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Thermal analysis of vacancy defects in quenched tin bronzes - α

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Investigation have been carried out on the thermal dilatation ($\Delta L/L_0$) and lattice parameters ($\Delta a/a_0$) of the α-solution of industrially smelted tin bronze type CuSn6P as a function of heating temperature from 20°C to 900°C after quenching within the temperature range 750÷910°C. These investigations have made it possible to determine the concentration of vacancies after quenching and heating up to 800°C and to assess preliminarily the formation energy of vacancies ($E_v^F \approx 0{,}5 \div 0{,}9$ eV) depending on the parameters of heat treatment.

1. INTRODUCTION

Tin bronzes belong to non-ferrous alloys largely used in industry. The technology of their production however is limited to the range of plastic treatment due to the minimum plasticity and the distinct intergranular brittleness at elevated temperatures of plastic deformation [1,2]. The reason for this brittleness have not been explicitly explained so far. Some hypotheses connected among others, with the role of point defects (vacancies and impurity atoms) in the process of nucleation and growth of intercrystalline fractures, require further experimental verification. There are only few date concerning the behaviour of vacancies during their heating after quenching, the formation of vacancy clusters or cavitations as well as their interaction with tramp elements or impurities particulary in the segregation at the grain boundaries and intercrystalline cavitation [3÷7]. Quenching to a lower temperature results in a considerable supersaturation of vacancies, a surplus of which (generated in the course of quenching) may affect the mechanical properties of the alloys. Heating of the alloys after quenching may lead to elimination of the lattice vacancies and also to the formation of their equilibrium concentration. The mechanism of eliminating the vacancies by heating can be modified by the solute-vacancy interacting prevailing in the alloy system [3,4]. Investigations on the kinetics of the elimination of vacancies frozen in the course of quenching have most often been carried out on polycrystalline samples measuring their resistivity. It has been found that the temperature of quenching and tempering exerted a large influence on the kinetics of this process. These investigations permitted also to determine the formation and migration energies of mono- and bivacancies in the tested alloys [5, 6].

The aim of these investigation employing dilatometric and X-ray crystal analyses of tin bronze CuSn6P was to determine the influence of the quenching temperature on the changes in the concentration of vacancies as a function of the heating temperature after quenching,

particularly within the range of temperature of the plasticity minimum, as well as to assess preliminarily the value of the energy of vacancy formation in the α-solid of tin-bronze.

2. EXPERIMENTAL PROCEDURES

Dilatometric and X-ray diffraction analyses were carried out on industrially melted tin bronze type CuSn6P (UE7P) produced by Trefimetaux (France) – the chemical composition of which is to be seen in Table 1.

Table 1
Chemical composition of the investigated tin bronze

Alloy	Chemical composition in % wt.									
	Sn	P	Bi	Pb	Sb	As	S	Fe	Zn	Cu
CuSn6P	6,7	0,42	<0,01	<0,10	<0,01	<0,025	≤0,001	0,018	0,046	rest

The samples used for dilatometric analysis with a diameter of 6 mm and length of 20 mm were subjected to diffusion annealing for 5h at 720°C in argon atmosphere and then quenched in water from 750, 850 and 910°C after one hour holding time. The investigation were performed on a differentiating Linseis dilatometer within the temperature range of 20÷910°C at a heating rate of 60°C/h, pressure 10^{-5}Torr, amplification 7500 times, precission of recording $\Delta L/L = 2x10^{-4}$ and temperature $\Delta t \pm 2$°C.

In order to determine the lattice parameters of the α-solute of tin bronze as function of heating temperature, an X-ray diffraction analysis was carried out, applying a high-temperature diffractometer Simens D500 in the temperature range 20÷850°C. For this purpose the radiation of a $\lambda CuK\alpha_1$ – anode and a graphite monochromater were used. The samples were prepared in the form of powder with a granulation of 0,020 mm, which was annealed for 1,5 h at a temperature of 450°C in hydrogen atmosphere. A layer of this powder about 0,1 mm think was placed on the surface of the Pt-Ta sample holder resistant-heated in a high-temperature chamber with a dynamic vacuum of about 10^{-3} Torr. The temperature was measured by means of a PtRh-Pt thermo-couple adjacent to the sample holder. The diffraction lines was recorded by means of step-scanning ($\Delta\theta$ = 0,01°2θ) counting the impulses in constant time of 7÷300 sec., depending on the intensity of the diffraction line. The influence of the dilatation of the sample holder was adjusted basing on the angle position of the diffraction lines (111) and (311) Pt. The lattice parameter of the α-solution was determined basing on the corrected values of the inter-plane distances applying the least squares method. The precision of measurements $\Delta a/a_0$ was of the order $3x10^{-3}$.

The concentration of vacancies as a function of heating temperature was determined according to the relation [7]:

$$C'_V(T) - C_V(T_r) = 3 \cdot \left[\frac{\Delta L}{L_0} - \frac{\Delta a}{a_0} \right] \tag{1}$$

where: $C'_v(T)$ – concentration of vacancies after quenching from the temperature T,
$C_v(T_r)$ – concentration of equilibrium vacancies at the heating temperature T_r after quenching,
ΔL – total elongation (contraction),

Δa – change of the lattice parameter in the course of heating,
L_0, a_0 – length of the sample and lattice parameter after quenching.

3. RESULTS AND DISCUSSION

The analitically determined values of the lattice parameter for three samples of α-tin bronze and various numbers of diffraction lines as a function of heating temperature after quenching have been presented in Fig.1. It has been found that changes of the lattice parameters are monotonous from 3,6700 $\dot{A}$ to 3,7243 $\dot{A}$, respectively at temperatures of 43°C and 796°C.

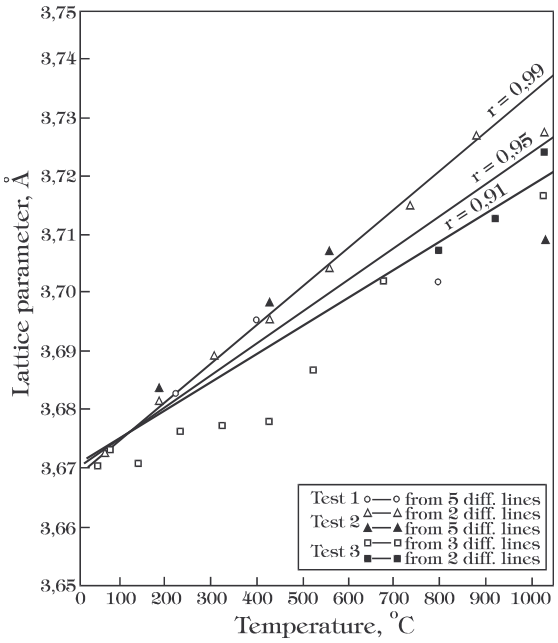

Fig. 1 Dependence of the crystalline lattice parameter of α-tin bronze on the heating temperature

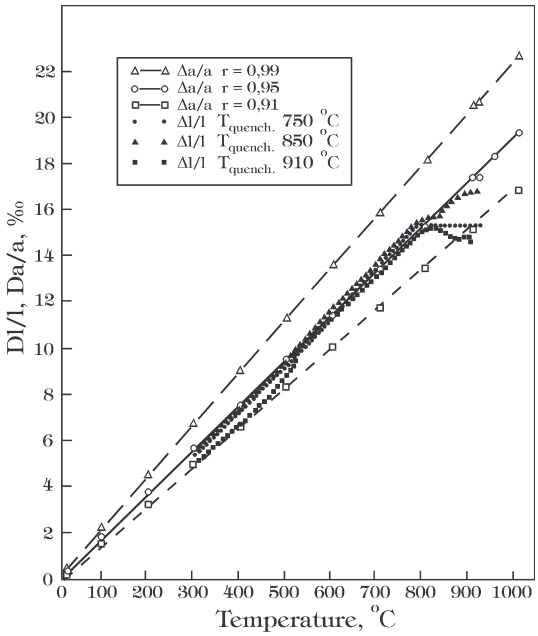

Fig. 2 Dependence of changes of the lattice parameters ($\Delta a/a_0$) and thermal dilatation ($\Delta L/L_0$) on the heating temperature for α - tin bronze

For comparative investigation with the dilatometric analysis, a linear regression a = f(T) has been applied with the coefficient of correlation r = 0,95.

The results of measurements of the thermal dilatation $\Delta L/L_0$ for samples quenched from 750, 850 and 910°C and heated up in the range from 20°C to 880-910°C have been presented graphically in Fig.2.

A comparison of the results of dilatation curves makes it possible to distinguish between two fundamental temperature zones, viz. between 20°C and 800°C and above 800°C. It has been found that the values of elongation increase, in general, proportionally with the heating temperature to about 780-800°C. Above this later temperature the values $\Delta L/L_0$ take a somewhat different course, depending on the quenching temperature. An isothermal holding of the samples at 900°C for about 50h leads to their distinct contraction, amounting relatively to 0,01-0,02. A comparative analysis has shown that in the temperature range of 20-470°C the

slope coefficient of the regression lines $\Delta L/L_0 = f(T)$ and $\Delta a/a_0 = f(T)$ is similar amounting to about 0,0177-0,0199. At temperature exceeding 500°C this coefficient increases with the growth of quenching temperatures, amounting to 0,0201; 0,0229 and 0,0284, respectively, for the quenching temperatures 750, 850 and 910°C – Table 2.

The course of the curves $\Delta L/L_0 = f(T)$ within the temperature zone 800-900°C is probably connected with the elimination of vacancies or changes of the lattice parameters of the α – solution. It may also be explained by the local melting or sliding of the grain boundaries due to the stress of the dilatometer head. An exact explanation of the recorded dilatation effects would require further complementary investigations.

Table 2

Experimental values $\Delta L/L_0$ for the determination of the regression lines $\Delta L/L_0=f(T)$

Heating temperature °C	Temperature of quenching °C					
	750		850		910	
	$\Delta L/L_0$[‰]	r	$\Delta L/L_0$[‰]	r	$\Delta L/L_0$[‰]	r
100	1,3081		2,0466		1,1869	
200	3,3009		3,8190		3,0669	
300	5,2938	0,999	5,5914	0,999	4,9469	0,999
400	7,2866		7,3638		6,8270	
450	8,2831		8,2499		7,7670	
470	-		-		8,1430	
470	-		-		8,0953	
500	-	-	9,5110	0,999	8,9471	0,996
530	-		-		9,7989	
600	-		11,8096		-	

The results of calculations of the vacancy concentration in the heating temperature range of 20÷800°C are to be seen in Fig.3. The shape of the curves indicates a slight effect of the elimination of vacancies to 500°C and their generation above this temperature. Taking into account the observed changes in the concentration of vacancies with the heating temperature are small (C_V (800°C)<$2x10^{-3}$) and analysing the errors in the determination of $\Delta L/L_0$ and $\Delta a/a_0$ it must be stated that the concentration of vacancies has been calculated on the boundary of method detection, and therefore it is difficult to draw definite conclusion. Basing on the result of C_V (T) the formation energy of vacancies has been assessed preliminarily by means of the graphical method (Fig.4) and applying the relation:

$$\ln C_V(T) = \frac{E_V^F}{k} \cdot \frac{1}{T} + \ln C_0 \qquad (2)$$

where: E_V^F - formation energy of vacancies in eV,

k – Bolzman constant $8,617 \cdot 10^{-5}$ eV/K,

T – heating temperature in K.

It has been found that probable calculated values of the formation energy are 0,9 eV and about 0,5 eV for the quenching temperatures 850 and 910°C, respectively.

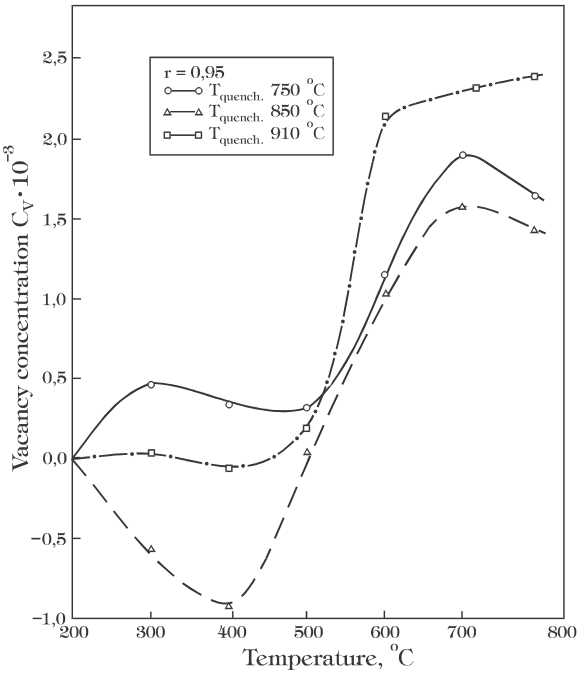

Fig. 3 Dependence of vacancy concentration on the heating temperature at different quenching temperatures for α-tin bronze

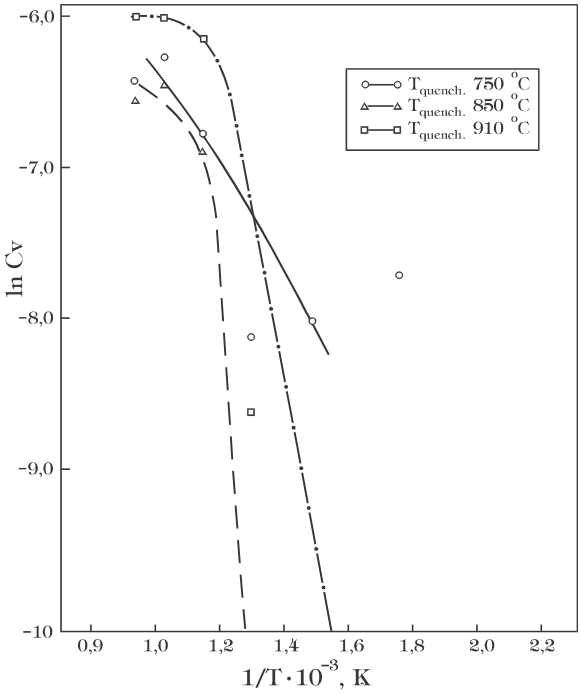

Fig. 4 Logarithmic dependence of the vacancy concentration on the inversed heating temperature for α-tin bronze

Dilatometric investigations were supplemented by measurements of the density of massive specimens applying mechanical balances with a precision of measurements of 0,01 mg. The applied immersion method warrants an absolute precision of density measurement $\Delta d/d \approx 10^{-3}$. A comparision of the results of density immediately after quenching from 850°C (d=8,704 g/cm^3) and after heating to 550°C (d=8,704 g/cm^3) justifies the statement that there is no distinct elimination of vacancies in the course of heating to 550°C, which coincides with the results of dilatometric investigation.

4. CONCLUSIONS

The performed investigations an α-tin bronze type CuSn6P lead to the following conclusions:

1. The lattice parameter of the investigated alloy changes after quenching proportionally with the heating temperature within the range 20÷800°C independently of the quenching temperature.
2. Changes in the thermal dilatation after quenching in the heating temperature range to about 780÷800°C are proportional to the changes of temperature. Above this temperature they take an unsteady state.
3. Changes of the vacancy concentration in the investigated range of heating temperature are somewhat lower than $2x10^{-3}$ and indicate the occurrence of a slight effect of vacancy elimination to the heating temperature 550°C.

4. The preminarily assessed formation energy of vacancies amount in the case of the determined alloy to about 0,9 eV and 0,5 eV at quenching temperatures 850°C and 910°C respectively.
5. Investigations concerning the density of massive samples of α-tin bronze carried out by means of the immersion method confirm the obtained results of dilatometric investigations.

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