Chemical Isolation of Precipitates in IF Steels

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The aim of the presented paper was to determine the critical conditions of the method of isolation of precipitates from IF steels with Ti and Nb microalloys or with their combination. The existence of a critical value of the time of isolation, dependent on the chemical composition of the precipitate, was demonstrated together with simultaneous changes of the chemical composition of precipitates.

A complete fixation of interstitially dissoluble carbon and nitrogen atoms by means of Ti and Nb alloys, or their combination, is characteristic of IF (interstitial free) steels. Their low yield point and favourable texture afford exceptional deep-drawing properties of these steels. The state of precipitation, which controls the process of formation of the structure and texture, plays a dominant role in these materials [1—3].

In this connection it is important to investigate the precipitation kinetics in individual junction points of the technological production process. Thermomechanical processing at cold rolling and recrystallization annealing belong among the most important of these points.

In majority of cases the state of precipitation is determined indirectly by measurements of some physical or mechanical properties. Direct examinations employ mostly transmission electron microscopy and chemical isolation [4—6]. Both methods have some advantages and disadvantages. The difficulties arise from a very low mass fraction of interstitial elements C and N the values of which vary within thousandths of a percent. Corresponding microalloying elements Al, Ti, and Nb also reach a thousandth part of a percent.

The aim of the presented paper is to compare the stability of the precipitates after the chemical isolation from IF steels before the start of recrystallization, at $\approx$ 50 % proportion of recrystallized grains, and after the finish of the process.

EXPERIMENTAL

Two types of IF steels designated B and C, together with the reference material A, free of microalloying additions, were used in experiments. The chemical composition of these steels is shown in Table 1.

The starting hot-worked material was subjected to 70 % cold deformation and then to recrystallization annealing in a saline bath at isothermal conditions, at temperatures 550 °C, 600 °C, and 700 °C and various times. Specimens used for precipitation studies were selected according to the results of metallographic analyses in such a way that they represented the state before the start of recrystallization, at $\approx$ 50 % proportion of recrystallized grains, and after the finish of the process. Designation of samples is shown in Table 2.

The method of precipitate isolation has been described in detail in [7]. The chemical agent consisted of 3 M-H_2SO_4 (thermostated at 64 °C; 80 cm^3 per 1 g of sample (filings) at point weighed amount), which appeared as optimal from the viewpoint of subsequent analyses (tested were also the following agents: 1.5 M-H_2SO_4 and 1 M-H_2SO_4 thermostated at 64 °C, and 2 M-HNO_3 at the temperature 25 °C).

Obtained precipitates were filtered through a SYNPOR filter (0.25 mm) [7], dried and weighed. The

Table 1. Chemical Composition of Steel

Element	Specimen		
	A	B	C
		w/%	
C	0.004	0.006	0.004
Mn	0.14	0.10	0.14
P	0.008	0.007	0.005
S	–	0.01	–
N	0.0022	0.0042	0.00509
Al	0.028	0.050	0.031
Nb	–	–	0.033
Ti	–	0.089	0.028

Table 2. Conditions of Processing of Specimens by Recrystallization Annealing (Temperature, Time, Recrystallized Portion w_r)

Conditions	Specimen					
	$A_0B_0C_0$	A_5	A_{90}	B_{110}	B_{500}	C_{20}
t/min	0	5	90	110	500	20
θ/°C	0	550	550	600	600	700
w_r/%	0	50	100	50	100	100

precipitate obtained by this method was used for additional chemical analyses together with the filtration mass.

The Method of Determination of Fe, Ti, Al, and Nb in the Precipitates

An addition of an acid mixture consisting of 5 cm^3 of H_2SO_4 (ρ = 1.84 g cm^{-3}), 5 cm^3 of HNO_3 (ρ = 1.4 g cm^{-3}), and 5 cm^3 of $HClO_4$ (ρ = 1.67 g cm^{-3}) to the precipitate (in a beaker) caused decomposition at elevated temperatures. The obtained mixture was heated until complete elimination of H_2SO_4 and $HClO_4$ fumes — the full annealing is necessary, caused by the incomplete removal of $HClO_4$ solution. The mixture is allowed to cool and 5 cm^3 of 6 M-HCl together with a small amount of H_2O are added. The present salts dissolve upon subsequent heating. This basic solution of the precipitate is transferred to a 50 cm^3 volumetric flask and aliquots are pipetted for determinations of Fe, Al, Ti, and Nb. Spectrophotometrical methods and the AAS method were used for analytical determinations of elements in the precipitate [7].

All determinations were carried out using anal. grade chemicals.

RESULTS AND DISCUSSION

The composition and size of precipitates (nitrides, carbonitrides, carbides, *etc.*) is a function of the temperature of their formation and the proportion of the C and N amount bound in these precipitates [8].

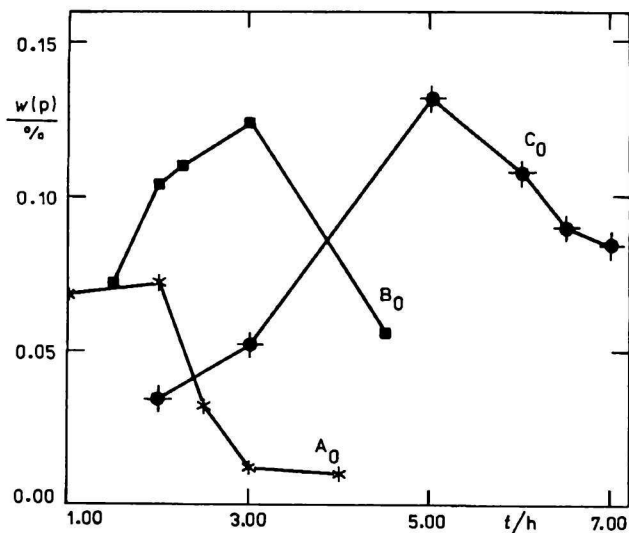Fig. 1 shows the dependence of the amount of precipitate in unannealed specimens on the time of

its isolation. One maximum was observed for each specimen type — $t_A \approx$ 2 h for A, $t_B \approx$ 3 h for B, and $t_C \approx$ 5 h for the specimen C. The time t_{crit}, i = A, B, C corresponds to the critical time of isolation. Isolation time below t_{crit} results in an incomplete extraction of precipitate in all these types. However, exceeding of this critical time causes dissolving of particles, which is demonstrated by decreased isolated quantities. It is clear that some more unstable parts of the grains are dissolved before t_{crit} (*e.g.* AlN), but for our study these ones are not so important. Dissolving conditions depend on the character of precipitates. Fig. 2 shows the dependence of the relative amount (mass fraction) of Fe in the precipitate on the time of precipitate isolation for unannealed specimens. Minimal quantities of Fe, Al (Fig. 3) and
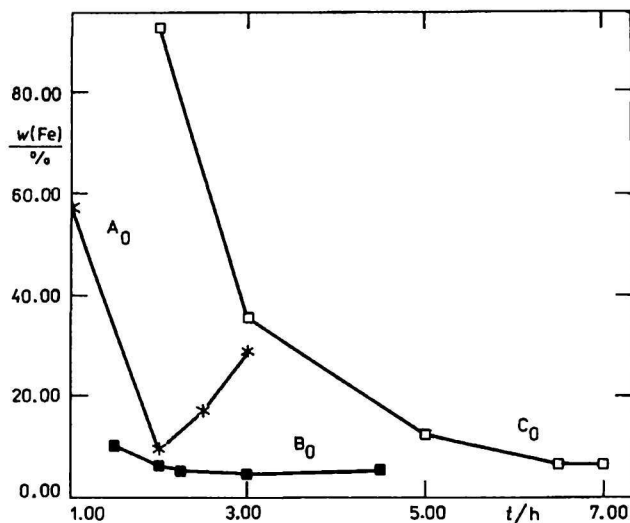

Fig. 2. Dependence of the mass fraction of Fe in precipitates of unannealed IF steels on the time of isolation.
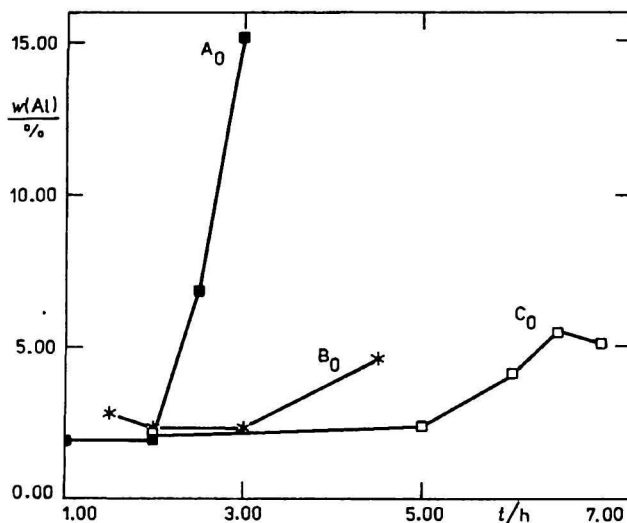

Fig. 1. Dependence of the mass fraction of precipitate of individual types of IF steels on the time of isolation. See Table 2 for used designation.

Fig. 3. Relationship between the mass fraction of Al in precipitates of unannealed IF steels and the isolation times.
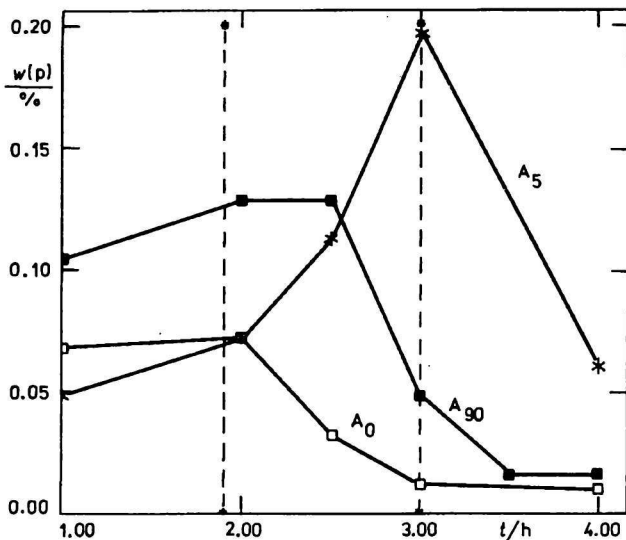
Fig. 4. Dependence of the mass fraction of precipitates in the type A steel at individual thermal regimens on the time of isolation. The vertical lines delimitate the zone corresponding to the maximal amount of the precipitate.
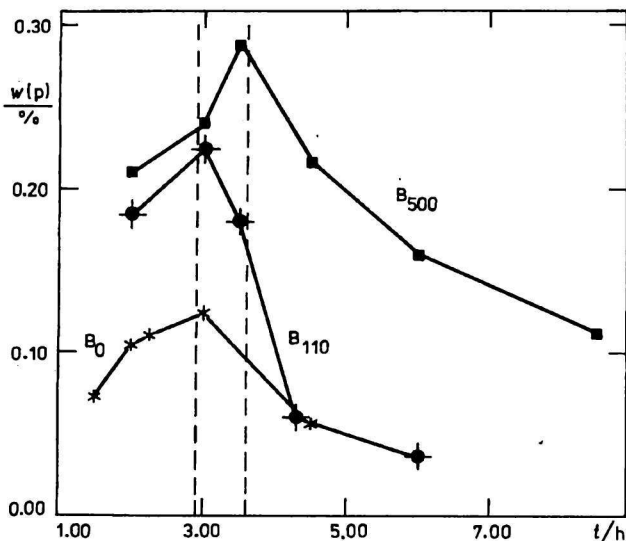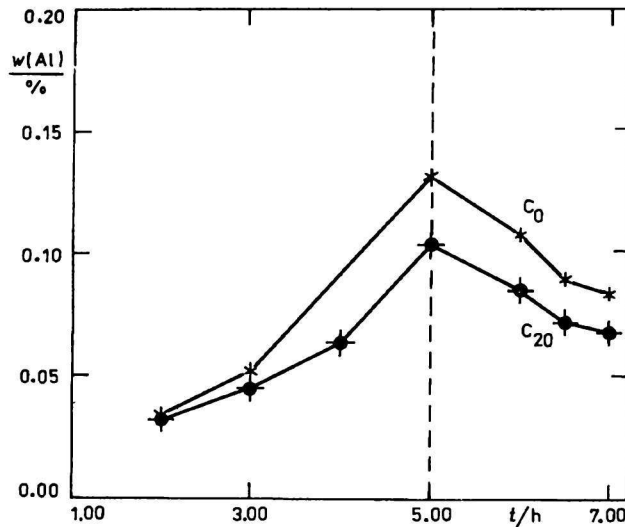

Fig. 6. Relationship between the mass fraction of Al in the type C steel at individual thermal regimens and the time of isolation. The vertical line delineates the zone of the maximal amount of the precipitate.

Fig. 5. Dependence of the mass fraction of precipitates in the type B steel at individual thermal regimens on the time of isolation. The vertical lines delimitate the zone corresponding to the maximal amount of the precipitate.

in our experiment). In case of the specimen B (Fig. 5) a moderate dispersion is observed around the t_B value, *i.e.* the isolation time value, which provides the maximal precipitate quantity. In case of the specimen A (Fig. 4) the maximal dispersion in the vicinity of t_A is observed within 1 h. According to [8], the presence of nitrogen in steels (and at the same time in precipitates) is considerably influenced, besides the chemical composition, by the thermal processing of specimens — a number of nitrides are subjected to changes upon heating. Our results indicated the lowest stability of Al nitrides at thermal processing [5—7] and, on the contrary, the highest stability of nitrides or carbonitrides of Nb. This knowledge must be taken into account as in experiments as in evalu-
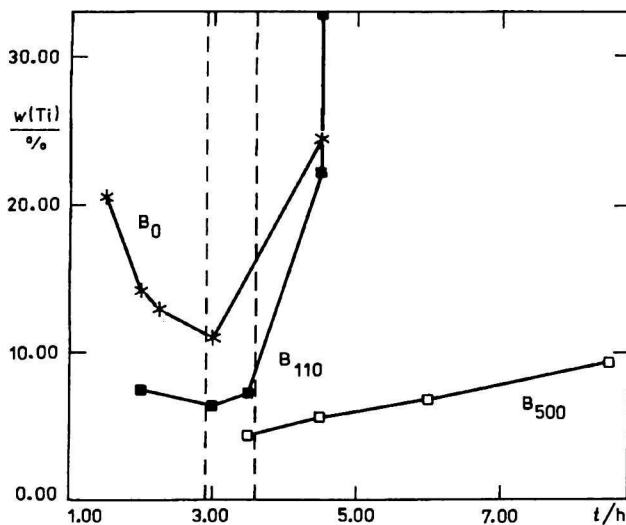
Ti are observed at sites of maximal amounts of precipitates, however, at times exceeding the critical times of specimens B or C, the precipitates of which contain Ti, or Ti and Nb, an increase of the relative proportion of Al, Ti, and Nb is observed, which is ascribed to the fact that the chemical "resistance" of the precipitate to the action of a chemical agent is determined by the amount of nitridic nitrogen bound to Al, Ti, and Nb.

Figs. 4—6 show the dependence of the amount of precipitates on the time of their isolation for different annealing states. It is obvious that in case of the specimen C (Fig. 6) t_C is independent of the time of annealing (at least for the time up to 20 min, used

Fig. 7. Relationship between the mass fraction of Ti in precipitates of the type B steels and the time of isolation at different thermal regimens.
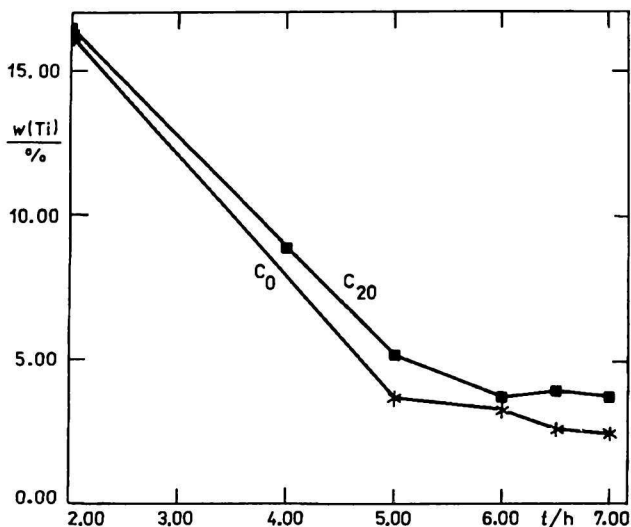
Fig. 8. Relationship between the mass fraction of Ti in precipitates of the type C steels and the time of isolation at different thermal regimens.
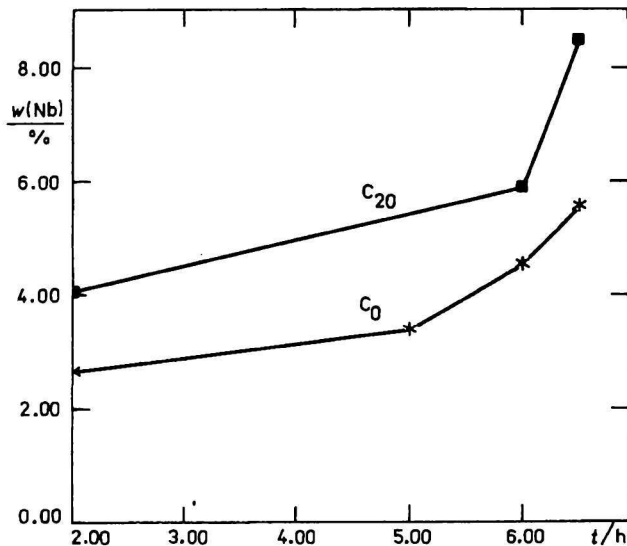

Fig. 10. Relationship between the mass fraction of Nb in precipitates of the type C steels and the time of isolation at various thermal regimens.
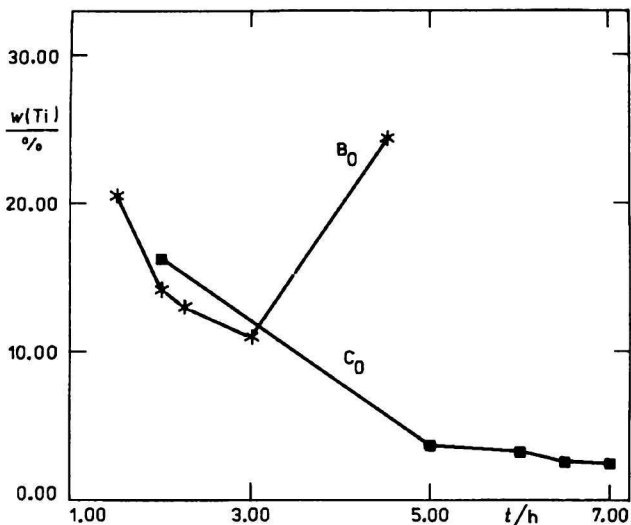

Fig. 9. Relationship between the mass fraction of Ti in precipitates of the unannealed type B and C steels and the time of isolation.

ation of results and their comparison with the data of other authors.

Fig. 7 shows the dependence of the relative amount of Ti (mass %) in precipitates on the time of precipitate isolation for unannealed and annealed specimens B. The observed growth of Ti over the time zone (2—4.3 h) also suggests the thermal stability of Ti nitrides or carbonitrides. Fig. 8 shows the dependence of the amount of Ti in the specimen C on times close to t_C.

Figs. 8 and 9 illustrate the gradual decrease of Ti and Fig. 10 the parallel gradual increase of the amount of Nb. This points to the higher stability of Nb nitrides or carbonitrides in comparison with Ti nitrides or carbonitrides.

CONCLUSION

Extensive chemical isolation of precipitates from IF deep-drawing steels in 3 M-H_2SO_4, at 64 °C, after various states of thermal processing provided the following knowledge:

1. The amount of precipitates changes in dependence on the time of isolation in such a way that pronounced maxima are observed at the so-called critical time t_{crit} for each steel. This critical time depends on the chemical composition of the precipitate and the amount of nitridic nitrogen in the given precipitate. In case of steels in precipitates of which the AlN prevalence can be observed the critical zone $t_{crit} \approx$ 2—3 h arises according to the precipitation state. In steels with predominance of TiN or TiC, Ti(C, N) in their precipitates this range becomes narrower, $t_{crit} \approx$ 2.8—3.7 h, and it is shifted to longer times. Steels with predominance of Nb(C, N) in their precipitates show only one value of the critical time, $t_{crit} \approx$ 5 h, for different states of thermal processing of specimens.

2. Changes of chemical composition of precipitates occur during the process of isolation. Minimal or maximal values of elements Fe, Al, Ti, and Nb are observed in the zone of t.

3. Chemical analyses confirmed that AlN belongs to the least stable compounds in precipitates while Nb compounds are among the most stable ones (Nb(C, N), NbN, etc.). This result is independent of the fact whether or not the sample was subjected to thermal processing.

Finally we can stress that the stability of the precipitates in dependence on the temperature and on the various degree of the recrystallization annealing

is given by the dominant chemical element, e.g. for the A sample it is Al, for the B one it is Ti and for the C one Nb.

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Influence of the Binary Solvent Methanol—Water on the Values of Protonation Constants in the H+—Alanine System

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The H+—alanine system has been studied by the potentiometric method at 25 °C in 1.0 M water—methanol solution of $NaClO_4$ up to methanol mole fraction $x(CH_3OH) = 0.5$.

The values of protonation constants log K_n were obtained after experimental data evaluation of the function $E = f(V)$ with the assistance of purpose-made computer programs KALIBR.SKE and AC.BAZ, improved with MAGEC and ESAB2M programs.

The effect of various nonaqueous and mixed solvents on the values of equilibrium and rate constants of chemical reactions is known for a long time already [1—5].

For instance, the effect of such solvents on acid-base and transport properties seems to be promising for the application of organic solvents in isotachophoresis [6]. In comparison with organic solvents the mixed aqueous—organic solvents seem to be more advantageous. Trace amounts of water in pure organic solvents can have a great influence on the properties of some solutions and dissolved compounds and the experimental conditions can become hardly reproducible. One of the very advantageous qualities of methanol is its full-range miscibility with water. Further advantage of the water—methanol

mixture is its higher boiling point in comparison with pure methanol.

Dey and co-workers [7—9] have systematically studied the protonation constants of amino acids in various mixed solvents. Our work deals with determination of the first and second protonation constant of DL-alanine by the potentiometric method in binary methanol—water solvent at various volume ratios of the two components at 25 °C.

EXPERIMENTAL

All chemicals used in the experiment were of anal. grade. The solutions were prepared with the use of deionized and redistilled water (conductivity < 10⁻⁶ S) and methanol (Lachema, Brno) dried over molecular sieves (4A) and distilled. The middle fraction was

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