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Mechanical Properties of Some Cu-based Alloys

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The purpose of this paper is to present experimental results obtained on Cu-Ti, resp. Cu-Ni-Sn alloys. The relations between mechanical properties of those alloys and the internal structure development was examined. The internal structure was changed by isothermal ageing of the initially supersaturated solid solutions.

Both alloys decompose by spinodal reaction if the concentration of solute is appropriate. The kinetics of decomposition is influenced by the mechanical state of the alloys, particularly by the applied cold work. Experimental results of this kind are presented.

The dependence of the strain rate sensitivity coefficients on the internal structure was also studied. The purpose of this study was to understand better the deformation behaviour.

Účelem tohoto článku je uvedení některých experimentálních výsledků získaných při studiu mechanických vlastností slitin Cu-Ti a Cu-Ni-Sn. Vyšetřována byla zejména souvislost vybraných mechanických vlastností se změnami struktury, ke kterým dochází v průběhu rozpadu přesycených tuhých roztoků. Při vhodné koncentraci částečně rozpustné příměsi dochází u obou slitin k zahájení rozpadu spinodální reakcí. Rychlost a rozsah fázových změn jsou ovlivněny předchozí historií vzorků slitin, zejména předdeformací za studena. Jsou uvedeny základní experimentální poznatky o tomto jevu.

Pro bližší pochopení povahy deformačního procesu je studována závislost koeficientů rychlostní citlivosti napětí na vnitřní struktuře slitin, zejména na proměnném obsahu Sn ve slitinách Cu-Ni-Sn.

Целью статьи является обзор некоторых данных полученых при исследовании механических свойств сплавов Cu-Ti и Cu-Ni-Sn.

Исследована именно связь изобранных механических свойств с изменением внутренней структуры в течении распада пересыщенных твердых растворов. При подходящей концентрации примеси начинается этот распад спинодальной реакцией у обоих сплавов.

Холодная деформация перед старением имеет влияние на скорость и объем фазовых превращений в течении распада. В работе показаны экспериментальные данные касающееся этого явления.

Зависимость коэфициентов скоростной чувствительности напряжения от внутренней структуры образцов исследована с целью лучшего понятия протекающих деформационных процесов.

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1. Introduction

Supersaturated solid solution decomposes during appropriate ageing treatment. Created structures can differ as for spatial distribution of the different alloy constituents. Mechanical properties are mainly influenced by the details of internal structure. An important role is played by the systems in which modulated structures are created as a consequence of the decomposition process. Such systems are sometimes called "side band alloys" because of the occurence of the side bands or satelites in the neighbourhood of the diffraction maxima of the matrix. This phenomenon was firstly described by Daniel and Lipson (1) who studied the decomposition of the Cu–Ni–Fe alloy.

Binary system Cu–Ti resp. pseudobinary Cu–Ni–Sn alloy belongs to the class of the side-band alloys if the concentration of solute is appropriate. The influence of the internal structure changes on mechanical properties has been studied. The dependences of the parameters of the stress-strain curves and strain rate sensitivities on details of internal structure have been chosen as a measure of mechanical properties.

2. Experimental

Alloys of the following composition were used for the reported study. (See Table 1). Alloys were prepared by Metals Research Institute Panenské Břežany from the constituents of the 3N purity by vacuum melting. Ingots were gradualy cold rolled to the final thickness. Annealing treatment at 1073 K for 20 min was always performed aftes thickness reduction reached aprox. 80%. Rectangular specimens were machined from obtained sheets. Samples were then anneaed at 1073 K for various times in order to obtain suitable grain size. After anneal the samples were quenched into water bath. Ageing was performed at temperatures specified below.

Table 1.

		Alloy No	Cu (at %)	Ti (at %)	Ni (at %)	Sn (at %)
		0	98.4	1.6	0	0
		1	80.63	0	9·68	0·006
		2	90.11	0	9.81	0.08
Cu–Ni–Sn	I.	3	89.9	0	9.78	0.24
Sn < solubility limit		4	89.8	0	9.72	0·47
		5	89.1	0	9.9	0.99
		6	87.2	0	11.59	1.19
Cu–Ni–Sn	II.	7	apr. 88.6	0	apr. 9	apr. 2.4
Sn > solubility limit		8	89.4	0	7.59	3.02
		9	apr. 87.4	0	apr. 9	apr. 3.6

Samples were tested in tension using Instron 1195 testing apparatus. The temperature of deformation was controlled by Instron Temperature Cabined if the temperature used was higher then 273 K. Bath of liquid nitrogen or mixture ethanol + solid carbon dioxide helped to realize low temperature measurement.

Details of internal structure were generaly studied by means of Tesla BM 540 electron microscope. The wave length of the modulated structute was determined using HZG X-ray diffractometer. The optical metalography was performed using Neophot 2 optical microscope. Electrical resistivity measurement was performed using apparatus described in [2]. For details of experimental performing see [3].

3. Results and discussion

3.1. The Cu-Ti alloy

The homogenised samples were aged at 573 K for times in the range from 0 to 800 hours. All heat treatments were performed in the argon atmosphere. Aged specimens were then deformed at an initial deformation rate of $8 \times 10^{-5}\,s^{-1}$ at

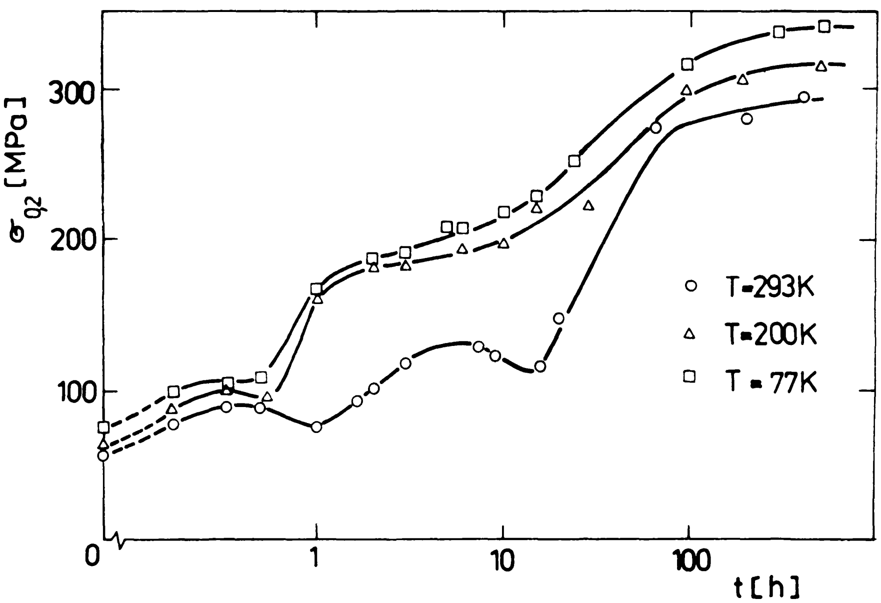

Fig. 1. The dependence of the proof stress on the time of ageing for Cu-Ti alloy.

temperatures 77 K, 200 K and 293 K. True stress-true strain curves were obtained and the dependences of the proof stress $\sigma_{0.2}$ (stress at 0.002 strain) on the time of ageing were drawn. These dependences are depicted in the Fig. 1. It can be seen that the curves can be divided into three parts (stages). Different stages are divided by the aproximate time of ageing $t_1 \approx 1$ hour and $t_2 \approx 20$ hours respectively. The values of the yield stress are strongly temperature dependent for $t_1 < t < t_2$.

It was firstly ascertained, that the behaviour of $\sigma_{0.2} = f(t)$ plots cannot be understood on the basis of any changes in the mean grain size or grain character respectively. No changes of these factors were observed by means of optical microscopy throughout the ageing. As TEM showed heterogenous precipitation neither in the grain boundary nor on the dislocations, it was concluded, that the changes of the internal structure (in the grain interior) must be responsible for the behaviour of the $\sigma_{0.2} = f(t)$ plots. On the basis of the diffraction data supplemented by the TEM and electrical resistivity measurement was developed the following model of the internal structure changes during ageing. Homogenised and quenched alloy is in the state of the supersaturated solid solution. Existence of the modulated structure was ascertained for time of ageing in the range 0 h $< t <$ 15 hours. The wave length (the mean distance between solute rich regions) of the modulated structure increases with the fourth root of the time of ageing (see Fig. 2). The wave vector of the concentration

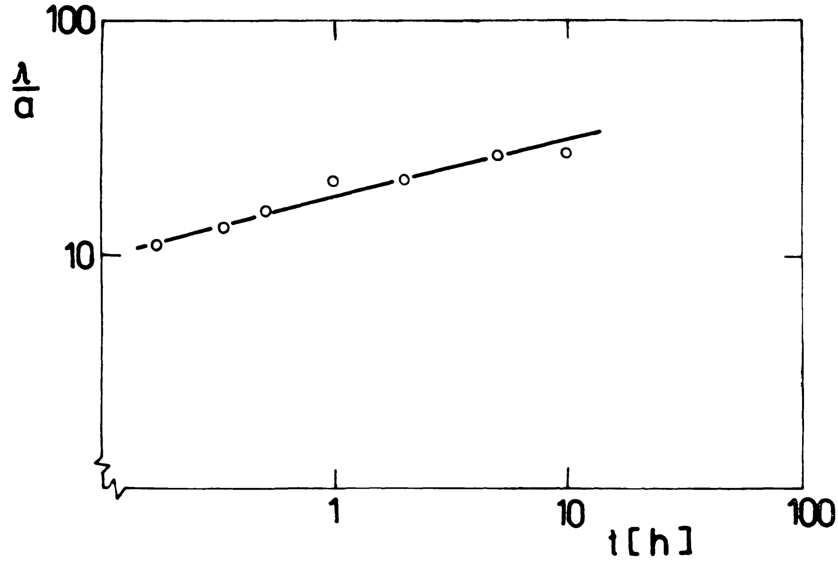

Fig. 2. The dependence of the wave length of the modulated structure on the time of ageing. (Cu-Ti alloy).

modulations is paralel to any $\langle h\ 0\ 0\rangle$ direction. For $t >$ 5 hours coexists modulated structure with particles of β'-Cu_4Ti phase as demonstrated by TEM. β'-phase is coherent with the matrix and its structure is crystalographicaly relative to the parental f.c.c. solid solution (see Fig. 3). On the basis of this model and discovered quantitative data of the kinetics of the phase transformation the following explanation of the $\sigma_{0.2} = f(t)$ plots was accepted: (The data of the $\sigma_{0.2} = f(t)$ curve obtained at 77 K were used).

1. Alloy quenched from temperature T = 1073 K is supersaturated solid solution of the Ti in Cu.

Agreement of the measured $\tau_0^{\mathrm{exp.}}$ and estimated value τ_0^{L} of the critical resolved shear stress (according to Labusch [4]) is quite good ($\tau^{\mathrm{exp.}}/\tau_0^{\mathrm{L}} = 0{\cdot}75$).

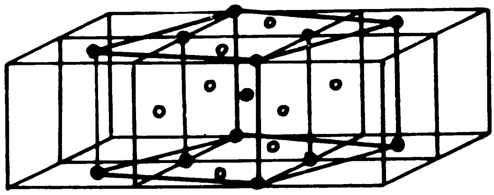

Fig. 3. Structure of the β'-Cu_4Ti phase.

2. Critical resolved shear stress of the alloy aged for h < t < 0·5 hour is fully determined by the coherent stress field of the harmonic modulated structure (cosine-like). It can be concluded, that the agreement of the measured and estimated value of the CRSS is good under the assumption, that the hardening of the material is caused by the interaction of the mixed (60°) dislocation with coherent field of the modulated structure (Kato [5]). For the interval 0·5 h < t < 15 h the cosine-like character of the concentration modulations is not preserved and the spatial distribution of the solute must be described by higher harmonics of the Fourier expansion. In such a case the use of any existing model of strengthening is not appropriate and qualitative estimations are not possible at present.

3. For $t > 15$ hours the strengthening is mainly determined by particles of the β'-phase. For qualitative comparison of the measured and estimated values of the CRSS the model developed by Balík and Saxlová (6) was used. That model respects morphology of the β'-phase and specific stress field created by the particles in the matrix. The dependence of the CRSS on the time of ageing was estimated on the basis of the measured data of kinetics of internal structure evolution. The estimated dependence was then compared with the experimental one. It could be concluded, that the agreement of both is good if one accepts the assumption, that the hardening of the alloy is determined by partly ordered net (distribution) of the β'-particles in the matrix for $t < 100$ hours and by fully ordered arrangement of those for $t > 100$ hours.

3.2. The Cu-Ni-Sn alloys

The set of the Cu–Ni–Sn alloy with constant concentration of Ni and variable Sn content was a subject of intense study. Alloys listed in tab. 1 can be divided into two groups. In the first one there are alloys with Sn content below the solubility limit (alloys No 1 – 5), while the second group contents the alloys, which are supersaturated solid solution (after appropriate heat treatment. The dependence of the CRSS on variable solute content (Sn) was firstly determined [7]. The temperature dependence of the $\sigma_{0.2}$ was determined and that is depicted for assorted alloys in Fig. 4. As it

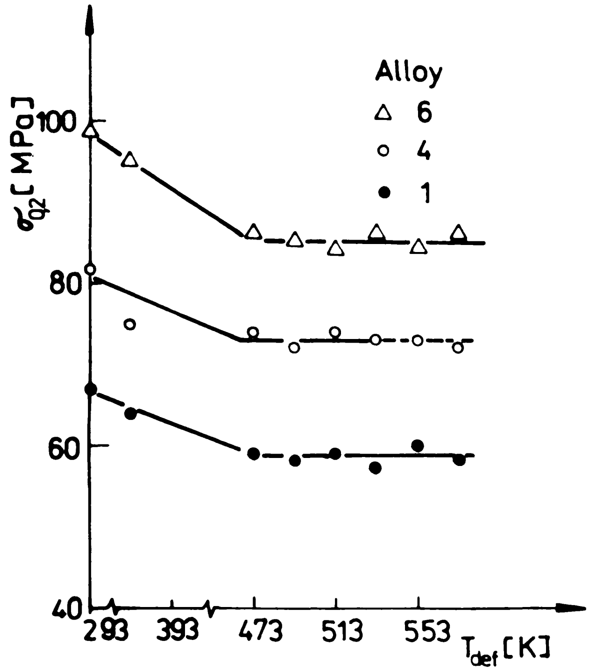

Fig. 4. The temperature dependence of the proof stress for the Cu-Ni-Sn alloys.

can be seen from Fig. 4, the temperature independent contribution to the yield stress for the alloy of groups I exists. The value of that contribution conveys to the $c^{2/3}$ law (Labusch [8]) quite well as can be seen from Fig. 5.

Ageing of the alloys of the second group was also studied [9]. Alloys No 6, 7, 8, 9 annealed at 573 K, 623 K and 673 K for various time have been studied. In the Fig. 6 the dependences of the proof stress $\sigma_{0.2}$ [obtained at room temperature] on the time of ageing are plotted for various temperatures of ageing and Sn content. On the basis of the model of the microstructure development described in more details for example in [9] it could be concluded:

1. All the alloys homogenised for 2 hours at 1073 K are supersaturated solid solutions.

2. Supersaturated solid solution decomposes during ageing either by the process of nucleation and growth or by spinodal reaction. The type of decomposition reaction depends on the initial Sn concentration.

3. Alloy with 1.2 at. % Sn is fully precipitation hardened by the particles of the originated by the process of nucleation and growth.

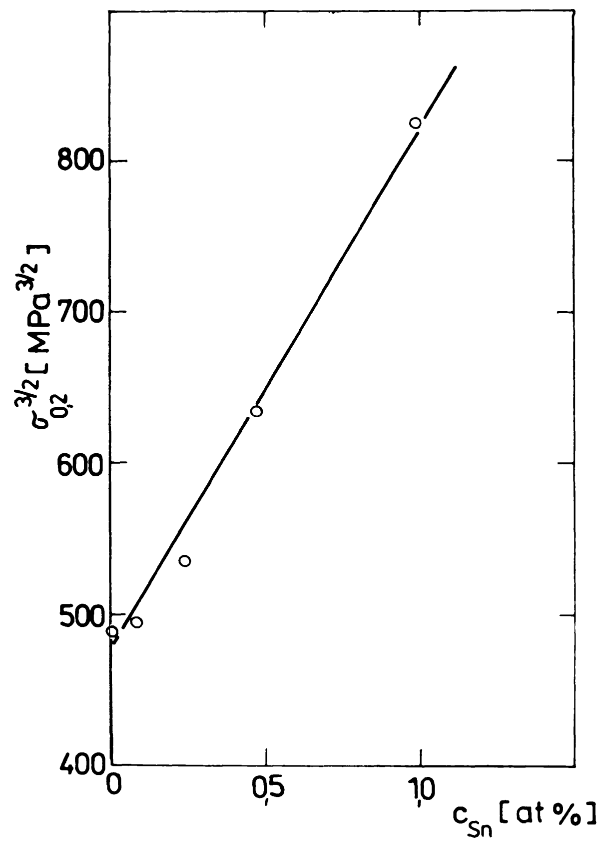

Fig. 5. The concentration dependence of the proof stress for the Cu-Ni-Sn alloys.

4. Alloys with higher Sn concentration decompose spinodaly and modulated structures are created during first stages of decomposition process. Solute rich regions of the modulated structure become internally ordered during prolonged ageing.

Ordering of the Ni_3Ti type with space group DO_{22} is characteristic for the medium times of ageing. Stable γ-phase with space group DO_3 originates later and its occurence is commonly connected with decrease of the proof stress $\sigma_{0.2}$.

An interesting result is depicted in Fig. 7.

The influence of cold rolling of the supersaturated solid solution No 8 on the dependence of the proof stress on time of ageing is seen. The strengthening maxima for the predeformed alloy are shifted to the shorter time periods as compared to the maximum of fully recrystalised alloy. Deeper study of this phenomena has been recently under way.

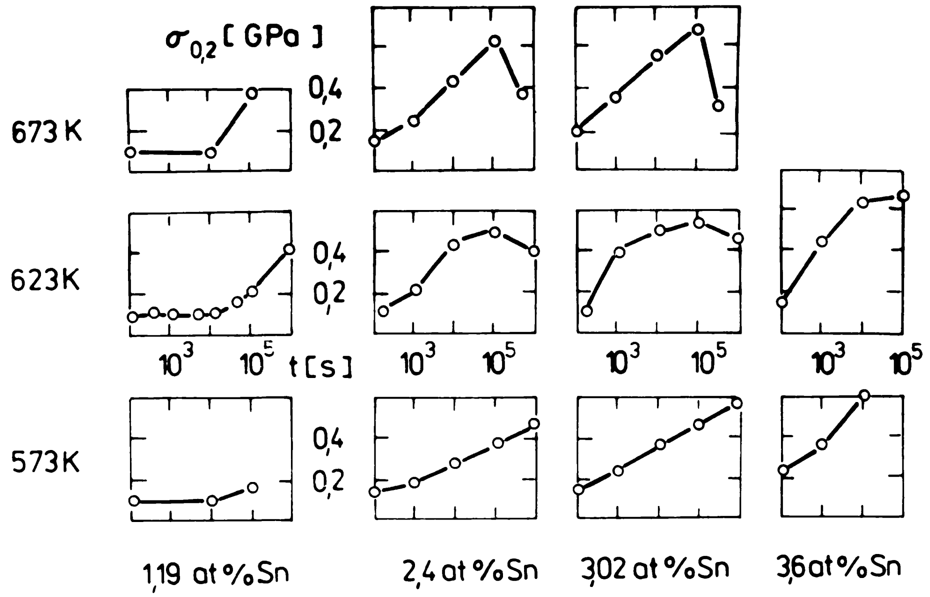

Fig. 6. The dependence of the proof stress on the time of ageing for the Cu-Ni-Sn alloys.

The flow stress of the crystals is commonly supposed to be a superposition of two contributions. The first one τ_Y, the so called yield stress, depends on strain rate $\dot{\varepsilon}$, temperature T and the details of internal structure which can be symbolised as $\{c\}$. The second component τ_D depends also on dislocation density (or more acurately on the dislocation substructure developed during deformation). If the flow stress τ is a simple sum of these components, the relation $\partial\tau/\partial \ln \dot{\varepsilon} = (M_Y - M_D)\,\tau_Y + M_D\tau$ holds if we denote $M_Y = \partial \ln \tau_Y/\partial \ln \dot{\varepsilon}$ and $M_D = \partial \ln \tau_D/\partial \ln \dot{\varepsilon}$. Experimentaly obtained relations of that type are known as a "Haasen plots" [10]. If the details of internal structure $\{c\}$ are changed (e.g. by alloying or by ageing), the influence of that change on both M_Y resp. M_D strain rate sensitivities can be separately studied according to Kocks [10].

The influence of Sn content on strain rate sensitivity coefficient M_Y resp. M_D were studied. Strain rate changes were used for this purpose. For the alloy No 8 the influence of ageing on both M_Y resp. M_D was also studied. The main results can be summarised as follows:

1. Increased Sn content influences both M_Y and M_D. Rising solute concentration causes the increase of the M_Y, whereas M_D decreases even to a negative value as solubility limit of Sn is passed. (See Fig. 8).

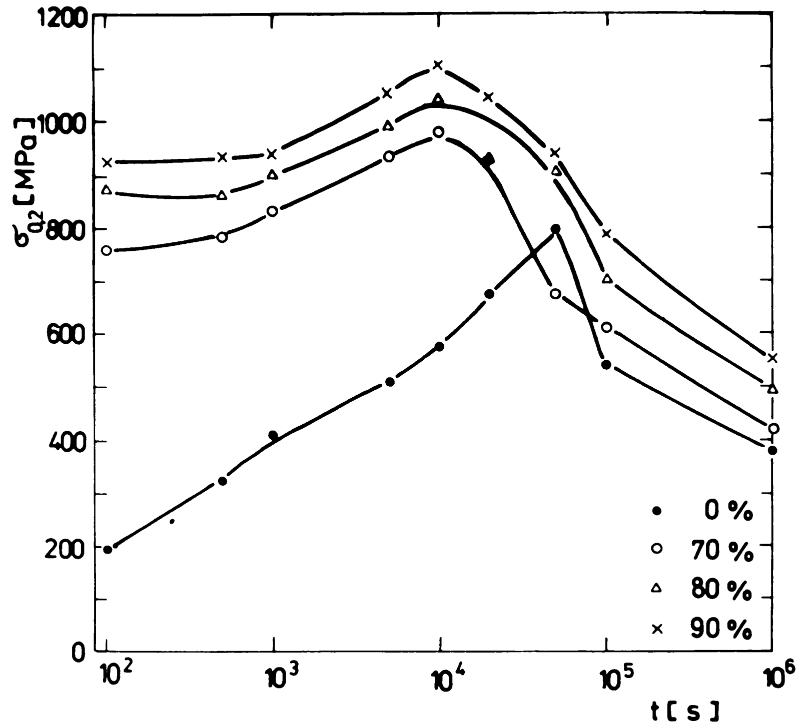

Fig. 7. The influence of cold rolling of the supersaturated solid solution on the dependence of the proof stress on time of ageing at 637 K for the Cu-Ni-Sn alloy No 8.

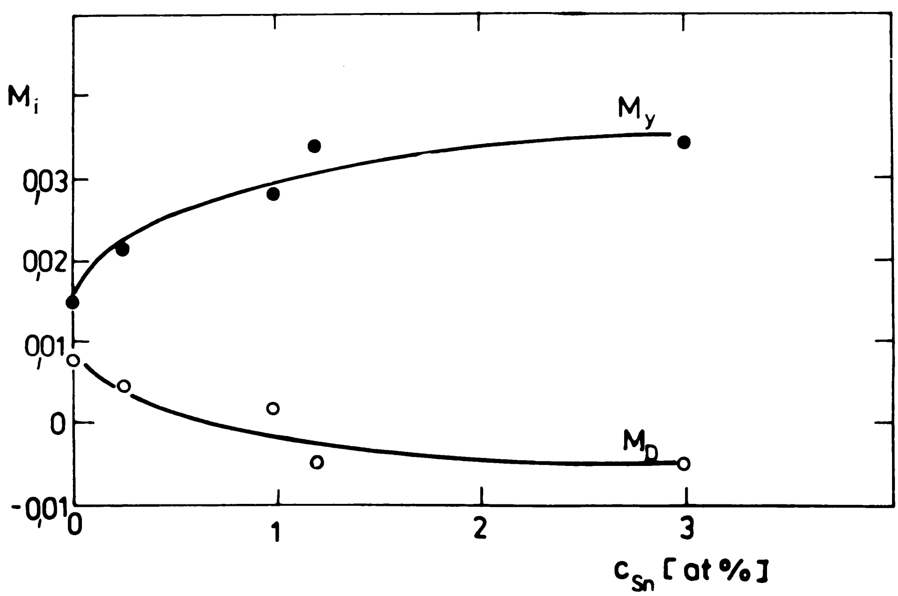

Fig. 8. The dependence of the strain rate sensitivity coefficients on the Sn content.

2. Aglomeration of solutes is suspected to explain the saturation of the growth of M_Y with increasing Sn concentration, whereas strain ageing is probably the reason for the negative values of M_D.

3. The ageing of the supersaturated solid solution influences both M_Y resp. M_D as well. As ageing proceeds, the initial relative high strain rate sensitivity of the yield stress decreases as concentration of the "free" solute decreases. (See Fig. 9).

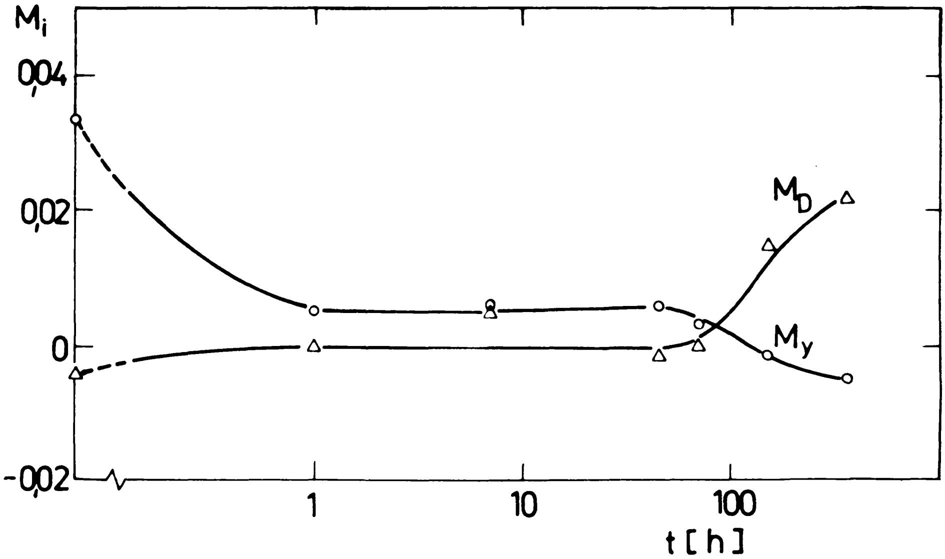

Fig. 9. The dependence of the strain rate sensitivity coefficients on time of ageing for the alloy No 8.

4. The occurence of the stable γ-phase has a dramatic effect on strain rate sensitivity coefficients. Stable γ-phase precipitates as a fine lamellar eutectics. Strain rate coefficient of the yield stress decreases to a negative values for such times of ageing, for which the lamellar γ-phase occurence is dominant structure freature. More detailed study of this problem is recently under way in connection with occurence of the jerky flow at appropriate temperatures and strain rates.

4. Conclusions

The main results of the presented study can be summarised as follows.

The studied alloys are solid solutions after appropriate homogenisation treatment followed by rapid water quenching. These solutions are supersaturated as for Cu–Ti alloy and Cu–Ni–Sn alloys with higher content of tin. (Alloys No 6, 7, 8, 9). The values of the critical resolved shear stress (CRSS) estimated from 0.002 proof stresses of the homogenised alloys are in good agreement with the Labusch's theory of the solid solution hardening [8].

If the supersaturated solid solutions are held at elevated temperatures (isothermal ageing) those decompose. The mode of this decomposition depends besides temperature of ageing mainly on solute concentration. If the Sn concentration in the Cu–Ni–Sn alloys is higher than 2·5 atomic percent, the sequence of the internal structure changes is the same as for Cu–Ti alloy. The modulated structure is present in early stages of ageing probably as a consequance of spinodal reaction. The modulated structure changes continuously into two-phase structure. The α-solid solution coexists with particles of the metastable phase.

A final product of the decomposition reaction is very fine (eutectics-like) structure with the lamelae of the stable phase. The critical stress depends on time of ageing nonmonotonously as a consequence of such internal structure development.

However, on the other hand, the alloy No 6 with 1·19 at. % Sn decomposes via nucleation and growth of the γ phase. The monotonous dependence of the CRSS on the time of ageing is characteristic for this decomposition process.

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