that in comparison with hardening and low temperature tempering, tempering in the secondary hardening temperature range leads to a marked increase in the strength of the steel with a decrease in plasticity. The sharpest reduction in the plasticity of the base steel is observed after tempering at  $450\text{--}475^\circ\text{C}$ , that is, at temperatures below the zone of maximum strengthening. This may be related to the presence of carbon atoms in the solid solution and primarily to the high density of distribution of highly dispersed mixed zone type accumulations formed from them and characteristic of the preprecipitation phase [1]. It should be noted that the processes occurring in the martensite in the preprecipitation stage weakly influence the values of impact strength obtained under conditions of loading with high deformation rates. This is also characteristic of the phenomenon of delayed failure. In turn as the result of tempering at a temperature corresponding to the temperature of maximum hardening

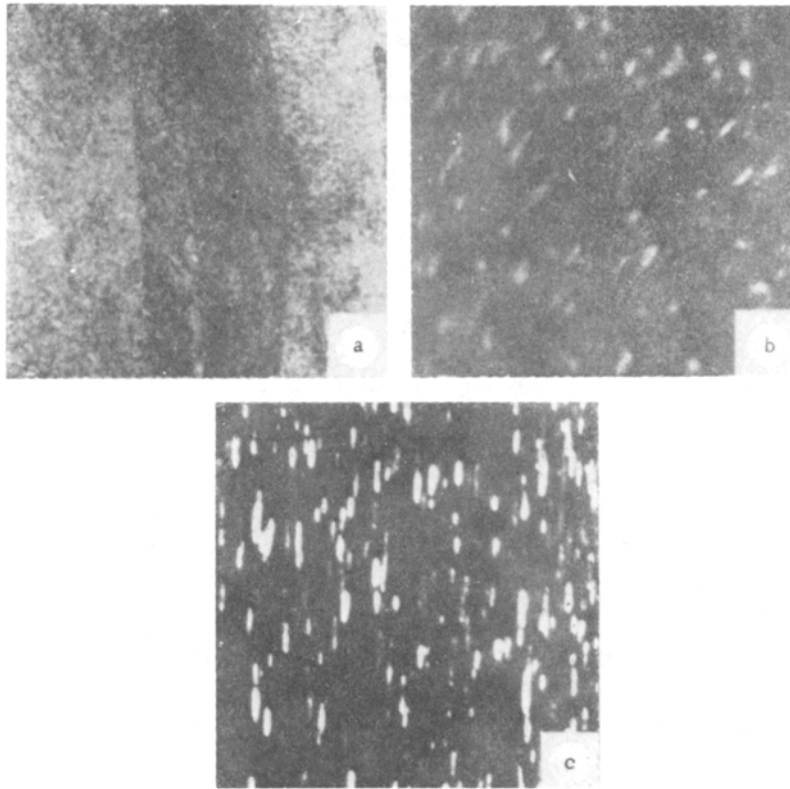


Fig. 2. Structure of Fe-Ni-Mo steel containing 10% Co after hardening and tempering at 500°C for 1 h (a, b) and at 550°C for 10 h (c): a) bright-field electron-microscopic image, 70,000×; b) autoion microscopic image of dispersed precipitates of an intermediate strengthening bct phase, ×500,000; c) dark-field image of particles of Mo<sub>2</sub>C carbide elongated in the [100]<sub>M</sub> direction, 70,000×.

and, consequently, of a high degree of linking of the carbon atoms with molybdenum, the plasticity of the base steel increases significantly (Fig. 1a). The plasticity and impact strength of this steel continue to increase in the overaging stage.

It was established that under the influence of alloying with cobalt the intensity of secondary hardening of the steels increases significantly, which leads to a strong reduction in the plasticity of the steels in the preprecipitation stage, especially with a content of 10-15% Co in them. It should especially be noted that the reduced plasticity of the cobalt-containing steels is not eliminated even in overaging of them, when significant loss of strength occurs.

Using the resource determined for increasing the plasticity and impact strength of the steels as the result of decreasing the hardening temperature from 1150 to 1100°C (a reduction in grain size to 10 μm and less complete solution of the carbide phases are obtained), it was possible to not only prevent brittle fracture of the steel after tempering in the range of maximum hardening temperatures but also to provide a quite high level of plasticity and impact strength. This in turn made it possible to obtain a high level of strengthening of the steels during secondary hardening (Fig. 1b). It should be noted that in this case with an increase in cobalt content in the steels after tempering at 500°C there is a significant increase in the tensile and yield strengths while with a content of 5-10% Co there is practically no change in their plasticity and impact strength. Only with 15% Co does the above shown reduction in plasticity and toughness of the matrix phase appear.

It was established that the steel containing 10% Co possesses the best combination of properties and after tempering at 500°C  $\sigma_t = 2450$  MPa,  $\sigma_{0.2} = 2250$  MPa,  $\delta \cong 4-5\%$ ,  $\psi \cong 22\%$ ,  $\alpha_1 = 200$  kJ/m<sup>2</sup>, and  $K_{IC} = 80$  MPa·m<sup>1/2</sup>.

The investigation of the process of secondary hardening of the steels was made by methods of diffraction electron and autoion microscopy and x-ray diffractometry. It was established that tempering at 500°C for 1 h, which causes the greatest strengthening of the

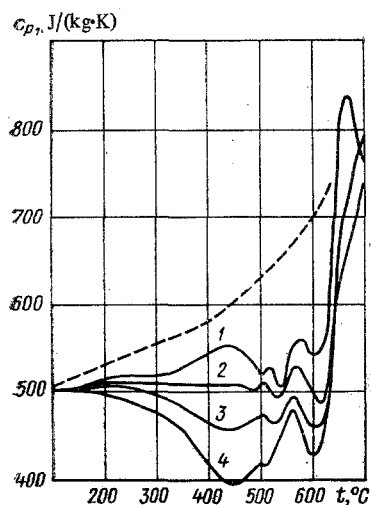


Fig. 3. The temperature relationship of the specific heat of hardened Fe-Ni-Mo steels with different cobalt contents (solid lines) and of the base steel after hardening and high-temperature tempering (broken line): 1) without cobalt; 2, 3, 4) 5, 10, and 15% Co, respectively.

steels, leads to changes in the martensite structure which are characterized by the appearance on the electron-microscopic images of a contrast from very dispersed precipitates (Fig. 2a). On the microelectron diffraction patterns diffraction reflections elongated in the  $[100]^*$  direction and corresponding to precipitates with a bct lattice apparently coherently bound to the bcc lattice of the martensite are revealed. The elongation of the reflections is caused both by the different degree of tetragonality of the lattice of different precipitates and by the change in it within the limits of a single precipitate. This is confirmed by the results of photographs of dark field images of precipitates in different "areas" of the elongated diffraction reflex and agrees with the data of [6]. The precipitation of the intermediate (before appearance of the cph  $\text{Mo}_2\text{C}$  carbide) strengthening bct carbide phase enriched with carbon and molybdenum in this case is also apparently stimulated by the presence of the coherent bond of the close in structure bct and bcc lattices of the precipitates and matrix, respectively. The microstresses occurring in the presence of such a bond are an additional factor in strengthening.

To investigate the distribution and form of the precipitates in the stage of maximum strengthening the most informative is the method of autoion microscopy. Figure 2b shows a hydrogen autoion microscopic image<sup>†</sup> of the structure of the steel containing 10% Co. On the background uniform in luminosity corresponding to the martensite matrix may be seen brighter areas the contrast of which is determined by the presence in the steel of areas of concentration inhomogeneity formed by atoms of carbon and alloy elements. The distribution of areas of concentration inhomogeneity in the volume of the alloy is statistically uniform and preferential formation of them close to any structural defects was not observed. The areas of contrast visible on the photomicrographs are different in form, lines and round. The size of the line areas is about 4 nm and of the round 2 nm. The results of observation of the time of existence of the image from the areas of different form during evaporation of the specimen material and the differences given above make it possible to conclude that the concentration inhomogeneities in the investigated state are rod-shaped areas with a ratio of dimensions of 1:2.

After tempering at 550°C for 10 h, when a marked loss of strength of the steels was already observed, in their structure there are formed comparatively coarse precipitates of cph  $\text{Mo}_2\text{C}$  carbide precipitates elongated in the  $\langle 110 \rangle_M$  direction (Fig. 2c) and linked (according to the data of analysis of microelectron diffraction patterns) with the lattice of the matrix by the Pitsch-Schrader orientation relationship, which is also confirmed by the results of [6]. It should be noted that in all of the investigated steels the process of precipitation

<sup>†</sup>The investigation was made by V. I. Kirienko.

of the carbide phase completely suppresses the reaction of formation of intermetallides, which occurs very intensely in carbide-free maraging steels of similar composition, especially if they contain cobalt [5].

As the result of their localness the methods of structural analysis used are not able to reveal the appreciable influence of cobalt content on the volume share of molybdenum carbide precipitates. To determine the influence of cobalt on the secondary hardening effect in tempering of the investigated steels a calorimetric method making it possible to establish the temperature conditions and sequence of the phase and structural transformations and also to give a quantitative determination of the degree of their development was used.

As the result of comparison of the temperature relationship of the change in "apparent" specific heat during heating of the hardened steel with the similar relationship after tempering at 640°C the temperature intervals of the reduction in specific heat indicating the occurrence of exothermic transformations were determined.

In the hardened base steel not containing cobalt in the secondary hardening temperature range at 500, 540, and 600°C there were observed three minimums in specific heat (Fig. 3, curve 1). The first thermal effect (at 500°C) is apparently related to decomposition of the residual austenite in the steel. After cold treatment it appears to a lesser degree. Taking into consideration that the calorimetric analysis was made under conditions of continuous heating and that the mechanical properties of the steels presented above were determined after isochronous tempering (for 1 h), it may be concluded that the effect of reduction in specific heat at 540°C corresponds to the maximum in secondary hardening and is caused by precipitation of metastable carbide phase. The minimum in specific heat appearing at 600°C obviously corresponds to the formation of the more stable modification of the carbide phase.

The intensity of the thermal effects of the transformations in tempering changes significantly with additional alloying of the steels with cobalt (Fig. 3). The reduction in specific heat observed in the base steel at 500°C, as must be expected, appears to a lesser degree with 5% Co and with cobalt contents of 10 and 15% is completely absent, which agrees with the rule shown above of the change in the quantity of residual austenite in hardened steels under the influence of cobalt. In turn with an increase in cobalt content those thermal effects which accompany the reactions of precipitation of the carbide phase are shifted in the direction of lower temperatures and increase significantly, which is an indication primarily of the increase in the quantity of carbide phase formed. In addition to these changes on the temperature relationship of "apparent" specific heat of the cobalt-containing steels there is observed an additional anomaly at about 450°C, the intensity of which increases with an increase in cobalt content. The appearance of such an anomaly at this particular temperature and only in the presence of cobalt obviously reflects the process of Fe-Co type close-range ordering in the matrix phase (similar to that observed in steels with a similar matrix composition [5]) and its increasing contribution to the secondary hardening effect, which together with the increase in the quantity of carbide phase caused the greater strengthening of the steels containing cobalt in tempering.

**Conclusions.** 1. Secondary hardening in tempering of carbon-containing iron-nickel martensite alloyed with molybdenum is caused by precipitation of metastable molybdenum carbide, which occurs with greater completeness and, in addition, on a background of the process of Fe-Co type close-range ordering in steels additionally containing cobalt.

2. As the result of use of the secondary hardening effect it is possible to obtain a high combination of mechanical properties in carbon-containing iron-nickel martensite-base steels alloyed with cobalt and molybdenum.

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## STRUCTURE AND PROPERTIES OF POWDER METALLURGY

### TUNGSTEN-FREE ROM2F3-MP HIGH-SPEED STEEL

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UDC 620.18:620.17:621.762:669.14.018.252.3

In connection with the limited alloy element raw material resources and the ever-increasing shortage of tungsten, at present it has become necessary to replace high-alloy high-speed steels with lower alloy ones, particularly those not containing tungsten [1].

It is known [2, 3] that the tungsten-free high-speed steels ÉI260 and ÉI277 possess approximately the same cutting properties as R18 high-tungsten steel in machining materials with a hardness of up to 250 HB. Of the earlier works devoted to a comparison of high-speed steels differing in composition, including tungsten-free ones with a low molybdenum content, the thorough investigation of Houdremont and Schrader [4] should be noted, although such a type of high-speed steel was patented\* by Armstrong in 1924. As for others proposed in recent years, tungsten-free low-alloy steels differ insignificantly in the content of the basic alloy elements. To obtain good cutting properties these steels include 2-3% V (more than in R18 steel), which decreases their grindability. With such a vanadium content in steels with a low tungsten and molybdenum content, a large quantity of hard VC carbides (about 3000 HV) is formed and the grindability is significantly reduced [2, 5], as the result of which ÉI260 and ÉI277 steels have not found wide use in industry.

The production of high-speed steel by the powder (granular) metallurgy method makes it possible to significantly increase cutting tool quality [6]. The high rate of crystallization provides a fine granular structure, a dispersed carbide phase (size less than 3  $\mu\text{m}$ ), and the absence of segregation, and therefore powder metallurgy high-speed steels possess a high combination of service and technological properties. Satisfactory grindability is provided even with a content in the steel of up to 6-8% V [7, 8].

This article presents the results of an investigation of the structure and properties of ROM2F3-MP powder metallurgy tungsten-free high speed steel, which is an analog of ÉI277 steel produced by the traditional method (Table 1).

The investigation was made on ROM2F3-MP steel by atomization in nitrogen using the method of the Tula Ferrous Metallurgy Scientific and Production Union with subsequent compacting of the powder by hot extrusion in 'Élektrostal' Plant. The oxygen and nitrogen contents in the compacts obtained did not exceed 0.025% each. The cooling rate in atomization, which depends upon the size of the powder granules, has a significant influence on the structure and phase composition of powder metallurgy high-speed steels [9, 10]. The powder of ROM2F3-MP steel was separated into the following fractions: finer than 50, 50-100, 100-200, 200-300, and coarser than 300  $\mu\text{m}$ . The cooling rate for each fraction was determined from the distance between the second order axes [11]. Depending upon the fraction size the cooling rate varies from  $10^4$  to  $10^5$  deg/sec (Table 2). The ROM2F3-MP steel powder for metallographic investigations was mixed in "Protakril" paste and after hardening was ground and polished normally. The microhardness was determined on a PMT-3 tester with loads of 0.5-2 N. The microstructure of the powder particles was revealed by etching in 2% nital. The microstructure of ROM2F3-MP steel powder particles is characteristic of powders obtained by gas

\*USA Patent 1496980.