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Role of Copper in Precipitation Hardening of High-Alloy Cr-Ni Cast Steels

Mirosław Gajewski

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The mechanism of strengthening with second-phase particles that results from heat treatment, i.e., precipitate hardening, plays an important role in modern alloys. The strengthening effect of such particles can result from their coherence with the matrix, inhibition of dislocation slip, inhibition of grain boundary slip, as well as hampering recovery processes due to dislocation network pinning. The results of investigations into high-alloy Cr-Ni-Cu cast steels precipitate hardened with highly dispersed ε phase particles are presented within. The influence of heat treatment on changes in microstructure, mechanical properties, and morphology of fracture surfaces obtained under loading have been analyzed. It has been demonstrated that, with the appropriate selection of heat treatment parameters, it is possible to control the precipitation of the hardening ε phase and, thus, to change the final mechanical and functional properties.

Keywords copper (Cu), duplex cast steel, ε phase, martensitic cast steel, precipitation hardening

1. Introduction

Corrosive and erosive action of water solutions containing Cl^- and SO_4^{-2} ions, for example, as well as solid particle pollutants, lead to costly failures and operational stoppage caused by premature machine part wear. These problems refer mainly to components of pump flow systems for coal and copper mine main drainage and also pumps operating in the sulfur industry or in seawater environments. Such problems can be solved by application of precipitate-hardened high-alloy Cr-Ni-Cu cast steels with a martensitic microstructure or "duplex-type" Cr-Ni-Mo-Cu cast steels with a ferritic-austenitic structure (Ref 1-8). The above-mentioned cast steels are characterized by high corrosion resistance and, at the same time, satisfactory abrasion resistance. As far as duplex cast steels are concerned, the appropriate ferritic-austenitic microstructure is obtained through the use of proper amounts of ferrite and austenite formers. The ferrite content can approach 80%.

High corrosion resistance of this type of cast steels results from the low C content (max ≈ 0.06%) and the presence of Cr, Ni, Mo, and Cu. Owing to transformations in Fe-Cu (Fig. 1), it is possible to obtain ε phase precipitation hardening of the martensite in martensitic cast steels and of ferrite in duplex cast steels.

In the periodic table, Cu is located next to Ni, and, similar to Ni, it dissolves better in austenite than in ferrite. In the Fe-Cu phase equilibrium diagram, at 1094 °C, a peritectic reaction occurs between the austenite containing 8.5% Cu and the fluid rich in Cu. This reaction results in a Cu solid solution (96% Cu) containing Fe. At 850 °C, there is a eutectoid transformation: austenite containing 45% Cu decomposes into 1.4% Cu ferrite and ε phase. Copper solubility in ferrite decreases with the decrease in temperature, and at room temperature it is lower than 0.2%.

Because of the eutectoid transformation and the change in Cu solubility in ferrite, it is possible to apply two kinds of heat treatment:

- At Cu content up to 1.4%: rapid cooling from the supersaturated ferrite, i.e., after soaking at 800-850 °C, followed by aging, which leads to the precipitation hardening with ε phase.
- At higher Cu contents: rapid cooling from the austenite phase field to achieve supersaturated ferrite, and then aging, which results in the precipitation of a high dispersion of ε.

Copper occurrence in high-alloy Cr-Ni cast steels improves resistance to chemical attack, e.g., HCl, H_2SO_4, and H_3PO_4 acids, as well as to that of hydrogen at high pressure. Additionally, austenitic steels have higher resistance to stress corrosion cracking. The presence of Mo enhances Cu anticorrosive action.

Apart from the anticorrosive and hardening effect, Cu significantly increases fluidity, which makes these alloys particularly applicable to light-section castings of complex shapes. High castability allows manufacturers to use lower temperatures in tapping and mold pouring. That, in turn, is favorable to the refinement of the cast steel microstructure and significantly reduces susceptibility to microshrinkage and shrinkage porosity.

Impeller oil pumps working at 370 °C, with the use of catalysis particles whose main component is Al_2O_3, demonstrate strong abrasive action and provide an excellent example of advantageous Cu addition prolonging service life. The service life of pumps, whose individual structural elements were made of martensitic cast steels (max 0.15% C-(11.5-14.0)% Cr and max 0.06% C-(11.5-14.0)% Cr-(3.5-4.5)% Ni) amounted to ~400 h. LOH16N5Cu3 martensitic cast steel (Table 1), hardened and aged at 450 °C, prolonged pump life to over 3000 h.

On the other hand, C content plays a significant role in

Mirosław Gajewski, Kielce University of Technology, Department of Materials Technology, al. Tysiaclecia P.P. 7, 25-314 Kielce, Poland. Contact e-mail: gajem@tu.kielce.pl.

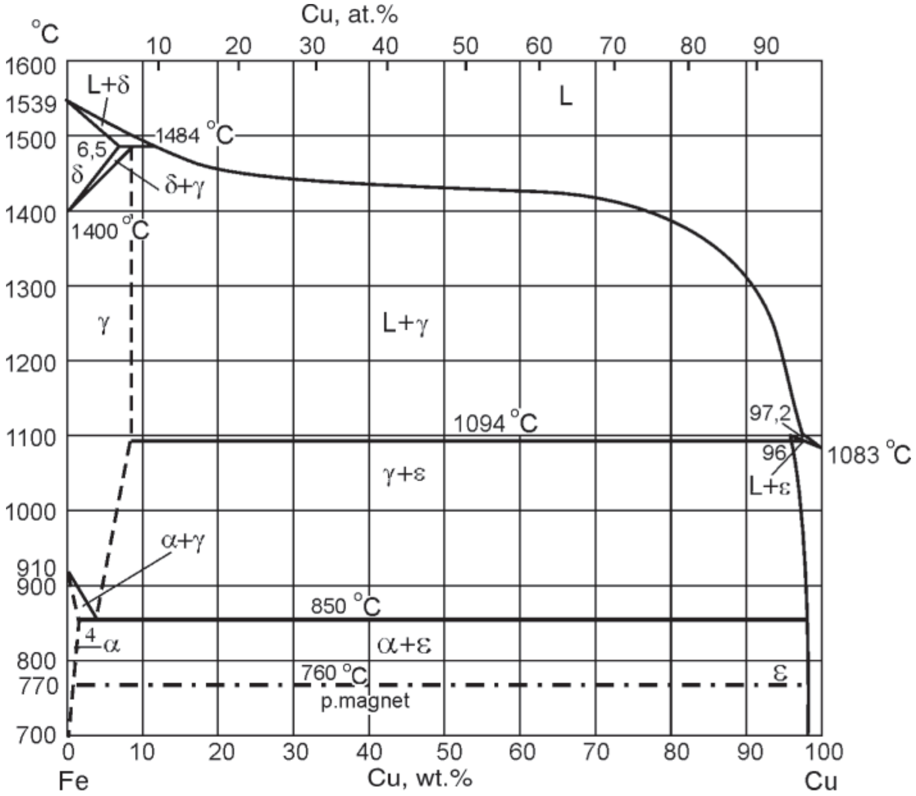

Fig. 1 Fe-Cu phase diagram (Ref 9)

Table 1 Chemical composition of precipitation hardened LOH16N5Cu3 cast martensitic and duplex LOH24N5M2Cu3 cast steels

Cast grade	Chemical composition, wt.%								
	C	Mn	Si	P	S	Cr	Ni	Mo	Cu
LOH16N5Cu3	Max	Max	Max	Max	Max	14.00	4.00	…	2.50
	0.06	1.00	1.00	0.03	0.03	16.00	6.00	…	3.00
LOH24N5M2Cu3	Max	Max	Max	Max	Max	23.00	4.00	2.00	2.50
	0.06	1.00	1.00	0.03	0.03	25.00	6.00	2.50	3.00

providing the cast steels with high corrosion resistance. It is confirmed by differences in the service life of pump rotors made of 22.5% Cr-8% Ni1.8% Mo-1.9% Cu cast steel and operated in mine water containing 50 mg/dm^3 chlorides. The rotor with C content of 0.18% was operated 770 h until failure, whereas the rotor with 0.10% C was operated for 2800 h. The service life of rotors made of duplex LOH24N5M2Cu3 cast steel (Table 1) exceeded 8000 h.

2. Experimental Results and Discussion

2.1 Precipitation Hardening of Cr-Ni-Cu Steel with Martensitic Microstructure and ε Phase

Hardening of LOH16N5Cu3 cast steel (Table 1) causes the formation of a complex microstructure consisting of lath martensite (Fig. 2a) and small amounts of austenite. On the boundaries of the martensite laths and on interior dislocations, secondary phases precipitate at a very high volume fraction. X-ray phase analysis showed that these phases are mainly ε precipitates. Impact-loaded specimens exhibited transgranular ductile fracture (Fig. 3a).

Aging at 450 °C changed the martensite character and dislocations density within the laths. Namely, a fairly systematic martensite dislocation structure, which existed in the hardened state, disappears to a certain extent after the 450 °C heat treatment. X-ray phase analysis revealed new ε precipitates. The microstructural character has indicated, however, the domination of the state immediately preceding ε phase particle precipitation from the martensitic matrix. Such a state, characterized by Cu content fluctuation and its atom concentration in selected areas of the martensite crystal lattice, constitutes the primary factor contributing to hardening (Table 2). The as-cast steel hardness increases from 341 to 430 HB. An increase in yield strength of about 300 MPa is also worth noting. The morphology of the fracture surface also highlights these changes, becoming transgranular with a high number of jogs and changes in the crack direction (Fig. 3b). Only minor traces of ductile fracture are observed.

Indications of cracking are found on the fracture surfaces. Because very little ductility is associated with the second-phase particles on the fracture surface, this might indicate their coherence with the matrix. Raising the aging temperature to 475 °C causes the enhancement of ε phase precipitation. At the

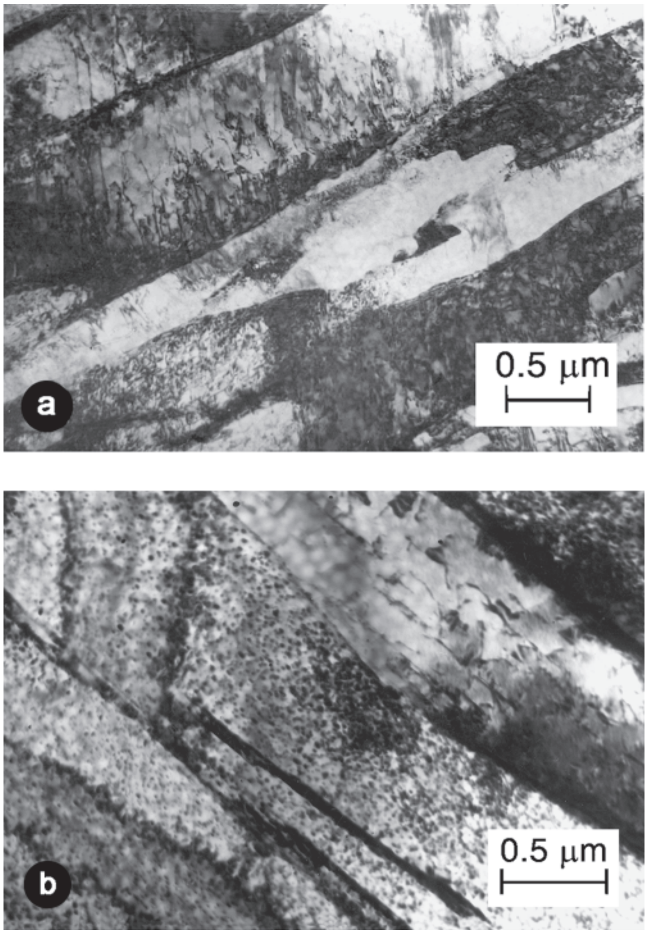

Fig. 2 LOH16N5Cu3 cast microstructures: (a) heat treatment at 1050 °C/oil hardening; (b) +500 °C aging

same time, the density of dislocations in the martensite decreases even further. Such microstructural changes result in minor changes to the mechanical properties than those following the 450 °C aging treatment, but the character of the changes is exactly the same.

Aging at 500 °C leads to further increase in the weight percent and size of the ε particles. The particles become visible (Fig. 2b). At the same time, the density of dislocations in the martensite decreases significantly. Still, yield strength remains high, and while impact resistance increases compared with the other heat-treatment temperatures, it is still lower than the tempered microstructure. The other mechanical properties, i.e., R_m (UTS), A_5 (% elongation), Z (% reduction in area), and HB (Brinell hardness) are only slightly changed or remain at the same level after hardening. This supports the supposition that the ε particles assist in hardening the martensite. Such an action compensates the lower martensite hardness as a result of dislocation annihilation through recovery. Structures of this kind are characterized by high stability at operating temperatures up to 400 °C. The fracture surfaces of the impact specimens still show grain boundary fracture, but the fraction of ductile fracture has increased (Fig. 3c).

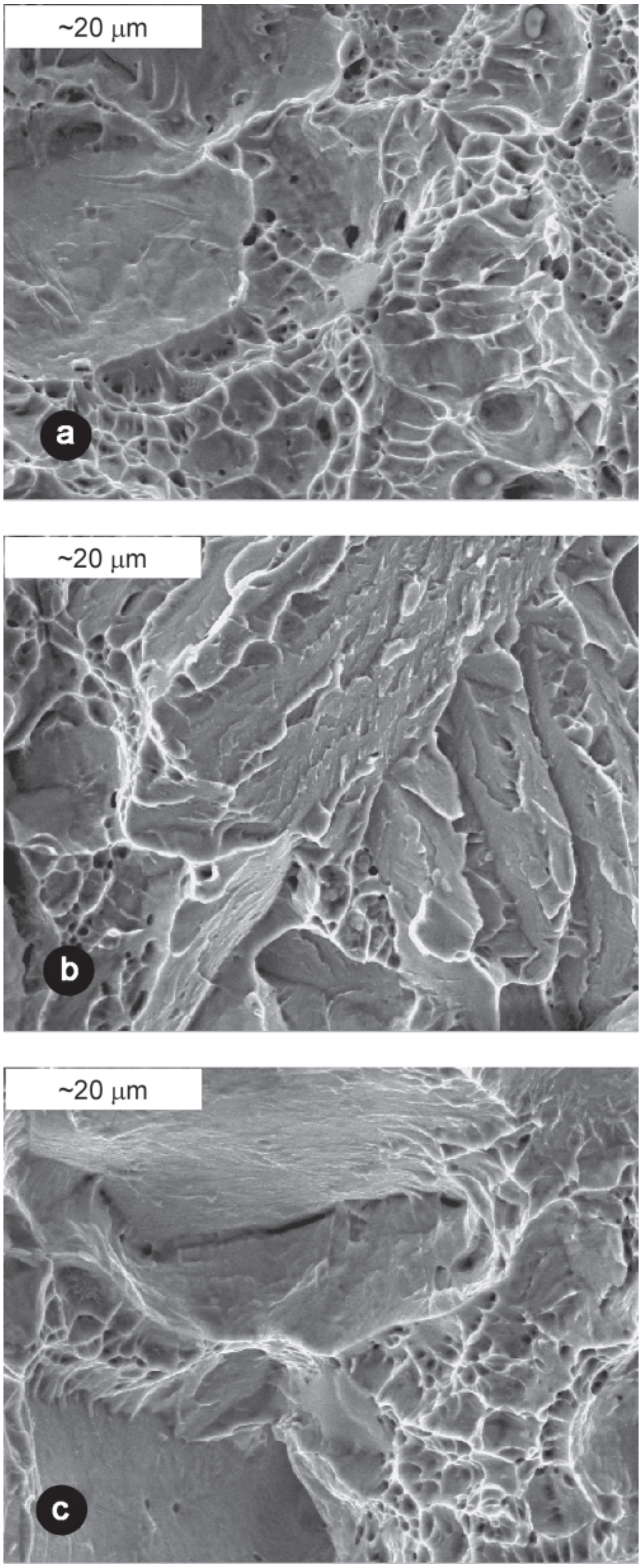

Fig. 3 Impact fracture surfaces of LOH16N5Cu3 cast steel: (a) heat treatment at 1050 °C/oil hardening (b) + 450 °C and (c) 500 °C

The final advantageous effect of heat treatment on the cast steel under consideration depends on its chemical composition. All deviations from the preset values of alloying elements lead to significant microstructural changes in the hardened state. It is possible to harden the alloy by precipitation of ε in such cases, although achieving it is far more complicated and the final general effect is not always satisfactory. Investigations into 0.050% C-0.74% Mn-0.12% Si-17.50% Cr-5.20% Ni-2.70% Cu cast steels confirm the above. To achieve precipitation hardening in this cast steel, the heat treatment consisted of

Table 2 Mechanical properties of LOH16N5Cu3 cast steel and secondary phase contents after various heat treatments

Heat treatment	$R_{0.2}$, MPa	R_m, MPa	A_5, %	Z, %	KCu_2, J/cm^2	HB	Secondary phase content, wt.%
H: 1050 °C/2 h/oil	895	1081	15.0	44.0	64.0	341	0.95
H: 1050 °C/2 h/oil SU: 450 °C/10 h/air	1196	1290	7.5	12.0	15.0	430	1.22
H: 1050 °C/2 h/oil SU: 475 °C/10 h/air	1115	1198	10.5	19.0	18.0	363	1.58
H: 1050 °C/2 h/oil SU: 500 °C/10 h/air	974	1063	17.0	42.0	36.0	341	1.76

H, hardening; SU, hardening aging

Table 3 Mechanical properties of 0.05C-17.5Cr-5.2Ni-2.7Cu cast steel and secondary phase contents after various heat treatments

Heat treatment	$R_{0.2}$, MPa	R_m, MPa	A_5, %	Z, %	KCu_2, J/cm^2	HB	Secondary phase content, wt.%
H: 1050 °C/2 h/oil	285(a)	752	48.5	56.0	315	156	0.52
H: 1050 °C/2 h/oil SU: 500 °C/5 h/air	345(a)	738	34.0	53.5	345	156	1.05
H: 1050 °C/2 h/oil SW: 750 °C/5 h/air	575	1092	17.0	35.0	85	293	2.65
H: 1050 °C/2 h/oil SW: 750 °C/5 h/air SU: 500 °C/5 h/air	920	1015	10.5	24.0	25	321	4.32

(a) Clear yield strength, R_e. H, hardening; SW, initial hardening; SU, hardening-aging

Table 4 Mechanical properties of LOH24N5M2Cu3 cast steel and secondary phase contents after various heat treatments

Heat treatment	$R_{0.2}$, MPa	R_m, MPa	A_5, %	Z, %	KCu_2, J/cm^2	HB	Secondary phase content, wt.%
P: 1050 °C/2 h/oil	492	679	25.0	59.0	194.0	229	0.47
P: 1050 °C/2 h/oil SU: 500 °C/10 h/air	650	885	18.0	29.0	38.0	293	1.10
P: 1050 °C/2 h/oil SU: 500 °C/10 h/air	630	847	25.0	38.0	46.0	285	1.30

P, solution; SU, hardening-aging

an initial hardening heat treatment, followed by an intermediate aging heat treatment, and ending with a final hardening-aging treatment. After the hardening heat treatment, the cast microstructure consisted of lath martensite, austenite, and small amounts of delta ferrite. $M_{23}C_6$ carbides and ε precipitates. The steel hardness in this condition was low at 156 HB (Table 3).

Precipitation hardening through intermediate aging was not possible at temperatures between 450 and 500 °C, and was only achieved after the austenite had transformed into martensite. Intermediate aging was therefore carried out at 750 °C. While the cast steel was soaking at this temperature, the $M_{23}C_6$ carbides precipitated and coarsened, which led to lowering of Cr and C content in the austenite, thus increasing the M_s temperature. The change in the austenite chemical composition enabled the martensitic transformation to occur during cooling to room temperature. In this way, the mechanical properties improved considerably (Table 3). On the other hand, ductility and impact resistance deteriorated dramatically. The main reason for this was fraction of $M_{23}C_6$ carbides that precipitated on the prior austenite boundaries (Fig. 4a). A final hardening-aging heat treatment at 500 °C led to the desired precipitation hardening. Because in the hardening-aging heat treatment, simultaneously with the precipitation of ε in the martensite, precipitation of $M_{23}C_6$ continued, this time chiefly on the boundaries of the martensite laths and non-transformed austenite (Fig. 4b). Strength increased, but ductility and impact resistance deteriorated even further. On the impact fracture surfaces, brittle intergranular fracture is observed (Fig. 5).

2.2 "Duplex-Type" Cr-Ni-Mo-Cu Cast Steel Hardened with ε Phase

The LOH24N5M2Cu3 cast steel in the supersaturated state consists of ferrite, austenite and a small amount of ε precipitates (Table 4). The ε particles are found exclusively in the ferrite (Fig. 6a). Impact surfaces exhibit transgranular fracture characteristics. On these surfaces numerous jogs and changes

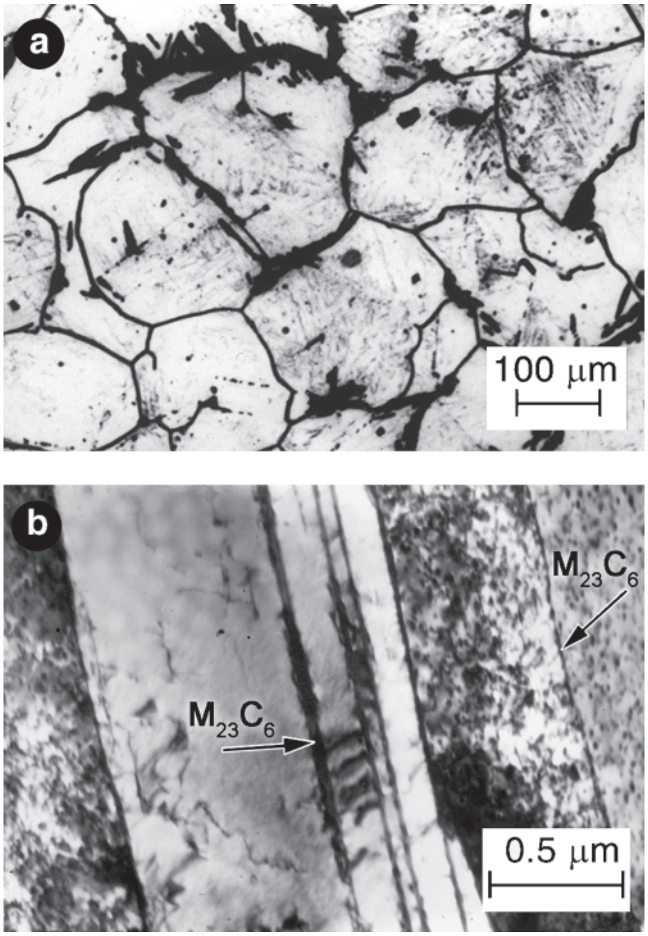

Fig. 4 0.05C-17.5Cr-5.2Ni-2.7Cu cast microstructures: (a) heat treatment at 1050 °C/oil hardening + 750 °C heat treatment and (b) +500 °C

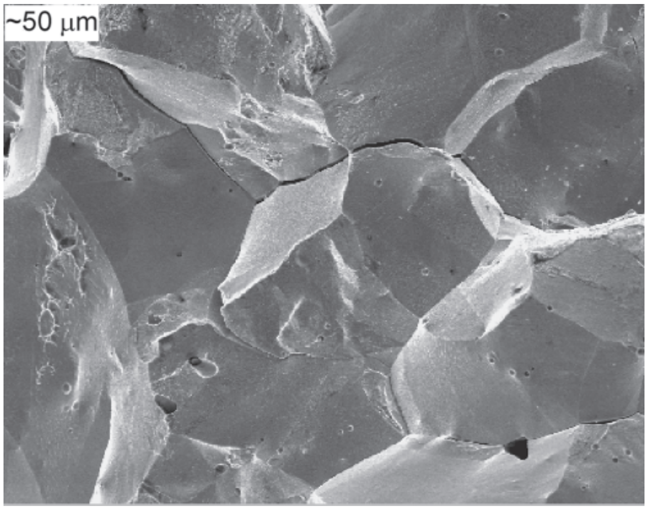

Fig. 5 Impact fracture surfaces of 0.05C-17.5Cr-5.2Ni-2.7Cu cast steel: heat treatment at 1050 °C/oil hardening + 750 °C + 500 °C

in the cracking directions, as well as areas of ductile fracture, are seen (Fig. 7a).

At 450 °C the aging of this cast steel causes dramatic precipitation of a high volume fraction of ε in the ferrite (Fig. 6b). At the same time, the density of dislocations in the austenite

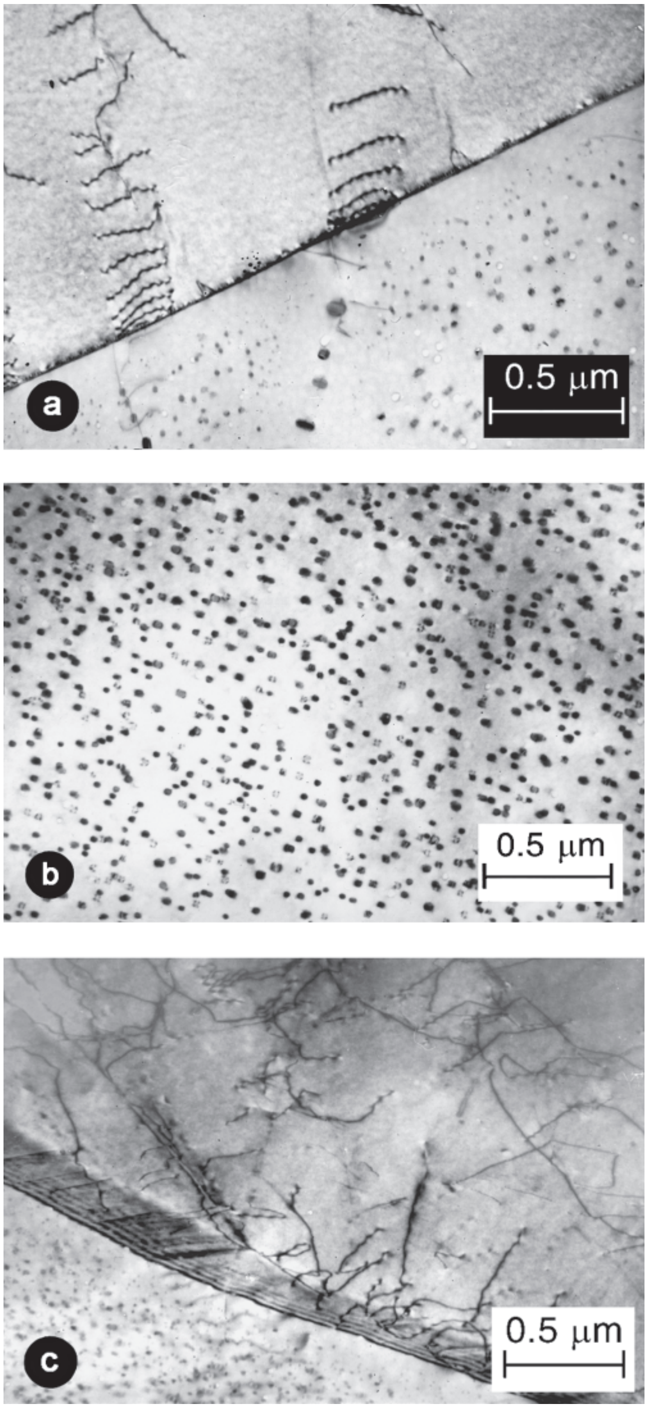

Fig. 6 LOH24N5M2Cu3 cast microstructures: (a) heat treatment at 1050 °C/oil solution treatment; (b, c) +450 °C

increases (Fig. 6c) with the interphase γ-α boundary showing a high dislocation density. The above-mentioned microstructure changes contributed to the improvement in mechanical properties. However, ductility continued to be low, as exhibited in the change in impact resistance from 194.0 to 38.0 J/cm^2. The morphology of impact specimen fracture surfaces underwent considerable change. Fracture is still transgranular (Fig. 7b), but there are now traces of ductile rupture on the surface. The predominant fracture morphology indicates structure strengthening (Fig. 7c), which might result from ε phase coherence with the matrix.

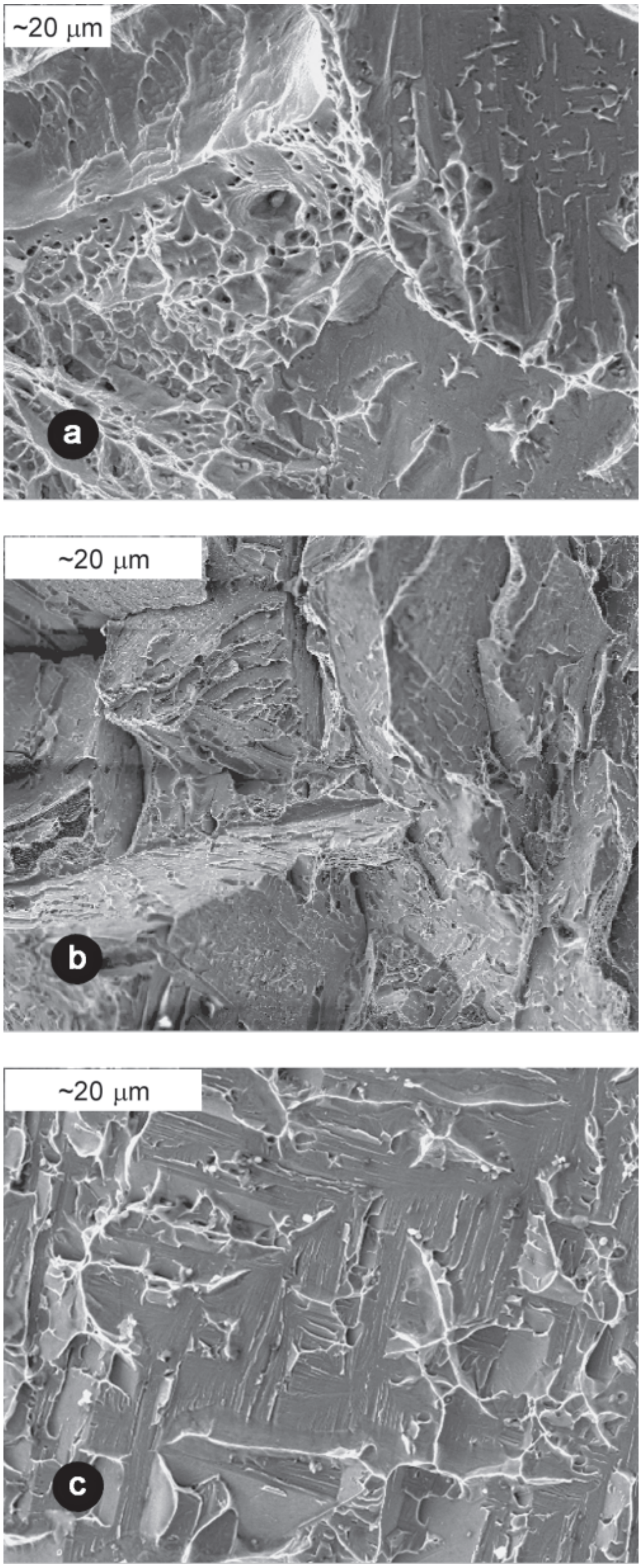

Fig. 7 Impact fracture surfaces of LOH24N5M2Cu3 cast steel: (a) heat treatment at 1050 °C/oil solution heat treatment; (b, c) +450 °C

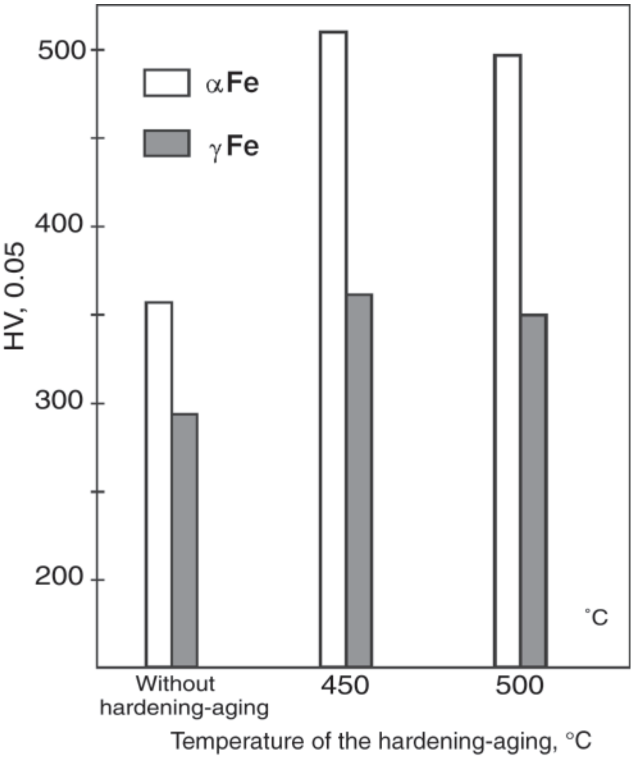

Fig. 8 Ferrite and austenite microhardness in LOH24N5M2Cu3 cast steel after solution heat treatment and aging at 450 and 500 °C

Aging at 500 °C does not produce a further significant increase in the ε participation. The size of the ε particles are, however, noticeably larger. In comparison to samples aged at 450 °C, strength was lower, whereas ductility and impact resistance improved. The general character of the impact specimen fracture surfaces did not change, yet the number of jogs and changes in cracking direction increased. Small areas of ductile rupture appeared as well.

Microhardness measurements showed a general increase in the LOH24N5M2Cu3 cast steel hardness after aging at 450 and 500 °C, consistent with ε phase hardening of the ferrite and austenite (Fig. 8). Whereas the precipitation of ε phase particles is responsible for the increase in ferrite hardness, the main reason for austenite improved hardness is thought to be its higher dislocation density due to the stress caused by the development of ε precipitation in the ferrite.

The investigation has shown a considerable influence of cooling rate (solution treatment) on the degree of the solid solution saturation with Cu, and later the intensity of development of ε precipitation during aging heat treatments. Increasing the rate prevents earlier (already in cooling) ε precipitation and facilitates more advantageous mechanical properties after aging, especially for the duplex cast steels.

3. Conclusions

High-alloy Cr-Ni-Cu precipitate-hardened cast steels provide a good material for the manufacture of pumps and other equipment used in the mineral processing and power industries.

An obvious advantage of these cast steels is the control of ε precipitation during heat treatment, thus changing the final mechanical and functional properties. The effect of heat treatment depends on the degree of coherence and dispersion of the ε precipitate as well as on the volume fraction of secondary-phase particles.

The results of the investigations indicate that it is necessary to adhere to the designed chemical composition of the cast steels. This is particularly important for the martensitic cast steels because obtaining a microstructure with too large a quantity of untransformed austenite is definitely disadvantageous. Consecutive heat treatments can lead to austenite transformation into martensite with ε precipitate hardening. Ductility as represented by % elongation and reduction in area, as well as impact strength, are lower than desired, which at this time precludes their practical application.

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